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PREPARATION OF ACETOPHENONE FROM ALPHA-METHYL STYRENE

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2 Claims. (Cl. 260—592)

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The present invention is primarily concerned with the preparation of certain nitrogenous addition compounds of aralkenes as well as with the utilization of these addition compounds as intermediates for the preparation of aromatic carbonyl compounds. The invention also contemplates starting with crude hydrocarbon mixtures, such as petroleum oil fractions, as source materials for the required nitrogenous intermediates.

I have discovered that olefinic compounds generally, react quantitatively with nitrogen tetroxide, while only selected types of olefins, such as aralkene-1 compounds, for example styrene and its homologues, also react quantitatively with nitrogen trioxide as well as with nitrogen tetroxide. If the reaction is carried out in the presence of a mixed hydrocarbon fraction, the nitrogenous addition products thereby formed in either case from these aromatic olefinic compounds can be readily separated for example from cycloaliphatic and acyclic hydrocarbons or their addition products that may be present in the reaction mixture, as well as from unreacted aromatic carbocyclic compounds free from side chain unsaturates. Accordingly, an excellent method is thereby provided for preparing hydrocarbon fractions free from undesired olefinic unsaturates. The nitrogenous addition compounds formed, furthermore, can be employed as useful intermediates for the preparation of valuable organic compounds, particularly by conversion to carbonyl compounds such as aldehydes and ketones, as hereinafter appears. Thus, starting with relatively inexpensive crude hydrocarbon fractions, such as petroleum or other mineral oil distillates, one can readily obtain not only relatively pure fractions of desired saturated aliphatic or aromatic hydrocarbons, but in addition a convenient source is furnished for important intermediates, and conversion products of these intermediates.

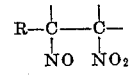
The purification of petroleum and other mineral fractions generally, is more fully described and claimed in my copending application, Serial No. 725,725, filed of even date herewith. The present application is more particularly concerned with the nitrogenous addition compounds of aromatic olefins, such as those formed from compounds of the styrene type.

In accordance with the invention, a hydrocarbon oil containing an aralkene-1 compound, such as styrene or its homologues, is treated with an oxy compound of nitrogen selected from the group consisting of nitrogen trioxide and nitrogen tetroxide under conditions avoiding thermal

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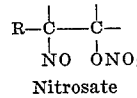
decomposition. As a result of the principal reaction, the olefinic side chain reacts to form nitroso addition compounds such as nitrosites and nitrosates respectively, which can be easily separated from the unreacted components by steam distillation or other means such as selective solvent extraction, as will hereinafter appear. The nitrosites and nitrosates thus formed, with or without previous separation from the unreacted components, may be further converted in accordance with the invention to aromatic carbonyl compounds, such as ketones and aldehydes, by reaction with an alkaline material, also under conditions avoiding thermal decomposition.

The reaction of the designated nitrogen oxides with the olefinic hydrocarbons takes place in either vapor or liquid phase. In such reactions between aralkene-1 compounds and N_2O_3 or N_2O_4, the addition of the nitrogen oxide takes place selectively at the olefinic double bond. According to related reactions described in the literature, with N_2O_3 the nitroso compounds formed are believed to correspond to the structure



Nitrosite

while with N_2O_4 the compounds obtained are believed to have the structure



Nitrosate

Since other tautomeric arrangements are also possible and likewise consistent with the observed reactions of these nitroso compounds herein described, the exact arrangements shown in the formulae are not material to the present invention, and applicant does not desire to be bound thereby. R in the above formulae represents a hydrocarbon radical of the benzene series (which may be nonfunctionally substituted) including thereby polycyclic hydrocarbon radicals such as naphthalene and alkylated naphthalenes, and the indicated free bonds may be attached to hydrogen or to alkyl radicals.

The physical state of these nitroso compounds depends to a large extent upon their purity. For instance, styrene nitrosites and α-methyl styrene nitrosites, when relatively pure, are crystalline; the nitrosates are more often oily, although in some instances crystalline nitrosates of styrene

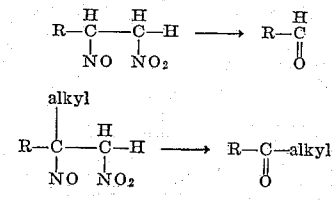
derivatives are obtained. In reactions involving the treatment of a hydrocarbon mixture containing aralkene-1 compounds with N_2O_4, the hydrocarbon mixture is contacted with the N_2O_4 under such conditions that the strongly exothermic reaction takes place preferably in the range of 80 to 100° F. The desired temperature range may be obtained by controlling the rate of admission of the N_2O_4 vapors and by the further provision of heat exchange if necessary or desired. The N_2O_4 may be obtained in vapor form from any suitable source such as by volatilization of liquid nitrogen tetroxide at suitable temperatures. The N_2O_4 vapor is introduced directly into the body of the hydrocarbon liquid and thorough contact of the reactants may be enhanced by agitation during treatment. The completion of the reaction is readily ascertained by the cessation of the exothermic phenomenon (significant temperature decline) and by the marked formation of brown fumes above the surface of the liquid being treated. When it is observed from these indications that the reaction has gone to completion, further addition of N_2O_4 should be stopped. Any excess N_2O_4 in the reaction products may be destroyed by the addition of water to convert the same to nitric and nitrous acids, or by other well known methods such as the addition of aqueous solutions of sulfamic acid as is done in the azo dye industry, or by the addition of aqueous solution of urea to destroy nitrous acid.

The reaction with N_2O_3 is conducted generally in a similar manner. N_2O_3 may be derived from any suitable source, such as by reaction of an acid with a nitrite under conditions insuring the absence of any oxidizing agent. The nitrogen trioxide is contacted with the olefin-containing hydrocarbon liquid with control of flow rate and temperature similarly to that described above in the N_2O_4 treatment. Completion of the reaction is indicated by the cessation of the exothermic phenomenon or the appearance of excess N_2O_3. In the case of the nitrosites particularly, separation of the reaction products is readily effected by physical means, since the reaction products are generally solids (crystalline), or in cases where gummy or oily materials are formed, they are sufficiently different in density and other properties from the unreacted portions to permit physical separation. Unless all of the desired nitrogenous addition compounds formed are solid materials, it is preferred to effect separation by steam distillation, and even in instances where solid products are involved, steam distillation may be employed to advantage.

The described reaction of N_2O_3 and N_2O_4 takes place not only with aralkene-1 compounds but also with acyclic, and non-aromatic cyclic, conjugated diolefins. Significant differences in the reactions of N_2O_3 and N_2O_4, however, were observed with mono-olefins, such as those present in hydrocarbon distillates boiling in the gasoline boiling range. Although N_2O_4 does react with these mono-olefin compounds to form nitrosates, as a general rule N_2O_3 does not so react or reacts only to a limited extent in some instances, as in the case of cyclo-hexene and di-isobutylene.

I have observed that some of the indicated nitrogenous addition compounds of olefins, for instance styrene nitrosite, on long standing apparently undergo a rearrangement, since they become less reactive with alkaline substances to form the carbonyl compounds. To obtain maximum yields of the desired carbonyl compounds, therefore, it is preferred to employ freshly prepared nitrosites or nitrosates. The character of the change which takes place on standing cannot be fully explained, but I have also observed that styrene nitrosite treated with ferrous sulfate or with hydrochloric acid, similarly is rendered less-reactive with alkali to form the carbonyl compounds. Also after refluxing styrene nitrosite in water at or near boiling, only very small yields of benzaldehyde are obtained by subsequent reaction with alkaline solutions and appreciable amounts of nitrobenzene are formed.

The nitrogenous addition compounds formed with either the N_2O_3 or N_2O_4, are converted to carbonyl compounds such as aldehydes and ketones, in accordance with the invention, by reaction with an aqueous solution of an alkaline material. Whether aldehydes or ketones will be formed depends upon the arrangement of the carbon atoms in the starting olefin, as illustrated by the following equations:



It will be readily understood that it is not necessary to employ a crude petroleum hydrocarbon fraction as the starting material for the preparation of the nitrosites or nitrosates; relatively pure raw materials may be used. One of the more important advantages of the present invention, however, lies in the ability to resort to crude distillates containing the desired olefins preferably in a fraction of narrow boiling range. Thus, a crude naphtha produced by high temperature cracking may be solvent extracted to produce an extract containing aromatic materials including styrene, olefins, and diolefins. By treatment with N_2O_4, nitrosates are formed of the unsaturated materials, which may then be separated from substantially pure saturated aromatics, inasmuch as the reactions to form these nitroso compounds apparently go to completion. Alternatively, one may employ N_2O_3 for the treatment of the solvent extract, whereby the nitrosites of the styrene type compounds and of the conjugated diolefins are formed, leaving substantially unreacted the mono-olefin content of the naphtha. The aromatics may be further purified by the removal of these remaining olefins by treatment with N_2O_4 to form the nitrosates of the olefins. The nitrosates and nitrosites may be removed from the treated naphtha as by distillation. Thus, the naphtha may be steam distilled, leaving the nitrosite or nitrosate as a residue. If desired, the nitrosite or nitrosate may be precipitated by dilution of the treated naphtha with petroleum ether or the like and then removed as by filtration or decantation. Alternatively, the nitrosate or nitrosite in the treated naphtha may be decomposed and the unreacted portions of the naphtha then separated, as by distillation.

Although nitroso compounds of the type above described are decomposed thermally to an uncontrollable variety of different decomposition products, in accordance with the present invention, an entirely different type of decomposition is effected by reaction of the nitroso compounds with aqueous alkaline materials, under controlled conditions. Temperatures at which the nitroso compounds tend to undergo thermal decomposition

should be avoided to favor good yields of the desired carbonyl derivatives. Any of a number of inorganic bases or alkaline materials may be employed for effecting the decomposition of the nitroso compound, such as alkali—and alkali earth metal hydroxides or carbonates and alkali metal bicarbonates; for example, caustic soda, sodium carbonate, sodium bicarbonate; calcium carbonate, magnesium carbonate, etc. Although ammonium hydroxide is operative for the purpose, lower yields are generally obtained therewith because of side reactions of NH_3 with the nitrosates or nitrosites.

Organic bases would be expected to have the same tendency to side reactions as occurs with the ammonium hydroxide. For maximum yields, to preclude or diminish side reactions, it is preferred to employ the more strongly alkaline materials in dilute aqueous solution.

For optimum results, the quantity of alkaline material employed should be about or at least that furnishing hydroxyl ions in an amount which is the molal equivalent of the nitroso compound to be reacted. A lesser amount of alkaline material, being insufficient to react with all of the nitrogenous product present, naturally results in reduced yields. Too great an excess of alkaline material on the other hand also progressively decreases the yield because of the increasing tendency to promote side reactions. It was found as a general rule that good yields were obtainable with 10% aqueous solutions of sodium hydroxide in an amount about double the weight of the nitrosate or nitrosite present.

In the initial reaction of the N_2O_3 or N_2O_4 with the olefin containing fraction, a wide range of temperatures may be employed; formation of nitroso compounds have been obtained at temperatures ranging from below 32° F. (with liquid butene) to somewhat above 130° F. It is preferred, however, to carry out the reaction at about room temperature or slightly above as in the range of 80 to 100° F. At low temperatures the yields are poorer and less stable reaction products are obtained, while at temperatures above 100° F. the tendency towards undesirable side reactions increases. The use of superatmospheric pressure is unnecessary and it is preferred to carry out the reaction at atmospheric pressure or if desired at subatmospheric pressures. Higher pressure may be used when it is not extended to the point of causing undesirable side reactions such as oxidation, nitration, and others which may occur. The reaction of the nitrogen oxides with the indicated unsaturated hydrocarbons proceeds rapidly so that time limitations are imposed only by operating conditions to assure completeness of the reaction. For complete reaction the amount of nitrogen oxide, whether it be N_2O_3 or N_2O_4, should be at least one mol of the oxide for each bond of olefinic unsaturation. Excess nitrogen oxide should be destroyed, as described.

No universal rule can be stated as to the choice between the use of N_2O_3 and N_2O_4 in the formation of the nitroso compound as an intermediate. It was found that better yields of benzaldehyde were obtainable from styrene nitrosite, whereas in the preparation of acetophenone better yields were obtained from α-methyl styrene nitrosate than from the corresponding nitrosite. The reaction of the styrene- and α-methyl styrene nitroso compounds with aqueous alkaline solutions to yield respectively benzaldehyde and acetophenone begins to take place at room temperature; at higher temperatures the reaction proceeds more rapidly. In the case of benzaldehyde and similar products which are recovered by steam distillation, the reaction is preferably conducted simultaneously with such distillation. Temperatures above those encountered in steam distillation should in any event be avoided; although formation of the aldehyde does occur at the higher temperature, the yield of pure aldehyde is decreased because of undesirable side reactions such as polymerization of the aldehyde, formation of sodium benzoate, or the like. In the case of acetophenone and like compounds, conditions similar to those described in connection with benzaldehyde are preferably employed. Even if the separation of the aldehyde or ketone is not to be effected by steam distillation, it is nevertheless advisable to avoid the higher temperatures in the reaction of the nitroso compound with the alkaline material. The reaction of the alkaline material with nitrosate or nitrosite occurs relatively independently of pressure, so that pressure considerations are concerned mainly with the equipment limitations, time of operation, and temperature limitations.

The selectivity and effectiveness of the described nitrosation method in removing olefinic unsaturates from hydrocarbon mixtures, is illustrated by the following typical experiment:

Example I

A sample of a synthetic mixture of paraffin-naphthene base (acid treated gasoline range material) containing 10% styrene, was treated with N_2O_3 until excess of nitrous fumes showed completion of reaction. The precipitate formed during the reaction was separated by filtration and the residual oil, 90% by volume of the original, was washed with about 5 volumes of 10% caustic solution, then washed with a small amount of sodium bisulphite solution to remove traces of benzaldehyde, again washed with a small amount of 10% caustic solution, then water washed to remove excess caustic, dried over calcium chloride, and distilled to 294° F. cut-point. The distillate had the following properties, indicating complete removal of styrene.

Refractive index (n_D^{20}), 1.4189

Specific gravity (d_4^{20}), 0.7523

Bromine number (ASTM), 0.0

Specific dispersion, $\frac{(n_F - n_C)}{d} 99$

In the above example the reference to "acid treated gasoline range material" denotes a residue resulting from treatment of a gasoline fraction with acid in conventional manner for analytic determination of the amount of aromatics and olefins by their absorption in the treating acid. The residue consisted essentially of paraffins and naphthenes, which residue was washed and neutralized, then dried. This washed residue gave no reaction with nitrogen oxides and was therefore satisfactory as a diluent or carrier for olefinic materials being tested.

To further show the selectivity of the reaction of the designated nitrogen oxides with olefinic materials preliminary experiments were carried out with aromatic hydrocarbons, such as benzene, which were found to be substantially non-reactive.

The formation of the nitroso compounds with olefinic unsaturates present in a crude hydrocarbon distillate, and the production of carbonyl

compounds therefrom are illustrated in the following examples:

Example II

A hydrocarbon synthetic mixture which included approximately 10% styrene and 90% acid treated gasoline range material was treated with N_2O_3 at room temperature until presence of excess N_2O_3 indicated completion of reaction. The crystalline precipitate which formed, was separated by filtration, washed with water, petroleum ether, and alcohol, and dried in vacuum at room temperature. A part of the now white to cream colored crystalline precipitate was mixed with aqueous 5% NaOH solution (approximately 20 cc. NaOH solution per gram of precipitate) and the resulting mixture was distilled until no more oil came over with the water. The distillate contained a colorless oil slightly heavier than water and with a strong odor of benzaldehyde.

To identify the benzaldehyde, the distillate was made slightly basic with a small amount of 10% NaOH aqueous solution and then oxidized with cold saturated $KMnO_4$ solution which was added in small increments until the persistence of the purple permanganate color indicated substantially complete oxidation of the solution.

The oxidized solution was acidified with HCl (conc.) and decolorized with H_2SO_3. A white crystalline precipitate formed upon acidification and was recovered by filtration. The filtrate was extracted with chloroform to recover any remaining material similar to the crystals and added, after separation from the chloroform to the main crystalline body. The melting point of the crystalline material was determined and found to be 250° F., the same as the melting point of U. S. P. benzoic acid.

Example III

A hydrocarbon fraction, distilled from a sample of dehydrogenated cumene boiling entirely at 260° F. at atmospheric pressure and containing approximately 90.0% α-methyl styrene was treat- with N_2O_4 with cooling to prevent temperature rise above 100° F. until excess N_2O_4 fumes indicated completion of reaction. The weight of the sample increased to 156% during this treatment. The treated sample was washed with water to remove excess N_2O_4 and unreacted hydrocarbons separated by steam distillation; the residue being the nitrosate. This liquid residue, specific gravity 1.23, was treated with approximately twice its volume of 10% NaOH solution and steam distilled. The distillate, which was identified as impure acetophenone, contained 80% by volume of material boiling within the range of 393° to 397° F., which portion amounted to approximately 40% by volume of the original α-methyl styrene.

This product is sufficiently pure for most industrial uses of acetophenone. Further purification may be effected, if desired, in the usual manner, for instance by redistillation or solvent extraction, or a combination of these steps.

Example IV

A sample of α-methyl styrene nitrosite was obtained by reacting a hydrocarbon fraction, similar to that used as the starting material in the preceding example, with N_2O_3 at room temperature until completion of the reaction between the N_2O_3 and the hydrocarbon was evidenced by no further evolution of heat on absorption of the N_2O_3. This methylstyrene nitrosite was purified in similar manner to the preceding example and the ketone

formed by reaction with sodium hydroxide solution as before. The only odor of the product was that of acetophenone, but the purity was considerably less than that obtained from the corresponding nitrosate as indicated by the boiling range in which 80% was found to boil between 354° F. and 405° F.

A purer nitroso compound can be obtained by a treatment of the original olefin-containing fraction with SO_2 prior to the treatment with the nitrogen oxide, the SO_2 treatment being carried out generally as described in my U. S. Patent 2,410,042 of October 29, 1946. The following example further illustrates the combined treatment.

Example V

(A) A synthetic sample comprised of 90% by volume of reformer naphtha from the destructive distillation of coal and 10% by volume of added styrene was subjected to treatment at room temperature with N_2O_3, to segregate the styrene as the nitrosite. When completion of the reaction was indicated by presence of excess N_2O_3, the precipitate formed was recovered by filtration. The results of two such treatments on portions of this sample showed removal of styrene (as the nitrosite) in amounts of, respectively, 9.7% and 10.1%. Discrepancies in yields indicate presence of impurities, in the gummy precipitate, which were removed by washing the precipitate prior to drying.

(B) Another portion of the original sample was saturated with SO_2 gas at approximately room temperature. After standing for about two and one-half hours, the oil was decanted from the small amount of blackish precipitate which had formed and settled during standing. The oil was washed several times with water and then washed twice with 10% by volume portions of 10% NaOH solution to remove excess SO_2. The separated oil was then subjected to a steam distillation. The recovered oil amounted to about 91% of the original sample.

The treated and distilled oil was then subjected to treatment with N_2O_3 in the same manner as the treatments effected on the samples in the paragraph (A). This time a fine white precipitate of styrene nitrosite was obtained. An alcohol extraction of the crystalline precipitate showed the presence of only traces of impurities. The result of this final treatment showed the removal of styrene (as the nitrosite), as based on the original sample, of 10.9%, indicating the presence of a small amount of styrene in the reformer naphtha. The experiment further indicated that purer styrene nitrosite is obtained by the preliminary treatment of the oil with SO_2.

The original sample had a bromine number of 34.4. After treatment in paragraph (A) the residual oil had bromine number of 18.1, while after treatment in section (B) it had a bromine number of 16.1.

The above described combined treatment with SO_2 and nitrogen oxide can be advantageously employed where the nitroso compound or carbonyl derivative therefrom is desired in unusually pure form. In addition, it will be understood that with a purer form of the nitroso compound better yields of the desired carbonyl compound requiring less extensive purification, are obtained.

Obviously many modifications and variations of the present invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and therefore only such limita-

tions should be imposed as are indicated in the appended claims.

The present application is a continuation-in-part of my application, Serial No. 528,948 filed March 31, 1944, now abandoned.

I claim as my invention:

1. The method of producing acetophenone which comprises reacting a hydrocarbon fraction rich in α-methyl styrene with N_2O_4 to form a nitrosate of said α-methyl styrene, continuing the reaction under controlled conditions maintaining the temperature thereof not in excess of 100° F. and until excess N_2O_4 forms indicating completion of the reaction, steam distilling the product to separate unreacted hydrocarbons leaving a residue containing said nitrosate, treating said residue with about twice its volume of 10% NaOH solution and steam distilling the alkaline reaction mass, thereby obtaining a distillate containing acetophenone.

2. The method in accordance with claim 1 wherein said hydrocarbon fraction is a purified

fraction obtained by treating a mineral oil fraction rich in α-methyl styrene, with sulfur dioxide in vapor form at approximately room temperature, removing any precipitate formed, washing the oil to remove excess sulfur dioxide, and steam distilling the washed oil.

GEORGE R. BOND, JR.

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