

1

3,115,506

DERIVATIVES OF 1,4-BISMETHYLENE CYCLOHEXANE AND 1,4-BISMETHYLENE CYCLOHEXADIENE AND PROCESSES OF PREPARATION

Donald S. Acker and Dale C. Blomstrom, Wilmington, Del., assignors to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware
No Drawing. Filed Mar. 28, 1960, Ser. No. 17,753
14 Claims. (Cl. 260—396)

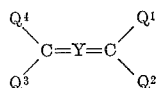
This invention relates to a new class of chemical compounds and to their preparation and more particularly to 1,4-bis(disubstitutedmethylene)cyclohexanes, -cyclohexadienes, -alkylcyclohexanes, and -alkylcyclohexadienes. The invention also comprises the amine and alkali and alkaline earth metal organic oxide condensation products of tetracyanoquinodimethane and C-alkyltetracyanoquinodimethanes, i.e., 1,4-bis(dicyanomethylene)cyclohexadiene and 1,4-bis(dicyanomethylene)alkylcyclohexadienes.

This application is a continuation-in-part of our co-pending applications Serial No. 762,282, filed September 22, 1958, and Serial No. 826,135, filed July 10, 1959, now abandoned.

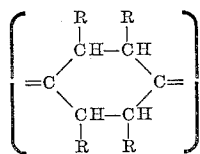
The thermographic process for copying of printed or written records uses a copy sheet bearing a substantially colorless coating which darkens on heating. When such a sheet is placed in contact with a text-bearing master and the assembly is exposed to a source of radiant heat, the portions of the copy sheet in register with text areas, particularly where they contain carbon, are heated much more rapidly than portions in register with blank areas of the master. The copy sheet is darkened only in those areas in register with text areas of the master and a copy is obtained. The color change in the copy sheet must take place at a temperature which otherwise causes no change in the copy sheet or master.

We have now found that 1,4-bis(disubstitutedmethylene)cyclohexanes and -cyclohexadienes are especially suitable as active ingredients in thermographic copying papers of the type described above. These new and useful compounds can be prepared by the condensation of 1,4-cyclohexanediones with a disubstitutedmethylene compound to yield 1,4-bis(disubstitutedmethylene)cyclohexanes, which by oxidation can be converted to the corresponding 1,4-bis(disubstitutedmethylene)cyclohexadienes. The substituents in the disubstitutedmethylene moieties are carboxyl groups and groups hydrolyzable to carboxyl.

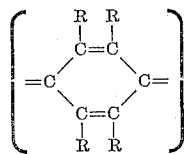
The products of this invention can be illustrated as follows:



where Q^1 , Q^2 , Q^3 , and Q^4 are carboxyl groups or groups hydrolyzable to carboxyl and Y is a 1,4-cyclohexadienylidene group



or a 1,4-cyclohexadienediylidene group

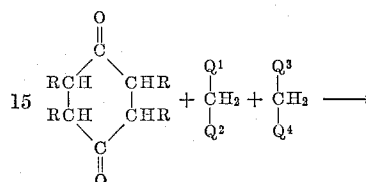


2

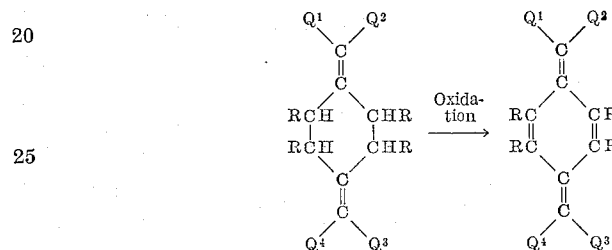
The preferred embodiments for Q^1 , Q^2 , Q^3 , and Q^4 include $COOR_1$, $CONR_2R_3$, COX , and CN , where R is hydrogen or alkyl of 1 to 8 carbons and R_1 , R_2 , and R_3 are hydrogen or hydrocarbyl groups containing up to 30 carbon atoms, and preferably up to 10 carbon atoms each, and X is halogen, i.e., fluorine, chlorine, bromine, or iodine.

The process of this invention can be illustrated as follows:

10



20



30

where the Q's are as defined above.

35

In the step of condensing 1,4-cyclohexanediones with a disubstituted methylene compound, the presence of a catalyst is necessary. The catalyst can be an acid or a base, or a salt which ionizes in water to give an acidic or basic solution. Thus there can be employed any of the wide variety of catalysts that have been shown useful in the Knoevenagel and aldol condensations. Active catalysts include hydrochloric acid, sodium and potassium carbonates, sodium and potassium cyanides, sodium acetate, ammonium acetate, piperidinium acetate, sodium bisulfite, sodium hydroxide, trisodium phosphate, diethylamine, zinc chloride, sodium methoxide, acidic or basic ion exchange resins, pyridine, piperidine, and the like.

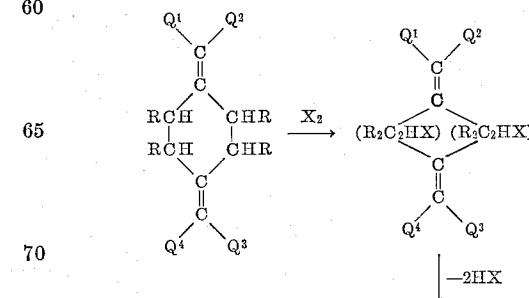
45

In the condensation step, water is always formed, and yields are sometimes improved if it is removed. This can be done by means of dehydrating agents, by simple distillation, or by refluxing the reaction mixture in the presence of an inert organic liquid immiscible with water, such as a hydrocarbon, and separating the water from the reflux condensate.

50

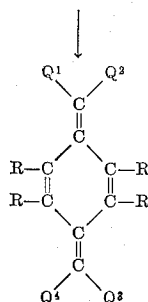
The step of oxidizing the 1,4-bis(disubstitutedmethylene)cyclohexanes to the corresponding cyclohexadienes can be carried out by direct oxidation, such as by the action of air, oxygen, a peroxide, or any direct chemical oxidant, or it can be carried out indirectly by halogenating and dehydrohalogenating as indicated in the following equation:

60



70

3



where X is chlorine or bromine. Alternatively the halogenation can be carried out by a halogenating agent such as, for instance, N-bromosuccinimide, phosphorus pentabromide, phosphorus pentachloride, and the like.

In the following illustrative examples, parts are by weight unless otherwise indicated. Example I represents a preferred embodiment of the invention.

EXAMPLE I

Part A.—1,4-Bis(Dicyanomethylene)Cyclohexane

A mixture of 140 parts of malononitrile, 112 parts of 1,4-cyclohexanedione, 63 parts of acetic acid, and 20 parts of ammonium acetate in 1760 parts of benzene is heated under reflux using a water separator for about two hours or until the theoretical amount of water has been removed. The reaction mixture is cooled and the solid product which precipitates is collected by filtration and washed well with water. Recrystallization from ethyl acetate gives 159 parts (76.5% yield) of 1,4-bis(dicyanomethylene)cyclohexane, M.P. 197–212° C. A sample for analysis is prepared by several recrystallizations from ethyl acetate, M.P. 204–210° C.

Analysis.—Calcd. for $C_{12}H_{10}N_4$: C, 69.2; H, 3.9; N, 26.9. Found: C, 69.4; H, 4.1; N, 26.3.

Another and preferred technique in view of the noticeably higher yields and greater purity of the product therein obtained is illustrated in the following:

In an open glass reactor of internal capacity corresponding to 1,000 parts of water was placed 100 parts of 1,4-cyclohexanedione and 119 parts of malononitrile. The mixture was heated at steam bath temperatures until significant melting had occurred, at which point a solution of one part of β -alanine in 200 parts of water was added. The reaction vessel was heated at steam bath temperatures with occasional swirling until the formation of a few crystals was noted, at which point heating was discontinued. An exothermic reaction then began, and, when it had become sufficiently vigorous to cause the reaction mixture to boil, the reactor was placed in an ice/water bath until boiling had ceased, at which point the reactor and the still warm reaction mixture were removed from the cooling bath and allowed to stand until it had cooled essentially to room temperature. The nearly solid mass was then filtered and washed with water until the washings were colorless. The filter cake was air-dried and then washed with diethyl ether until the washings were colorless. After air-drying, there was thus obtained 180 parts (97% of theory) of 1,4-bis(dicyanomethylene)cyclohexane as white crystals melting at 216–217° C.

Part B.—1,4-Bis(Dicyanomethylene)Cyclohexadiene, i.e., 7,7,8,8-Tetracyanoquinodimethane (TCNQ)

A solution of 76.5 parts of 1,4-bis(dicyanomethylene)cyclohexane in 1174 parts of acetonitrile is stirred at 50° C. under a nitrogen atmosphere while 160 parts of N-bromosuccinimide is added in small portions over a 45-minute period. The reaction mixture is stirred at the same temperature for an additional 45 minutes. It is then chilled to –20° C. and a solution of 72 parts of pyridine in 714 parts of ether is added. After the reaction mixture is stirred at –15° to –20° C. for an additional 15 minutes, it is allowed to warm to room temperature. Cold

4

water is added and the precipitate which forms is collected by filtration and recrystallized from ethyl acetate to give 641 parts (84% yield) of rust-colored crystals of 1,4-bis(dicyanomethylene)cyclohexadiene, M.P. 289–291° C. (dec.). A sample for analysis is prepared by recrystallization from ethyl acetate. This product can be sublimed under high vacuum at 200° C. with 97% recovery. It sublimes, apparently unchanged, when heated above 250° C. at atmospheric pressure. When a few crystals are crushed between micro cover glasses and heated on a Fisher melting point block, a deep blue film forms on the glass plates starting at about 200° C.

Analysis.—Calcd. for $C_{12}H_4N_4$: C, 70.6; H, 2.0; N, 27.4. Found: C, 71.3; H, 2.0; N, 28.2.

Another technique for the halogenation/dehydrohalogenation procedure using a halogen directly as the halogenating reagent is illustrated in the following, which procedure generally results in a slightly purer product as evidenced by the higher melting point.

A mixture of 12 parts of 1,4-bis(dicyanomethylene)cyclohexane, 156 parts of acetonitrile, and 19.2 parts of bromine in a glass reactor was cooled with stirring using an external ice/water bath to 10° C. under an atmosphere of nitrogen. The reaction vessel was maintained in the ice/water bath, and a solution of 18.8 parts of pyridine in 23.5 parts of acetonitrile was added over a period of 15 minutes with continued stirring at such a rate that, with continued external cooling, the temperature of the reaction mixture remained at 0° C. The reaction mixture was then stirred an additional 30 minutes at 0° C., at which point the cooling bath was removed and the reaction mixture allowed to warm to 20° C. over a period of one hour, at which point 300 parts of cold water was added and the resultant solid removed by filtration. The filter cake was washed with water and air-dried, thereby affording 12.1 parts of crude TCNQ as a yellow solid melting at 293–295° C. with decomposition. After recrystallization from acetonitrile, there was obtained 9.3 parts (80% of theory) of pure TCNQ as rust-colored crystals melting at 293.5–296.0° C.

As stated expressly in the foregoing, the present invention is generic to the 1,4-bis(disubstitutedmethylene)cyclohexanes, -cyclohexadienes, -alkylcyclohexanes, and -alkylcyclohexadienes. The immediately foregoing examples have illustrated in detail the preparation of a representative 1,4-bis(disubstitutedmethylene)cyclohexane and a representative 1,4-bis(disubstitutedmethylene)cyclohexadiene. Application of substantially the same techniques, utilizing disubstituted C-alkylcyclohexane reactants, results in the formation of the corresponding 1,4-bis(disubstitutedmethylene)alkylcyclohexanes and -alkylcyclohexadienes. More specifically:

Part C.—2-Methyl-1,4-Bis(Dicyanomethylene)-Cyclohexane

To 43 parts of 2-methyl-1,4-cyclohexanedione was added 46.2 parts of malononitrile and 0.5 part of β -alanine dissolved in five parts of water. The mixture was heated for two hours at steam bath temperatures and then let stand overnight at room temperature. The solid product was washed with water and then with diethyl ether and subsequently air-dried. There was thus obtained 54 parts (71% of theory) of crystalline 2-methyl-1,4-bis(dicyanomethylene)cyclohexane melting at 186–194° C. after recrystallization from ethyl acetate. The infrared spectrum of the product was wholly consistent with the 2-methyl-1,4-bis(dicyanomethylene)cyclohexane structure. The product exhibited a single absorption band in the ultraviolet region at 249 m μ with an extinction coefficient of 26,000.

Analysis.—Calcd. for $C_{13}H_{10}N_4$: C, 70.2%; H, 4.5%; N, 25.2%. Found: C, 70.1%; H, 4.8%; N, 25.0%.

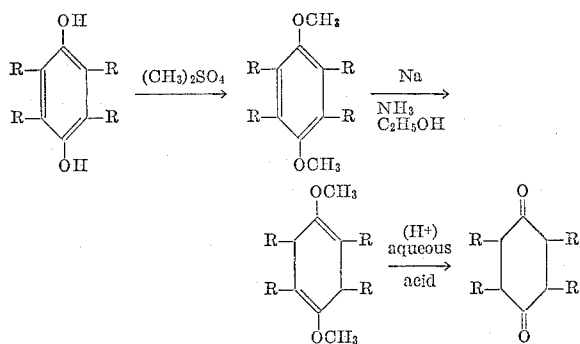
5

Part D.—2-Methyl-1,4-Bis(Dicyanomethylene)
Cyclohexadiene

To a solution of 20 parts of 2-methyl-1,4-bis-(dicyanomethylene)cyclohexane and 28.8 parts of bromine in 290 parts of acetonitrile cooled with an external ice/salt bath was added 28.3 parts of pyridine slowly over a period of about twenty minutes with stirring while maintaining the external cooling. After the addition was complete, the reaction mixture was stirred for an additional one-half hour with cooling and then for two more hours at room temperature, at the end of which time 555 parts of cold water was added. The resultant solid product was removed by filtration and washed with 230 parts of cold water. The crude 2-methyl-7,7,8,8-tetracyanoquinodimethane (MeTCNQ) was dissolved in 706 parts of acetonitrile. After filtration, the filtrate was heated with decolorizing charcoal, filtered, and cooled to room temperature. The resultant clear filtrate was concentrated to a volume corresponding to 50 parts of water under a stream of nitrogen. On filtration and air-drying, there was thus obtained 3.6 parts (18% of theory) of pure MeTCNQ as dark tan microcrystals melting at 193–195° C. and exhibiting a single absorption maximum in the ultraviolet region at 396 mμ with an extinction coefficient of 45,600. The infrared spectrum was wholly consistent with the MeTCNQ structure.

Analysis.—Calcd. for C₁₃H₆N₄: C, 71.5%; H, 2.8%; N, 25.7%. Found: C, 71.3%; H, 3.4%; N, 25.8%.

The C-alkyl-1,4-cyclohexanediones from which the 1,4-bis(disubstitutedmethylene)alkylcyclohexanes and -alkylcyclohexadienes of the present invention are prepared, as per the preceding Example I, Parts C and D, are themselves conveniently obtained by the Birch reduction with sodium and liquid ammonia in ethanol of the diethers of the corresponding C-alkylhydroquinones, some of which are available commercially, in accord with the following stoichiometry, using dimethyl sulfate and accordingly the dimethyl ether as illustrative.



EXAMPLE II

A mixture of 284 parts of 1,4-bis(dicyanomethylene)-cyclohexane and 222 parts of selenium dioxide in 3,914 parts of acetonitrile is heated under reflux for six hours and filtered hot to remove any insoluble material. The solvent is then removed by evaporation under reduced pressure. A solid residue remains which is recrystallized from ethyl acetate and then sublimed to yield 45 parts of 1,4-bis(dicyanomethylene)cyclohexadiene. After recrystallization of this sublimed product from ethyl acetate, a product melting at 290–292° C. (dec.) is obtained.

By substitution of other active methylene compounds for malononitrile in the condensation with 1,4-cyclohexanedione as shown in Example I, other 1,4-bis(disubstitutedmethylene)cyclohexanes and the corresponding 1,4-

6

bis(disubstitutedmethylene)cyclohexadienes of this invention can be prepared as shown in the following table:

TABLE

Active Methylene Compound	1,4-bis (disubstituted-methylene)cyclohexane	1,4-bis (disubstituted-methylene)-cyclohexadiene
Diethyl malonate...	1,4-bis (diethoxy-carbonylmethylene)cyclohexane.	1,4-bis(diethoxycarbonylmethylene)cyclohexadiene.
Malonamide.....	1,4-bis(dicarbamoylmethylene)cyclohexane.	1,4-bis(dicarbamoylmethylene)cyclohexadiene.
Ethyl cyanoacetate.	1,4-bis(cyano(ethoxycarbonyl)methylene)cyclohexane.	1,4-bis(cyano(ethoxycarbonyl)methylene)cyclohexadiene.
Cyanoacetamide....	1,4-bis(carbamoyl-cyanomethylene)cyclohexane.	1,4-bis(carbamoyl-cyanomethylene)cyclohexadiene.

The products of this invention can also be prepared by other means. For example, 1,4-bis(dicyanomethylene)cyclohexane can be hydrolyzed by the action of concentrated solutions of sulfuric acid or sodium hydroxide. By adjusting the time of the hydrolysis reaction and the concentration of the solution, products can be prepared in which one, two, three, or four of the cyano groups are hydrolyzed to carboxyl groups. In a similar way, 1,4-bis(dicyanomethylene)cyclohexadiene can be partly or completely hydrolyzed to the corresponding carboxylic acid derivatives.

These carboxylic compounds are converted to the corresponding acid chlorides by reaction with thionyl chloride. The acid chlorides are converted to the corresponding acid fluorides, bromides, or iodides by interchange with hydrogen fluoride, hydrogen bromide, or hydrogen iodide in the presence of the corresponding alkali metal halide salt, as shown by Wagner and Zook in "Synthetic Organic Chemistry," John Wiley & Sons, 1953, method 338, page 548. For example, 1,4-bis(dicarboxymethylene)cyclohexane reacts with thionyl chloride to yield 1,4-bis(di(chlorocarbonyl)methylene)cyclohexane which can be treated with sodium hydrogen fluoride to yield 1,4-bis(di(fluorocarbonyl)methylene)cyclohexane or with sodium hydrogen bromide to yield 1,4-bis(di(bromocarbonyl)methylene)cyclohexane. The corresponding 1,4-bis(di(halocarbonyl)methylene)cyclohexadienes can be similarly prepared from 1,4-bis(dicarboxymethylene)cyclohexadiene.

The use of the 1,4-bis(disubstitutedmethylene)cyclohexanes and 1,4-bis(disubstitutedmethylene)cyclohexadienes of this invention for preparing thermographic images is illustrated as follows:

A hot solution of about four parts of 1,4-bis(dicyanomethylene)cyclohexadiene in about 600 parts of dioxane is brushed onto photographic paper stock. After the coated paper is dried at room temperature, it is pressed for five seconds against metal relief images (nickel foiled electrotpe) heated at various temperatures. With the relief image at 165° C. a faint brownish yellow image is formed. With the relief image at 188–200° C. a deep brown image is obtained. Under similar conditions, uncoated photographic paper does not give any coloration when pressed against hot metal relief images.

The 1,4-bis(disubstitutedmethylene)cyclohexadienes of this invention are also useful for reducing to the corresponding 1,4-bis(disubstitutedmethyl)benzenes. This may be illustrated as follows:

A solution of 1,4-bis(dicyanomethylene)cyclohexadiene in glacial acetic acid is treated with a molecular excess of thiophenol and allowed to evaporate to dryness. The residue is extracted with ether, and the remaining solid is recrystallized from ethanol to yield 1,4-bis(dicyanomethyl)benzene melting at 244–245° C.

Analysis.—Calcd. for C₁₂H₈N₄: C, 69.9; H, 2.93; N, 27.2. Found: C, 70.14; H, 2.97; N, 27.45.

As another example, a mixture of 41 parts of 1,4-

7

bis(dicyanomethylene)cyclohexadiene, 80 parts of mercaptoacetic acid, and 1049 parts of glacial acetic acid is heated at reflux under a nitrogen atmosphere for 15 minutes. When the hot reaction mixture is diluted with 1000 parts of water and then cooled in ice, 1,4-bis(dicyanomethyl)benzene crystallizes as white needles. After the product has been washed with water and dried, it weighs 36 parts (80% yield) and melts at 241–243° C.

The 1,4-bis(disubstitutedmethyl)benzenes can also be interconverted. For instance, refluxing of 0.3 part of the above 1,4-bis(dicyanomethyl)benzene (which also can be termed *p*-phenylenedimalononitrile), for 3.5 hours with 24 parts of methanol containing 0.173 part of water while passing a rapid stream of dry hydrogen chloride gas through the solution, resulted in hydrolysis of the nitrile groups and conjoint esterification of the resulting carboxylic acid groups. Dilution of the reaction mixture with water afforded 0.783 parts (79% of theory) of 1,4-bis-[di(methoxycarbonyl)methyl]benzene, i.e., *p*-phenylenebis(dimethyl malonate), as a granular crystalline precipitate melting at 149–151° C. Repeated recrystallization from benzene/pentane mixtures resulted in raising the melting point to 151.5° C. to 152.0° C.

Analysis.—Calcd. for $C_{16}H_{18}O_8$: C, 56.8%; H, 5.4%. Found: C, 56.8%, H, 5.4%.

The 1,4 - bis(disubstitutedmethylene)cyclohexadienes can also be prepared by suitable dehydrogenation of the 1,4-bis(disubstitutedmethyl)benzenes. Thus, a solution of 0.96 part of the above *p*-phenylenebis(dimethyl malonate), 0.35 part of sodium methoxide, and 79 parts of methanol was refluxed under nitrogen for 1.25 hours, and the reaction mixture was then evaporated to dryness under reduced pressure. The residue was covered with about 50 parts of benzene and iodine was added slowly with swirling until a permanent iodine color remained in the benzene solution (approximately 0.3 part of iodine was required). The reaction mixture was filtered, and the filter cake was slurried with an aqueous solution of potassium iodide and sodium bisulfite to remove excess iodine. The mixture was filtered, and the filter cake was washed first with water and then with hexane. There was thus obtained as a yellow-green solid 0.245 part (26% of theory) of crude 1,4-bis[di(methoxycarbonyl)methyl]cyclohexadiene, which can also be referred to as cyclohexa-2,5-diene-1,4-diylidenebis(dimethyl malonate), and more concisely as 7,7,8,8-tetra(methoxycarbonyl)quinodimethane. On recrystallization, the purified 7,7,8,8-tetra(methoxycarbonyl)quinodimethane was obtained as bright yellow, prismatic needles which did not exhibit a distinct melting point but appeared to gradually polymerize on heating. The compound exhibited a single absorption band in the ultraviolet region at 368 $m\mu$ with an extinction coefficient of 47,000.

Analysis.—Calcd. for $C_{16}H_{16}O_8$: C, 57.1%; H, 4.8%. Found: C, 57.5%; H, 4.9%.

The 1,4-bis(disubstitutedmethyl)benzenes can also be prepared by other methods, as illustrated below.

To the alcohol-free sodium ethoxide from 12 parts of sodium there is added 293 parts of ethyl carbonate, 87 parts of toluene, and 39 parts of *p*-xylylenedicyanide. This mixture is heated with stirring until material (mostly ethanol) begins to distill through a distilling column attached to the reactor. Toluene is added to the reaction mixture at the same rate that distillate is collected until the head temperature reaches 115° C. This process requires the addition of about 217 parts of toluene. To the cooled reaction mixture there is added 300 parts of water and 42 parts of glacial acetic acid. The oil that separates is collected, and the aqueous phase is extracted with two 71-part portions of ether. The combined oil and ether extracts are dried over magnesium sulfate and freed of volatile material by distillation at 15 mm. pressure at 80–100° C. The oil that remains is distilled, and the portion that boils at 223° C./2.7 mm. to 231° C./2.0 mm. is collected. The resulting 1,4-bis(cyano(ethoxycar-

8

bonyl)methyl)benzene weighs 33 parts (44% yield) and crystallizes slowly to a moist solid when stored at room temperature. The infrared spectrum of this material shows bands at 4.45 microns ($-\text{C}\equiv\text{N}$) and 5.72 microns (ester $\text{C}=\text{O}$). When an ethanol solution of this material is mixed with ammoniacal silver nitrate, a silver mirror forms, and the solution develops a deep blue color.

The usefulness of the 1,4-bis(disubstitutedmethyl)benzenes as photographic developers is illustrated in the following paragraph.

A photographic developer solution is prepared by dissolving one part of 1,4-bis(dicyanomethyl)benzene in 1000 parts of 5% aqueous sodium bicarbonate solution containing one part of potassium bromide. A strip of positive photographic emulsion is exposed under a stepwedge. In a photographic dark room the exposed film is immersed in the above developer solution for four minutes. It is then fixed in hypo and washed by conventional photographic procedures. The developed strip shows a density gradation corresponding to the variation of exposure under the stepwedge and good differentiation between exposed and unexposed areas of the emulsion.

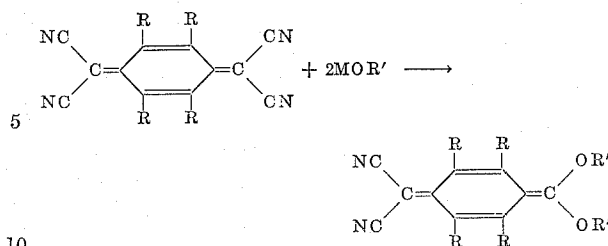
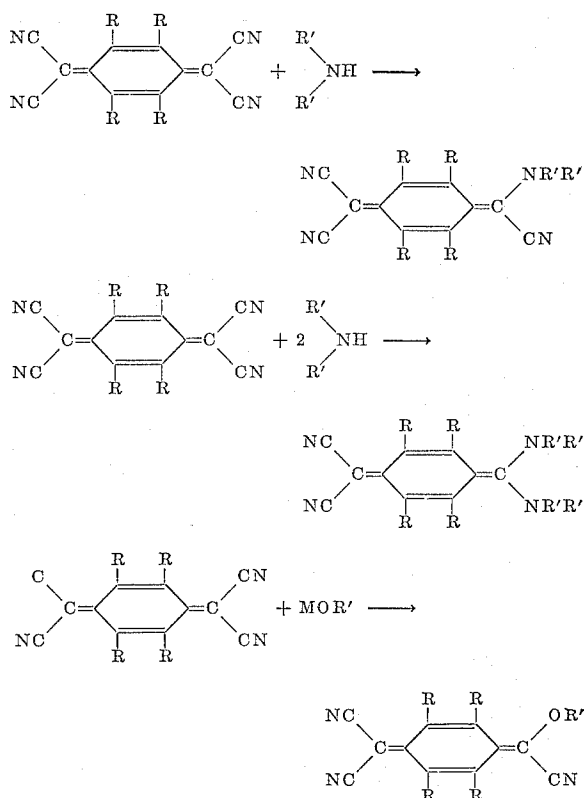
As given in detail in the foregoing Example I, Parts C and D, for the specific 2-methylsubstituted-1,4-bis(disubstituted) cyclohexane and -cyclohexadienes there involved, viz., the bis(dicyanomethylene) compounds, the preparative techniques therefor are substantially identical with those given in detail in the preceding discussions for the compounds without the alkyl substituent. In similar fashion, the mono-, di-, tri-, and tetraalkyl-substituted bis(difunctionally substituted methylene) compounds of the present invention are prepared. More specifically, using 2,3 - dimethyl-1,4-cyclohexanedione and malononitrile, there are obtained 2,3-dimethyl-1,4-dicyanomethylenecyclohexane and -cyclohexadiene. Similarly, from 2,3,5-trimethyl- and 2,3,5,6-tetramethylcyclohexane-1,4-diones, there are obtained the corresponding 2,3,5-trimethyl- and 2,3,5,6-tetramethyl - 1,4 - dicyanomethylene-cyclohexanes and -cyclohexadienes. Similarly, from 2-n-octylcyclohexane-1,4-dione and malononitrile there are obtained 2-n-octyl - 1,4 - dicyanomethylenecyclohexane and -cyclohexadiene. From 2-isopropyl-1,4-cyclohexanedione and 2-tertiary butyl-1,4-cyclohexanedione with malononitrile, there are obtained the corresponding 2-isopropyl- and 2-tertiary butyl-1,4-dicyanomethylene-substituted cyclohexanes and cyclohexadienes.

As the degree of chain branching in the various alkyl, i.e., monovalent saturated, hydrocarbyl substituents, increases and as the number of carbons in said substituents also increases, molecular packing factors tend to make the preparation of the compounds with increasing number of such substituents more difficult. However, within the realms of the 8-carbon atom limit assigned to each alkyl substituent on the 2-, 3-, 5-, and 6-ring carbons, it is possible to prepare tetrakis straight chain hydrocarbyl substituted compounds. More specifically, from 2,3,5,6-tetrakis-n-octyl-1,4-cyclohexanedione and malononitrile, the corresponding 2,3,5,6-tetrakis-1,4-dicyanomethylene-cyclohexane and -cyclohexadiene are obtained.

While the foregoing has been specifically directed to malononitrile as the diacid-substituted methylene compound, the same applies as illustrated in detail in the various sections of the foregoing Example I to other difunctionally substituted methylene compounds. Thus, from diethyl malonate, malonamide, ethyl cyanoacetate, cyanoacetamide, and the like, with the alkyl 1,4-cyclohexanediones there are obtained, respectively, the 1,4-bis(diethoxycarbonylmethylene)-, 1,4 - bis(dicarbamoylemethylene)-, 1,4 - bis[cyano(ethoxycarbonyl)methylene]-, 1,4-bis(carbamoylcyanomethylene) - alkylcyclohexanes and -alkylcyclohexadienes. The interconversions between the various difunctionally substituted methylenecyclohexanes and -cyclohexadienes illustrated specifically in the various sections of foregoing Example I likewise apply to the just enumerated illustrative alkyl-substituted

products of this invention. The conversion of the various products to the bis-substituted aromatic structures, i.e., where the bridging quino ring has been converted to a benzene ring, also similarly applies to the alkyl-substituted derivatives.

The present invention is also generic to the mono- and diamino and mono- and diether condensation products of 7,7,8,8-tetracyano-p-quinodimethane and 7,7,8,8-tetracyano alkyl-substituted-p-quinodimethanes and to the preparation thereof from, respectively, one and two molar proportions of the requisite amino hydrogen-bearing amine and alcoholic hydrogen-bearing alcohols and phenols, said hydroxy compounds being used in the form of their alkali metal and alkaline earth metal salts. In the manner of U.S. Patents 2,762,810, -832, and -833 concerning the amino and ether condensation products of tetracyanoethylene, the new 7,7,8,8-tetracyanoquinodimethane and 7,7,8,8-tetracyano-alkyl-substituted quinodimethanes likewise react with one to two molar proportions of amino hydrogen-bearing amines and hydroxyl hydrogen-bearing alcohols and phenols in the form of their salts to split out from one to two molar proportions of HCN and form the corresponding 7-mono- and 7,7-diamino and 7-mono- and 7,7-diether-substituted 8,8-dicyano-p-quinodimethanes, which substitution or condensation products likewise form a specific part of the present invention. The stoichiometry can be represented by the following four illustrative equations, wherein R is as before, i.e., hydrogen or alkyl of up to 8 carbons; M is an alkali metal or alkaline earth metal; and the R's, which can be alike or different, are hydrogen, aliphatic, cycloaliphatic, aromatic, alkaromatic, araliphatic or aralicyclic monovalent hydrocarbon radicals free of acyclic carbon-carbon unsaturation and of any substituents carrying Zerewitinoff active hydrogen and generally of no more than 18 carbons each. These radicals can contain heterocyclic atoms, such as oxygen, nitrogen, or sulfur, and can also be together joined pairwise to form carbocyclic or heterocyclic structures within the indicated limitations carrying the indicated pendant amino hydrogen- and hydroxyl hydrogen-containing substituents:



The 7, 7, 8, 8-tetracyano-p-quinodimethane and 7,7,8,8-tetracyano-alkyl-substituted p-quinodimethanes of the present invention form charge-transfer compounds or complexes with organic and organo-inorganic Lewis bases, including specifically such Lewis base compounds carrying amino hydrogen or hydroxyl hydrogen substituents. As just stated in the immediately preceding section, such substituents also undergo the HCN condensation-type reaction to form the also new 7-mono and 7,7-di- amino- and -ether-substituted-8,8-dicyano-p-quinodimethanes. As to which will be obtained with the various amino hydrogen and alcoholic hydrogen-bearing Lewis bases, this is, as is true of all chemical reactions, a function of the relative reactivity of the respective amino hydrogen and hydroxyl hydrogen-bearing compounds. In many instances, both types of products will be obtained simultaneously, and depending upon the rigor of the reaction conditions applied, the equilibrium can be shifted more to the formation of charge-transfer compounds or to the amine or ether condensation products. In general, the charge-transfer compound will form first and the reaction can be stopped at this point by carrying it out at lower temperatures or by running the reaction for only a short period of time. Running the reaction at modest to elevated temperatures or in the presence of mild to gross excesses of the amino hydrogen- and alcoholic hydrogen-containing Lewis bases will result in a tendency toward the formation of more of the amino or ether condensation products.

Generally speaking, the reaction will be effected at modest temperatures, most conveniently in the range of room temperature, and usually in the presence of inert diluents. Suitable such diluents include, for convenience, the liquid ethers, hydrocarbons, nitriles, and amides free of Zerewitinoff active hydrogen, such as tetrahydrofuran, acetonitrile, propionitrile, dimethylformamide, dimethylacetamide, the hexanes, pentanes, and the like. The products are obtained directly by the addition of either the tetracyanoquinodimethane to the amino hydrogen-bearing or hydroxyl-bearing coreactant, the latter in salt form, or vice versa. If mono-substituted condensation products are desired, only one molar proportion of the hydrogen-bearing coreactant will be used. If the disubstituted condensation products are preferred, excesses of the hydrogen-bearing coreactants will be used. The products are obtained directly at relatively short reaction times and are generally quite intensely colored. The products can be purified by conventional recrystallization techniques from suitable solvents or conventional solution/precipitation techniques from suitable solvents and adjusted concentrations of nonsolvents, sometimes also as a function of temperature.

The following examples in which the parts given are by weight are submitted to fully illustrate but not to limit the 7-mono- and 7,7-diamino- and -ether-substituted-8,8-dicyano-p-quinodimethanes.

EXAMPLE III

To a warm solution of one part of TCNQ in 83.8 parts of anhydrous THF was added 0.212 part (0.61 molar proportion based on the TCNQ) of pyrrolidine. The initially green solution turned a gray-purple color. The reaction mixture was allowed to stand at room temperature for 17 hours, then cooled in an ice/water bath, and

finally filtered. After air-drying, there was thus obtained 0.360 part (49% of theory) of 7,8,8-tricyano-7-pyrrolidinoquinodimethane as fine, purple-black needles which appeared to begin to melt at 233° C. and did not melt completely up to 300° C. After recrystallization from acetonitrile, the 7,8,8-tricyano-7-(1'-pyrrolidino)quinodimethane was obtained as fine, purple-black needles which did not melt up to 405° C., although some blackening occurred.

Analysis.—Calcd. for $C_{15}H_{12}N_4$: C, 72.6%; H, 4.9%; N, 22.6%. Found: C, 72.9%; H, 4.7%; N, 22.5%.

The infrared spectrum showed no absorption attributable to N—H. The strong absorption bands at 2175 and 2200 cm^{-1} are assignable to conjugated nitrile groups. The 7,8,8-tricyano-7-(1'-pyrrolidino)quinodimethane is useful as a gasoline dye in imparting a light violet color to white gasoline.

EXAMPLE IV

To a warm solution of one part of TCNQ in 88.8 parts of THF was added 1.7 parts (4.9 molar proportions based on the TCNQ) of pyrrolidine. After a few minutes a yellow, crystalline compound began to precipitate. The reaction mixture was let stand at room temperature for three days and then cooled in an ice/water bath and filtered. The yellow, crystalline product was washed with cold THF and then with diethyl ether to afford 1.2 parts (84% of theory) of 8,8-dicyano-7,7-di(1'-pyrrolidino)quinodimethane as yellow crystals melting at 292–300° C. with decomposition. After two recrystallizations from methanol, the pure 8,8-dicyano-7,7-di(1'-pyrrolidino)quinodimethane was obtained as pale yellow crystals melting at 304–307° C. with decomposition.

Analysis.—Calcd. for $C_{18}H_{20}N_4$: C, 73.9%; H, 6.9%; N, 19.2%; N.E., 292.4. Found: C, 73.9%; H, 7.0%; N, 19.0%; N.E., 290.

The infrared absorption spectrum showed no absorption characteristic of N—H groups and strong absorption bands at 2175 and 2130 cm^{-1} assignable to conjugated nitrile groups.

A piece of composite cloth containing joined integral areas woven from different fibers was heated for one hour in a dye bath containing 0.02 part of 8,8-dicyano-7,7-di(1'-pyrrolidino)quinodimethane, 200 parts of water, and a small amount of dimethylformamide, and 20 parts of a solution of a commercial dispersing agent. At the end of this dyeing cycle the cloth was removed and water-washed. The silk, wool, and nylon portions of the composite cloth were dyed yellow. This color was fast to soaping.

EXAMPLE V

To a mixture of 0.5 part of 7,8,8-tricyano-7-(1'-pyrrolidino)quinodimethane and 35.5 parts of THF was added 0.851 part of pyrrolidine. The reaction mixture turned green, and yellow crystals slowly began depositing therefrom. The reaction mixture was let stand five hours under room temperature and the yellow, crystalline product isolated by filtration. After washing with diethyl ether and drying, there was thus obtained 0.465 part (80% of theory) of 8,8-dicyano-7,7-di(1'-pyrrolidino)quinodimethane as yellow crystals melting at 276–281° C. with decomposition. After recrystallization from methanol, the pure 8,8-dicyano-7,7-di(1'-pyrrolidino)quinodimethane was obtained as yellow crystals melting at 289.5–311° C. with decomposition. Mixed melting point with the dicyanodipyrrolidinoquinodimethane obtained directly from TCNQ and pyrrolidine was 286.5–299.5° C. with decomposition, thus showing the products to be identical. The infrared spectrum of the product from pyrrolidine and the tricyanopyrrolidinoquinodimethane was also substantially identical with that of dicyanodipyrrolidinoquinodimethane.

EXAMPLE VI

To a warm solution of two parts of TCNQ in 222 parts of THF was added 0.89 part (1.25 molar proportions based on the TCNQ) of n-butylamine. The resultant dark solution was let stand at room temperature for 48 hours and then concentrated at reduced pressure to a dark solid. This was dissolved in dilute aqueous sodium hydroxide solution and undissolved material removed by filtration. The filtrate was washed with about one part of a 1:1 by volume pentane/diethyl ether mixture and the deep red, aqueous layer was taken. After acidification with dilute aqueous hydrochloric acid solution, the resultant dark purple precipitate was removed by filtration, washed with water, and dried. There was thus obtained two parts (82% of theory) of 7-n-butylamino-7,8,8-tricyanoquinodimethane as purple crystals. The product was purified by dissolving it in THF and reprecipitation therefrom by careful addition of n-hexane. There was thus obtained 1.44 parts of pure product as a purple powder melting at 159–169.0° C.

Analysis.—Calcd. for $C_{15}H_{14}N_4$: C, 72.0%; H, 5.6%; N, 22.4%; M.W., 246. Found: C, 71.6%; H, 5.7%; N, 21.8%; M.W., 232, 247.

The infrared spectrum exhibited absorption in a region characteristic of the N—H linkage and showed a triplet in the nitrile region. The ultraviolet and visible spectra exhibited absorption at 262 millimicrons and weaker absorption from 425 to 617 millimicrons. These spectral data are consistent with the view that the product is a mixture of the tautomers 7-n-butylamino-7,8,8-tricyanoquinodimethane and α,α',α' -tricyano- α -N-butylimino-p-xylene.

EXAMPLE VII

To a solution of 0.125 part of a mixture of 4.28 parts of TCNQ and 1.455 parts of p-phenylenedimalononitrile (dihydro TCNQ) in 13.3 parts of THF was added 0.11 part (3.0 molar proportions based on the methane) of n-butylamine. The reaction mixture immediately turned deep red and was allowed to stand under nitrogen at room temperature for 18 hours. The crystalline solid was removed by filtration and washed with tetrahydrofuran. On drying, there was thus obtained 0.110 part (75% of theory) of crude 7,7-bis(n-butylamino)-8,8-dicyanoquinodimethane as dull red crystals melting at 261–263° C. with decomposition. The solid was taken up in boiling methanol, treated with decolorizing charcoal, filtered, and the purified product precipitated with diethyl ether. The pale yellow crystals thus obtained melted at 264–266° C. with decomposition. Further recrystallization from methanol/water afforded pure 7,7-bis(n-butylamino)-8,8-dicyanoquinodimethane as pale yellow crystals melting at 270–275° C. with decomposition.

Analysis.—Calcd. for $C_{18}H_{24}N_4$: C, 72.9%; H, 8.2%; N, 18.9%. Found: C, 72.7%; H, 8.2%; N, 18.8%.

EXAMPLE VIII

To a warm solution of two parts of TCNQ in 266 parts of THF was added 2.92 parts (4.1 molar proportions based on the TCNQ) of n-butylamine. The mixture was allowed to stand at room temperature for 24 hours and the solid removed by filtration. The filter cake was washed with diethyl ether and dried. There was thus obtained 2.35 parts (81% of theory) of 7,7-bis(n-butylamino)-8,8-dicyanoquinodimethane as yellow crystals melting at 270–273° C. with decomposition.

Analysis.—Calcd. for $C_{18}H_{24}N_4$: N.E. 296. Found: 70 N.E., 300.

EXAMPLE IX

To a solution of four parts of TCNQ in 311 parts of THF was added a solution of 1.26 parts (3.8 molar proportions based on the TCNQ) of ammonia in 200 parts

of tetrahydrofuran. The resultant dark liquid reaction mixture was stored at room temperature for 69 hours under nitrogen. Upon filtration at the end of this period there was obtained 3.02 parts (82% of theory) of 7,7-diamino-8,8-dicyanoquinodimethane as a yellow-brown solid. A portion of the product was twice recrystallized from a mixture of dimethylformamide and THF to afford pure 7,7-diamino-8,8-dicyanoquinodimethane as yellow microcrystals which turned brown at 368° C. but did not melt up to 400° C.

Analysis.—Calcd. for $C_{15}H_8N_4$: C, 65.2%; H, 4.4%; N, 30.4%. Found: C, 65.4%; H, 4.6%; N, 30.5%.

The 7,7-diamino-8,8-dicyano product was still further characterized by hydrolysis under alkaline conditions to homoterephthalic acid, which would not be possible for the isomeric 7,8-diamino-7,8-dicyano compound.

A mixture of one part of the above 7,7-diamino-8,8-dicyanoquinodimethane, six parts of sodium hydroxide, and 25 parts of water was refluxed with stirring for five hours. The reaction mixture was then cooled and acidified with dilute hydrochloric acid. Upon filtration there was thus obtained 0.230 part of crude homoterephthalic acid as a light tan solid melting at 225–230° C. Recrystallization from diethyl ether afforded pure homoterephthalic acid as a white solid melting at 236–237° C. The mixed melting point with authentic homoterephthalic acid of melting point 241.5–242° C. was 239–241° C. The infrared spectrum of the hydrolyzed product is identical with that of the separately obtained sample of homoterephthalic acid.

EXAMPLE X

To a mixture of 0.3 part of 7,8,8-tricyano-7-(1'-pyrrolidino)quinodimethane in 220 parts of THF was added 0.74 part of *n*-butylamine. The reaction mixture was let stand four hours at room temperature and the solid product removed by filtration. There was thus obtained 0.18 part of crude 7-*n*-butylamino-8,8-dicyano-7-(1'-pyrrolidino)quinodimethane as a pale yellow solid melting at 105–134° C. with decomposition. After recrystallization from acetonitrile the pure 7-*n*-butylamino-8,8-dicyano-7-(1'-pyrrolidino)quinodimethane was obtained as pale yellow crystals melting at 267–269° C. with decomposition.

Analysis.—Calcd. for $C_{18}H_{22}N_4$: C, 73.4%; H, 7.5%; N, 19.0%. Found: C, 73.6%; H, 7.4%; N, 19.4%.

The same product was obtained by adding 0.085 part of pyrrolidine to a mixture of 0.08 part of 7-*n*-butylamino-7,8,8-tricyanoquinodimethane in 8.88 parts of THF. A precipitate formed immediately. The reaction mixture was let stand for 21 hours at room temperature and the solid then removed by filtration. The filter cake was washed with diethyl ether to afford 0.07 part of 7-*n*-butylamino-8,8-dicyano-7-(1'-pyrrolidino)quinodimethane as a yellow-red solid. After recrystallization from an acetonitrile/diethyl ether mixture, there was thus obtained 0.02 part of pure 7-*n*-butylamino-8,8-dicyano-7-(1'-pyrrolidino)quinodimethane as pale pink crystals melting at 261–262° C. with decomposition. A mixed melting point with the preceding product showed no depression (259.5–264° C. with decomposition). The infrared spectra of the two products were also identical.

EXAMPLE XI

To a mixture of 0.5 part of 7,8,8-tricyano-7-(1'-pyrrolidino)quinodimethane and 13.3 parts of THF was added 8.88 parts of THF saturated with dry ammonia. The mixture was stirred for 15 minutes and then allowed to stand at room temperature for two hours. After cooling in an ice/water bath, the yellow-tan crystals of crude 7-amino-8,8-dicyano-7-(1'-pyrrolidino)quinodimethane were removed by filtration. After drying, there was thus obtained 0.465 part (98% of theory) of the aminodicyanopyrrolidinoquinodimethane. After two recrystallizations from a mixture of dimethylformamide and diethyl ether,

the pure 7-amino-8,8-dicyano-7-(1'-pyrrolidino)quinodimethane was obtained as yellow microcrystals melting at 308.5–310° C. with decomposition.

Analysis.—Calcd. for $C_{14}H_{14}N_4$: C, 70.6%; H, 5.9%; N, 23.5%. Found: C, 70.5%; H, 6.1%; N, 23.9%, 24.1%.

EXAMPLE XII

To a solution of the two parts of TCNQ in 169 parts of THF was added 17.8 parts of THF containing 2.43 parts (5.5 molar proportions based on the TCNQ) of dimethylamine. The resulting solution was allowed to stand at room temperature for 17 hours and was then concentrated in vacuo to one quarter the original volume. The concentrate was diluted 50% by volume with diethyl ether and the resultant reaction mixture filtered. There was thus obtained 1.75 parts (74% of theory) of 7,7-bis(dimethylamino)-8,8-dicyanoquinodimethane as yellow crystals melting at 213–232° C. with decomposition. Recrystallization from a mixture of methanol and diethyl ether followed by recrystallization from a mixture of acetonitrile and diethyl ether afforded the purified 7,7-bis(dimethylamino)-8,8-dicyanoquinodimethane as yellow-orange crystals melting at 232–236° C. with decomposition.

Analysis.—Calcd. for $C_{14}H_{16}N_4$: C, 70.0%; H, 6.7%; N, 23.3%. Found: C, 70.0%; H, 7.0%; N, 23.2%, 23.5%.

EXAMPLE XIII

To a solution of two parts of TCNQ in 169 parts of THF was added a solution of 2.53 parts of THF containing 0.346 part (1.26 molar proportions based on the TCNQ) of dimethylamine. The solution turned dark green, and after one hour at room temperature dark crystals began to form. The reaction mixture was let stand for 20 additional hours at room temperature under nitrogen and the resulting purple mixture filtered to afford 0.765 part of crude product. After recrystallization from acetonitrile, the mixed 2/1 TCNQ/dimethylammonium anion radical and 7-dimethylamino-7,8,8-tricyanoquinodimethane product were obtained as black crystals. Acetonitrile solutions of the crystalline product exhibited the characteristic absorption in both the ultraviolet and visible spectra for the TCNQ radical-anion (394, 740, and 840 millimicrons) and in addition showed absorption at 578 millimicrons ascribable to the presence of 15–20% of the 7-dimethylamino-7,8,8-tricyanoquinodimethane.

EXAMPLE XIV

To a hot solution of one part of TCNQ in 54.8 parts of acetonitrile was added 7.22 parts (14.7 molar proportions based on the TCNQ) of diisopropylamine. The solution was allowed to stand under nitrogen for three days at room temperature and an aliquot taken therefrom for ultraviolet spectral analysis. The sample exhibited strong absorption in the range 415, 740, and 840 millimicrons characteristic for the 2/1 TCNQ/amine radical-anion charge-transfer compounds, i.e., here for the 2/1 TCNQ/diisopropylammonium compound. In addition, there were also absorption bands at 223 millimicrons and at 320 millimicrons, which bands are characteristic for the bis-aminodicyanoquinodimethane substitution products, i.e., in this instance for 7,7-bis(diisopropylamino)-8,8-dicyanoquinodimethane.

EXAMPLE XV

To a mixture of 0.25 part of 7,8,8-tricyano-7-(1'-pyrrolidino)quinodimethane, 3.9 parts of acetonitrile, and 0.94 part of dimethylformamide was added dropwise with stirring hydrazine hydrate until a homogeneous yellow solution was obtained (about .06 part required). A large volume of diethyl ether was added and the supernatant liquid decanted from the resultant orange oil which

15

separated. Trituration of the oil in the presence of acetonitrile, coupled with scratching, caused the oil to solidify. There was thus obtained 0.182 part (73% of theory) 8,8-dicyano-7-hydrazino-7-(1'-pyrrolidino)quinodimethane as an orange-yellow solid melting at 205–210° C. with decomposition. On precipitation from a solution of dimethylformamide containing a small amount of acetonitrile by addition of diethyl ether, the purified dicyanohydrazinopyrrolidinoquinodimethane was obtained as pale yellow microcrystals melting at 217–223° C. with decomposition.

Analysis.—Calcd. for $C_{14}H_{15}N_5$: C, 66.4%; H, 6.0%; N, 27.6%. Found: C, 66.2%; H, 6.0%; N, 28.1%.

An aqueous solution of the 8,8-dicyano-7-hydrazino-7-pyrrolidinoquinodimethane dyed wool, silk, and nylon yellow fast to soaping.

EXAMPLE XVI

A mixture of one part of TCNQ, three parts (5.0 molar proportions based on the TCNQ) of p-anisidine, 59 parts of acetonitrile, and 24.8 parts of pyridine was refluxed under an atmosphere of nitrogen for one hour and then allowed to stand under nitrogen at room temperature for 22 hours. The reaction mixture was concentrated in vacuo, and the resultant solid residue was suspended in diethyl ether and filtered. After drying, there was obtained 1.41 parts (73% of theory) of 7,7-bis(p-anisidino)-8,8-dicyanoquinodimethane as dark crystals melting at 292–298° C. After repeated precipitation from dimethylformamide solution by addition of diethyl ether, the purified product was obtained as yellow crystals melting at 288–294° C. with decomposition.

Analysis.—Calcd. for $C_{24}H_{18}O_2N_4$: C, 72.7%; H, 5.1%; N, 14.1%. Found: C, 72.9%; H, 5.2%; N, 13.8%.

EXAMPLE XVII

A mixture of one part of TCNQ, 9.82 parts (18.7 molar proportions based on the TCNQ) of benzylamine, and 88.8 parts of THF was refluxed for two hours under an atmosphere of nitrogen. The solution was then allowed to stand under nitrogen at room temperature for 63.5 hours and then concentrated in vacuo. The dark, oily residue thus obtained was left standing in contact with diethyl ether containing a small amount of THF for several days, during which time the residue solidified. There was thus obtained 0.6 parts (34% of theory) of 7,7-bis(benzylamino)-8,8-dicyanoquinodimethane as a yellow solid melting at 231–257° C. with decomposition. Precipitation from ethanol solution containing a small amount of diethyl ether by addition of n-hexane and from acetonitrile solution by addition of diethyl ether afforded the pure 7,7-bis(benzylamino)-8,8-dicyanoquinodimethane as yellow crystals melting at 244–246° C. with decomposition.

Analysis.—Calcd. for $C_{24}H_{20}N_4$: C, 79.1%; H, 5.5%; N, 15.4%. Found: C, 78.9%; H, 5.7%; N, 15.7%.

EXAMPLE XVIII

To a warm solution of one part of TCNQ in 47 parts of acetonitrile was added 0.4 part (1.36 molar proportions) of ethylenediamine. A green color formed, and a precipitate began to form immediately. After standing for 1.5 hours at room temperature, the mixture was filtered giving 0.927 part (90% of theory) of yellow-green solid 7,7-ethylenediamino-8,8-dicyanoquinodimethane which can also be named 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)imidazoline. Precipitation from dimethylformamide solution by the addition of ether gave a purified yellow solid product which did not melt up to 405° C.

Analysis.—Calcd. for $C_{12}H_{10}N_4$: C, 68.6%; H, 4.8%; N, 26.7%. Found: C, 68.1%; H, 4.8%.

16

EXAMPLE XIX

A mixture of 0.57 part of 7,8,8-tricyano-7-(1'-pyrrolidino)quinodimethane, 35.6 parts of methanol, and a catalytic amount of sodium methoxide was heated at steam bath temperatures until a yellow-red solution was formed. The solution was filtered and the solvent evaporated from the filtrate in vacuo. Cyclohexane containing a small amount of diethyl ether was then added to the residue and the resultant precipitate removed by filtration. There was thus obtained 0.277 part (48% of theory) of 8,8-dicyano-7-methoxy-7-(1'-pyrrolidino)quinodimethane as yellow crystals. After two recrystallizations from an about 1/2 part by volume acetone/diethyl ether mixture, the purified dicyanomethoxypyrrolidinoquinodimethane was obtained as yellow crystals melting at 128–129° C. turning blood-red at the melting point.

Analysis.—Calcd. for $C_{15}H_{15}N_3O$: C, 71.1%; H, 6.0%; N, 16.6%. Found: C, 71.4%; H, 6.0%; N, 16.3%, 16.6%.

The ultraviolet spectrum of the product exhibited characteristic absorption at 222 and 402 millimicrons. The infrared spectrum showed absorption at 2180 and 2140 cm^{-1} , characteristic of conjugated nitrile groups. There was no absorption characteristic of O—H or N—H groups.

EXAMPLE XX

To a stirred solution of 0.54 part of sodium methoxide in 79.3 parts of methanol was added rapidly under nitrogen a solution of one part of TCNQ in 102 parts of THF. The reaction mixture was let stand for one half-hour at room temperature and the orange solution then concentrated in vacuo to an oily residue. THF (88.8 parts) was added with stirring and the resultant precipitate removed by filtration. The filtrate was concentrated in vacuo to an orange oil which on treatment with diethyl ether solidified. Upon filtration there was obtained 0.7 part (67% of theory) of 8,8-dicyano-7,7-dimethoxyquinodimethane as a hygroscopic orange solid. The infrared spectrum of the product shows absorption at 2190 and 2130 cm^{-1} , characteristic of the conjugated nitrile function and is wholly in accord with the 8,8-dicyano-7,7-dimethoxyquinodimethane structure.

EXAMPLE XXI

To a stirred solution of 0.681 part of sodium ethoxide in 78.9 parts of ethanol was added a solution of one part of TCNQ in 88.8 parts of the THF over a period of 15 minutes under nitrogen. The reaction mixture was stirred at room temperature for an additional hour, and the green solution was then concentrated in vacuo to a brown gum which solidified on scratching in the presence of a THF/diethyl ether mixture. The resulting brown solid was heated to the reflux with 134 parts of THF and the resultant mixture filtered. The filtrate was concentrated in vacuo, giving a tan-green oil which solidified on scratching in the presence of a THF/diethyl ether mixture. Upon filtration there was obtained 0.87 part (73% of theory) of 8,8-dicyano-7,7-diethoxyquinodimethane as a yellow-tan solid melting at 187–200° C. with decomposition. The infrared spectrum of the product showed absorption at 2190 and 2140 cm^{-1} , characteristic of conjugated nitrile groups, and at 1675 cm^{-1} , characteristic of the $C=C(OR)_2$ group, at 1605 cm^{-1} characteristic of the $C=C(CN)_2$ group, and at 1080 cm^{-1} characteristic of the C—O—C group.

EXAMPLE XXII

To a warm solution of one part of TCNQ in 47 parts of acetonitrile was added 0.336 part (1.1 molar proportion based on TCNQ) of ethanolamine. Crystals began to precipitate almost at once. After standing 2.5 hours at room temperature, the mixture was filtered giving 0.570 part (55% of theory) of yellow-green crystals of 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)oxazolidine,

which did not melt up to 400° C. although extensive reddening occurs. Recrystallization from dimethylformamide-ether with the help of decolorizing charcoal give bright yellow microcrystals which did not melt up to 400° C.

Analysis.—Calcd. for $C_{12}H_9N_3O$: C, 68.2%; H, 4.3%; N, 20.0%. Found: C, 68.1%; H, 4.2%; N, 19.7%.

EXAMPLE XXIII

To a warm solution of one part of TCNQ in 77 parts of acetonitrile was added five parts (5.5 molar proportions based on TCNQ) of n-dodecylamine. The mixture was let stand at room temperature for three days and then filtered to give 2.37 parts (90% of theory) of waxy yellow 7,7-bis(dodecylamino)-8,8-dicyanoquinodimethane, M.P. 188–206° C. with decomposition. Two recrystallizations from acetonitrile afforded the purified product, M.P. 214–216° C. with decomposition.

Analysis.—Calcd. for $C_{34}H_{56}N_4$: C, 78.4%; H, 10.8%; N, 10.8%. Found: C, 78.3%; H, 10.9%; N, 10.6%.

EXAMPLE XXIV

To a mixture of one part of 7,8,8-tricyano-7-(1'-pyrrolidino)quinodimethane and 12 parts of acetonitrile was added approximately two parts of hydrazine hydrate. The resulting solution was treated with a large volume of ether, and the precipitated oil was separated and scratched in the presence of a 1/1 mixture of ether and acetonitrile which caused solidification. Filtration gave 0.560 part of orange solid which on recrystallization from dimethylformamide-ether gave 0.470 part of yellow solid which turns red at 215° C. but did not melt up to 400° C. Recrystallization from dimethylacetamide-ether afforded the pure 7,7-bishydrazino-8,8-dicyanoquinodimethane as a yellow solid which did not melt up to 400° C.

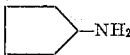
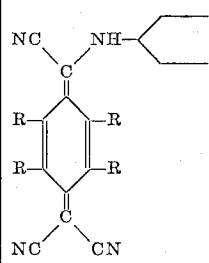
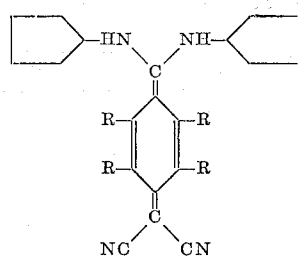
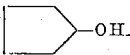
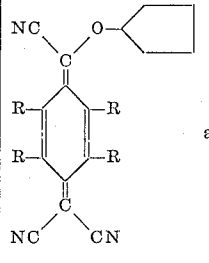
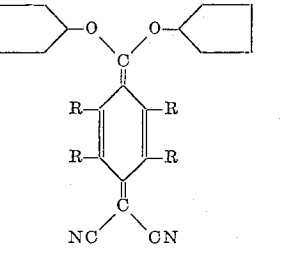
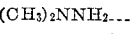
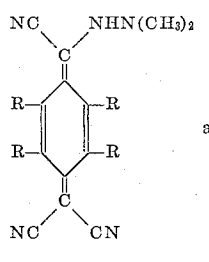
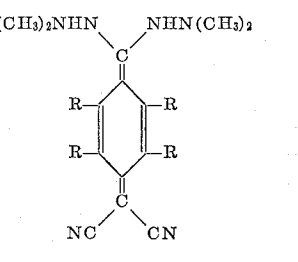
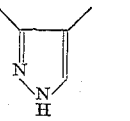
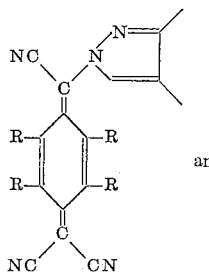
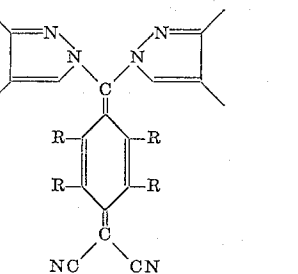
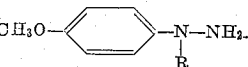
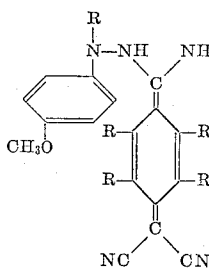
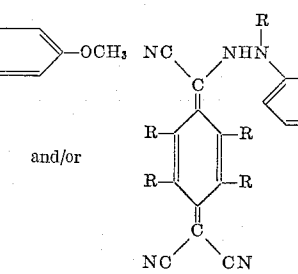
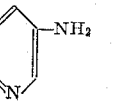
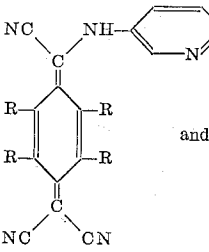
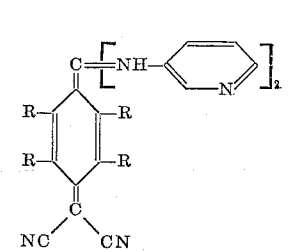
Analysis.—Calcd. for $C_{10}H_{10}N_6$: C, 56.1%; H, 4.7%; N, 39.2%. Found: C, 56.3%; H, 5.1%; N, 38.0%.

The infrared spectrum showed strong N—H absorption at 3300 and 3200 cm^{-1} and at 1680 cm^{-1} , conjugated $C\equiv N$ at 2175 and 2125 cm^{-1} , and no $—CH_2—$ absorption at 1460–1470 cm^{-1} .

As illustrated in the foregoing specific examples, a wide variety of amino hydrogen-bearing amines and hydroxyl hydrogen-bearing hydroxy compounds can be used in preparing the amino- and ether-substituted tricyano- and dicyanoquinodimethanes of the present invention. Also as illustrated in these specific examples, mixed type compounds likewise fall within the purview of the invention, i.e., 7,7-di-substituted-8,8-dicyanoquinodimethanes, wherein one of the 7-substituents is an amino substituent and the other is an ether substituent. These mixed substituents can likewise be together joined. Also as illustrated in the foregoing examples, mixed disubstituted amino and ether compounds, wherein two different amino or ether substituents are present in the same molecule, also form part of the present invention. These mixed disubstituted amino and ether compounds can, of course, be obtained by reaction of equimolar proportions of the two different amino hydrogen-containing or hydroxyl hydrogen-containing coreactants with one molar proportion of the tetracyanoquinodimethane. However, using such techniques it is obvious that mixtures of the two symmetrical disubstituted compounds with the desired mixed disubstituted compound will be obtained. If such mixed disubstituted products are desired, it will be preferred, as illustrated in these examples, that one molar proportion of one of the coreactants be reacted with one molar proportion or thereabouts of the tetracyanoquinodimethane to prepare as an intermediate the 7-mono-substituted-7,8,8-tricyanoquinodimethane which will then be reacted with one molar proportion of the second amino hydrogen- or hydroxy hydrogen-containing requisite coreactant to form the desired mixed disubstituted product.

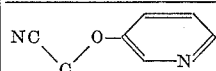
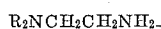
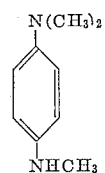
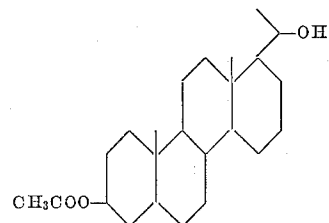
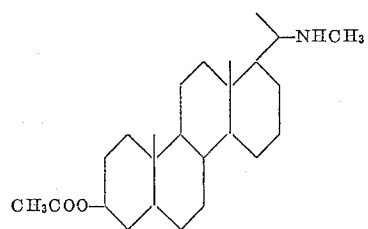
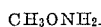
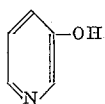
In addition to the foregoing detailed examples, further specific examples of the amino hydrogen-bearing and hydroxy hydrogen-bearing coreactants for reaction with tetracyanoquinodimethane and the alkyl-substituted tetracyanoquinodimethanes and the products obtained therefrom using the technique just specifically described are found in the following list where R is as before, i.e., hydrogen or monovalent saturated aliphatic hydrocarbon radical (alkyl) of no more than eight carbons:

Coreactant	Product
$H_2N(CH_2)_8NH_2$	
$HO(CH_2)_8OH$	
$HOCH_2OH$	

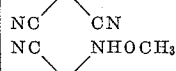
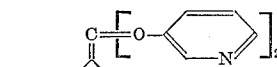
Coreactant	Product
	 and/or 
	 and/or 
	 and/or 
	 and/or 
	 and/or 
	 and/or 

Coreactant

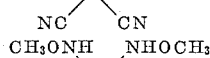
Product



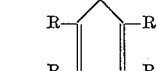
and/or



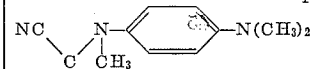
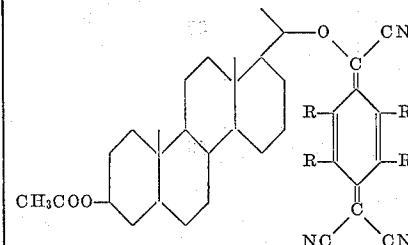
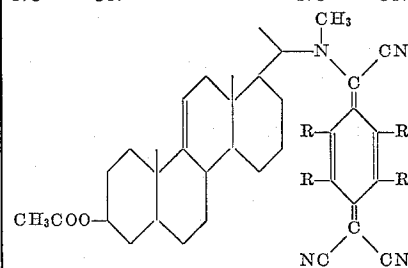
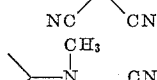
and/or



and/or

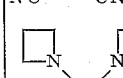
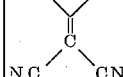
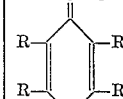


and/or

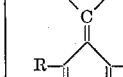
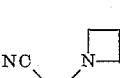


or

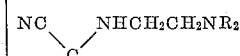
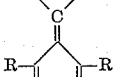
and or disubstitution product



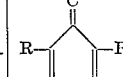
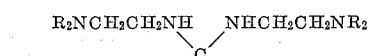
and/or



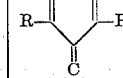
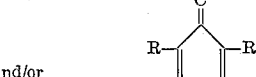
and/or



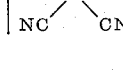
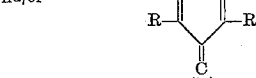
and/or



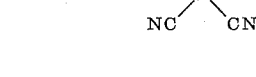
and/or

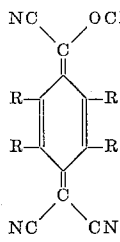
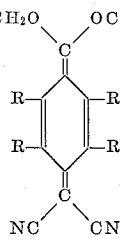


and/or



and/or



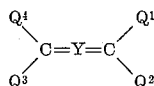
Coreactant	Product
$R_2NCH_2CH_2OH$	$R_2NCH_2CH_2O$
	

In all the foregoing primary amines, i.e., those carrying one or more $-NH_2$ substituents, one of the hydrogens on one or all of the said $-NH_2$ substituents can be replaced by a radical R' of the type discussed previously in the stoichiometry, which radical R' can be alike or different to the radical on which the said $-NH_2$ substituent is already pendent in the case of the primary amines.

As illustrated in the foregoing detailed examples, the mono- and diamino and ether or mixed amino ether condensation products of tetracyanoquinodimethane are generically colored compounds tending toward the deep shades which are generically useful as dyes, for instance, as gasoline dyes, as well as dyes for use in coloring textiles, threads, fabrics, and the like, by conventionally used dyeing techniques.

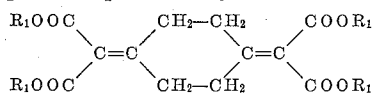
The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. Compounds represented by the formula



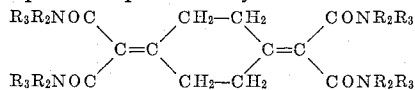
wherein Q^1 , Q^2 , Q^3 , and Q^4 are members of the class consisting of $COOR_1$, $CONR_2R_3$, COX , and CN , where R_1 , R_2 , and R_3 are selected from the group consisting of hydrogen and hydrocarbyl radicals of from 1 to 30 carbons and free of aliphatic unsaturation, and X is halogen, and Y is a member of the class consisting of 1,4-cyclohexadiylidene and alkyl-substituted 1,4-cyclohexadiylidene and 1,4-cyclohexadienediylidene and alkyl-substituted 1,4-cyclohexadienediylidene groups, said alkyl radicals being of from 1-8 carbons.

2. Compounds represented by the formula



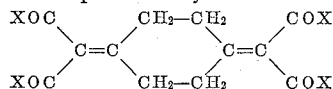
wherein R_1 is a hydrocarbyl radical of from 1 to 30 carbons and free of aliphatic unsaturation.

3. Compounds represented by the formula



wherein R_2 and R_3 are hydrocarbyl radicals of from 1 to 30 carbons and free of aliphatic unsaturation.

4. Compounds represented by the formula

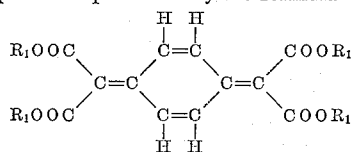


wherein X is halogen.

5. 1,4-bis(dicyanomethylene)cyclohexane.

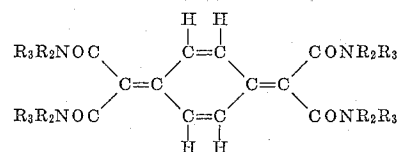
6. 1,4-bis(dicyanomethylene)-2-methylcyclohexane.

7. Compounds represented by the formula



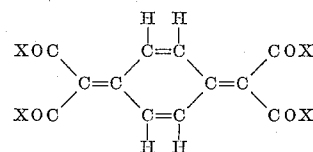
wherein R_1 is a hydrocarbyl radical of from 1 to 30 carbon atoms and free of aliphatic unsaturation.

8. Compounds represented by the formula



wherein R_2 and R_3 are hydrocarbyl radicals of from 1 to 30 carbons and free of aliphatic unsaturation.

9. Compounds represented by the formula

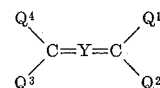


wherein X is halogen.

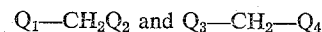
10. 1,4-bis(dicyanomethylene)cyclohexadiene.

11. 1,4-bis(dicyanomethylene)-2-methylcyclohexadiene.

12. Process for preparing 1,4-bis(bisubstitutedmethylene)cyclohexadiene compounds of the formula

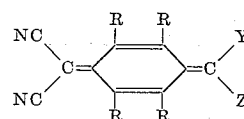


wherein Q^1 , Q^2 , Q^3 , and Q^4 are members of the class consisting of $COOR_1$, $CONR_2R_3$, COX , and CN , where R_1 , R_2 , and R_3 are selected from the group consisting of hydrogen and hydrocarbyl radicals of from 1 to 30 carbons and free of aliphatic unsaturation, and X is halogen, and Y is a member of the class consisting of 1,4-cyclohexadienediylidene and alkyl-substituted 1,4-cyclohexadienediylidene groups, said alkyl radicals being of from 1-8 carbons, which comprises reacting, in the presence of a catalyst, said catalyst being a member of the class consisting of acids, bases and salts which ionize in water to give acidic or basic solutions, a member of the class consisting of 1,4-cyclohexanedione and alkyl-substituted 1,4-cyclohexanediones, said alkyl radicals being of from 1-8 carbons, with from 1 to 2 disubstitutedmethylene compounds having the formulas



wherein the Q 's have the same significance as above, and isolating the 1,4-bis(disubstitutedmethylene)cyclohexane compound, which compound is then oxidized by halogenation/dehydrohalogenation reactions to the said 1,4-bis(disubstitutedmethylene)cyclohexadiene compound.

13. Compounds of the formula



wherein Y and Z are members of the class consisting of $-CN$, $-NR_1R_2$, and $-OR_1$ radicals, Y and Z being alike

25

or different, except that no more than one of Y and Z is cyano; R_1 and R_2 are members of the class consisting of hydrogen and monovalent hydrocarbon radicals of 1 to 18 carbon atoms free of aliphatic unsaturation; and R is a member of the class consisting of hydrogen and alkyl hydrocarbon radicals of from 1 to 8 carbon atoms. 5

14. Process for preparing compounds of claim 13 which comprises reacting a member of the class consisting of 7,7,8,8-tetracyano-p-quinodimethane and 7,7,8,8-tetracyano alkyl-substituted p-quinodimethanes, said alkyl radicals being of from 1-8 carbons, with from 1 to 2 molar proportions of a compound of the group consisting of 10



wherein R_1 and R_2 are members of the class consisting of hydrogen and monovalent hydrocarbon radicals of 1 to 18 carbon atoms free of aliphatic unsaturation and 15



wherein R_1 has the same significance as above and M represents a metal of the class consisting of alkali metals and alkaline earth metals. 20

26

References Cited in the file of this patent

UNITED STATES PATENTS

2,759,011	Soloway	Aug. 14, 1956
2,834,800	Trapp et al.	May 13, 1958
2,859,239	Trapp et al.	Nov. 4, 1958
2,953,454	Bergman	Sept. 20, 1960
3,004,042	Coppinger	Oct. 10, 1961
3,009,924	Schubert et al.	Nov. 21, 1961
3,042,519	Wainer	July 3, 1962

OTHER REFERENCES

- Chemical Abstracts, vol. 40, page 5025^a (1946).
 J. of Organic Chemistry, vol. 18, page 932 (1953) (Prowt).
 J. of Organic Chemistry, vol. 20, pages 13-32 (1955) (Talukdar et al.).
 Bailar: "Chemistry of the Coordination Compounds," pages 556-8 (1958).