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ALKYLATION PROCESS

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This invention relates to a process for the alkylation of alkylatable aromatic compounds with alkylating agents containing at least three carbon atoms in the alkylating group in the presence of catalytic proportions of phosphorus pentafluoride.

One object of this invention is to provide novel catalysts for the alkylation of alkylatable aromatic compounds with alkylating agents containing at least three carbon atoms in the entering (alkylating) group. Another object is to provide a process for the alkylation of aromatic hydrocarbons having at least one alkylatable nuclear carbon atom with an alkylating agent containing at least three carbons in the alkylating group in the presence of PF_5 or a material furnishing PF_5 under the alkylation reaction conditions. An additional object is to provide a process for the alkylation of aromatic hydrocarbons having at least one alkylatable nuclear carbon atom with a monoolefinic hydrocarbon containing at least three carbon atoms per molecule in the presence of PF_5. A further object is to provide a process for the selective alkylation of alkylatable aromatic hydrocarbons with a terminal vinyl olefin containing at least three carbon atoms per molecule in the presence of ethylene. These and other objects of our invention will become apparent from the ensuing description thereof.

We have discovered that PF_5, or materials which furnish PF_5, in the alkylation zone under the conditions of the alkylation reaction, such as benzenediazonium hexafluorophosphate, function as catalysts for the alkylation of alkylatable aromatic compounds with olefinic hydrocarbons or other alkylating agents containing at least three carbon atoms per molecule. Since the alkylation process of this invention is broadly applicable to a large variety of aromatic compounds and alkylating reagents containing at least three carbon atoms in the alkylating group, the preferred reaction conditions cannot be indicated for each possible instance of the application of this invention; these are, however, readily determinable by simple small-scale routine experimentation.

The alkylation process of the present invention may be practiced with a variety of aromatic compounds such as alkylatable aromatic hydrocarbons or alkylatable derivatives of aromatic hydrocarbons, for example, substitution products such as halogen-, hydroxy-, alkoxy-, or other substitution derivatives of aromatic hydrocarbons. Specific examples which are supplied for purposes of illustration but not as limitations include monocyclic aromatic hydrocarbons containing at least one alkylatable nuclear carbon atom, for example, benzene, toluene, the isomeric xylenes, ethylbenzene, n-propylbenzene, isopropylbenzene, the ethyl toluenes, the ethyl xylenes, pseudocumene, hemimellitene, sec-butylbenzene, t-butylbenzene, isodurene, diethylbenzenes, prehnitene, isoamylbenzene or the like. Examples of dicyclic aromatic hydrocarbons containing an alkylatable nuclear carbon atom comprise tetralin, naphthalene; alkyl naphthalenes, such as 1-methylnaphthalene, 2-methylnaphthalene, 1-isopropylnaphthalene, 2-ethylnaphthalene, 2,6-dimethylnaphthalene, isopropylnaphthalene, and the like; diphenyl, alkyl-substituted diphenyls; indene, alkylindenes, dihydroindenes and the like. The alkylation process of this invention may also be applied to tricyclic aromatic hydrocarbons such as anthracene, alkyl anthracenes, phenanthrene and even to alkylatable aromatic hydrocarbons containing more than three rings. Examples of alkylatable aromatic compounds (which may be considered as derivatives of aromatic hydrocarbons) include various phenolic compounds, such as phenol, pyrocatechol, resorcinol, hydroquinone, pyrogallol; phenolic ethers such as phenetole, anisole, phenyl t-butyl ether and the like. Also included are halogenated aromatic hydrocarbons such as chlorobenzene, dichlorobenzenes, bromobenzene, fluorobenzene, iodobenzene, 2-chloronaphthalene, orthochlorotoluene, parachlorotoluene, etc.

The alkylating reagent employed in our process is an olefinic hydrocarbon containing at least three carbon atoms per molecule, or a functional equivalent thereof under the alkylation reaction conditions in the presence of PF_5 catalyst. By the term "olefin-acting compound" as used herein, we intend to define olefins and compounds which function like olefins under the reaction conditions, i. e. they react with the aromatic compounds to substitute therein a group containing at least three carbon atoms. By way of example, we may employ as alkylating agents various monoolefinic hydrocarbons and mixtures thereof, specifically propylene, 1-butene, 2-butene, isobutylene, 1-pentene, 2-pentene, 3-methylbutene, 2-methylbutene, various hexenes, heptenes, octenes, 1-dodecene; mixtures of isomeric dodecenes derived from the polymerization of isobutylenes or isobutylene-n-butenes, or from propylene; cyclic monoolefinic hydrocarbons such as cyclopentene, various alkyl cyclopentenes, cyclohexene, alkyl cyclohexenes such as 1-methyl cyclohexene, 4-methyl cyclohexene or the like; aromatic olefins such as styrene, alpha-methylstyrene, vinyl toluenes, chlorostyrenes and the like; (2,2,1)-bicycloheptene and alkyl derivatives thereof, particularly the 4-alkyl(2,2,1)-bicycloheptenes, and the like. Especially desirable are olefins containing a terminal vinyl group, $=CH_2$.

We may also employ polyolefinic hydrocarbons containing at least three carbon atoms per molecule as alkylating reagents, particularly the diolefinic hydrocarbons. Examples of conjugated diolefinic hydrocarbons which we may employ include 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, piperylene, 4-methyl-1,3-pentadiene, 1,3-cyclohexadiene and the like. Examples of nonconjugated diolefinic hydrocarbons which we may employ include 1,5-hexadiene, dipentene and related terpenic hydrocarbons, and the like.

Olefin-acting compounds which we may employ as alkylating agents include various halohydrocarbons, alcohols, ethers, alkyl sulfates or the like containing at least three carbon atoms in the alkylating group. We may employ such halohydrocarbons as alkyl and cycloalkyl halides, especially chlorides or bromides, e. g., isopropyl chloride, n-propyl bromide, t-butylchloride, t-butyl fluoride, isopropyl fluoride, diisobutylene hydrochloride, cyclohexyl chloride, cyclohexyl fluoride, t-methylcyclopentyl chloride, benzyl chloride, 2,4-dichlorobenzyl chloride, bis(chloromethyl)benzenes, allyl chloride, methallyl chloride, 2,3-dichloro-2,3-dimethylbutane, 3-methyl-1,3-dichlorobutane and the like.

Examples of alcohols which may be employed in this invention include isopropyl, n-propyl, isobutyl, t-butyl, t-amyl, benzyl, cyclohexyl, t-methylcyclopentyl and t-octyl alcohols such as dimethylneopentyl carbinol. Various olefin-acting ethers may be employed as alkylating re-

agents in the process of this invention, for example, diisopropyl ether, methyl-t-butyl ether and the like. Other examples of olefin-acting compounds include various alkyl sulfates such as diisopropyl sulfate, dibutyl sulfates and the like.

Specific aspects of the process of the present invention are illustrated by the following examples.

Example 1

A mixture of toluene and propylene in the molar ratio of 1.1 to 1 was rocked in an autoclave with PF_5 in the concentration of one mol percent, based on propylene, at 25° C. for 4.5 hours and then allowed to stand an additional 16 hours. In detail, the following procedure was used. The autoclave was evacuated and 68 g. of toluene was introduced, following which 169 cc. of PF_5 gas was charged from a calibrated mercury displacement bulb. Propylene was then pressured into the autoclave at room temperature in the initial quantity of 28 g. The initial pressure was about 200 p. s. i. g. Upon completion of the reaction, the excess pressure in the autoclave was bled off and 88.1 g. of a liquid product of slightly reddish color was removed therefrom, washed with water and dried with anhydrous calcium chloride. Upon completion of the reaction, the product contained 47.2 weight percent toluene, 24.8 weight percent of a substantially equimolar mixture of meta- and para-cymene, 14.9 weight percent of diisopropyl-toluenes, small proportions of propylene trimers and tetramers, and 12.5 weight percent of alkylate containing 16 carbon atoms per molecule. The cymenes yield was 21.7% of theoretical and the diisopropyltoluene yield was 20% of theoretical.

Example 2

Into a 3-necked flask fitted with a reflux condenser were placed 200 g. of t-butylbenzene and 35 g. of 2-pentene. The flask was also provided with a thermometer and a PF_5 inlet tube extending below the liquid level. The mixture was heated to reflux and PF_5 gas was slowly introduced from a calibrated mercury displacement bulb. Over a 48 hour period the pot temperature increased from 85.5° C. to 107° C. A total of 612 cc. of PF_5 gas was added. The solution turned dark and opaque. Product was cooled, water-washed and dried over calcium chloride. The product weighed 210.5 g. Distillation yielded 12.4 g. of material boiling at 243° C., n_D^{20} 1.4828. The yield of the monoalkylate, based on 2-pentene, is 12.7% of theoretical.

Surprisingly, we have found that anhydrous liquid hydrogen fluoride exerts an inhibiting effect in alkylation, particularly in the alkylation of toluene by propylene, as shown by the following experiment which may be compared with Example 1. Reaction was effected between toluene and propylene in the molar ratio of 4.3, employing 2.4 mol percent of PF_5 and 13.4 mol percent of liquid anhydrous HF, based on the propylene, at 26° C. and 16 hours. The yield of alkylate was only 6 percent, based on propylene. The alkylate boiled at temperatures ranging upward from 170° C., and its refractive index (n_D^{20}) was 1.4902.

In the following table are recorded examples illustrating the alkylation of benzene by the appropriate alcohols to produce isopropylated, cyclohexylated and t-butylated benzenes in the presence of PF_5. In some of the examples benzenediazonium hexafluorophosphate was employed as catalyst. Reaction was effected by placing 2.5 mols of benzene and 0.5 mol of the alcohol in an Erlenmeyer flask. The resultant solution was cooled in an ice bath and approximately one-half mol of phosphorus pentafluoride was bubbled into the solution, causing it to become brown. The flask was then placed on a steam plate and the reaction mixture was refluxed for 2 hours. The reaction mixture was then allowed to cool to room temperature. It separated into two liquid layers, viz. an upper organic layer and a lower aqueous layer, the latter being separated and discarded. The organic layer was washed twice with 50 ml. portions of 10% aqueous NaOH and twice with 50 ml. portions of distilled water, following which it was dried for about 12 hours with calcium chloride and then distilled from sodium. When benzenediazonium hexafluorophosphate was employed, it was added directly as a solid to the mixture of feed stocks. The following data were obtained.

TABLE 1

Benzene alkylation

Ex.	Alcohol	Time (Hrs.)	Catalyst	C_6H_5R		$C_6H_4R_2$		Total, Percent of Theory
				Mols	Yield, Percent of Theory	Mols	Yield, Percent of Theory	
3	i-Propyl	2	PF_5	.170	34	.035	14	48
4	do	6	ϕN_2PF_6	.093	19	.066	26	45
5	t-Butyl	2	PF_5	.100	20	.042	17	37
6	do	2	ϕN_2PF_6	.069	14	.061	24	38
7	Cyclohexyl	2	PF_5	.198	40	.037	15	55
8	do	2	ϕN_2PF_6	.162	32	.058	23	55

In the above table, R represents the alkyl or cycloalkyl group which was substituted in the benzene nucleus, viz. isopropyl, t-butyl or cyclohexyl. The physical constants of the alkylation products were those shown in Table 2.

TABLE 2

Physical properties of mono- and p-dialkylbenzenes

Benzene	B. P., ° C./ mm. Hg	M. P., ° C.	n_D^{20}
Isopropyl-	151–2/747		1.4918
Cyclohexyl-	235–7/748		1.5241
t-Butyl-	167–9/744		1.4924
p-Diisopropyl-	206–8/741		1.4901
p-Dicyclohexyl-	190–6/15	103–4	
p-Di-t-butyl-	234/742	75–6	

In order to determine the position of the alkyl groups in the dialkylated benzenes, oxidation of the side chains to well-known benzene derivatives was used. The isomeric phthalic acids or their methyl esters differ widely in melting points. Two and five-tenths grams of diisopropyl benzene were refluxed with 300 ml. of 5 N nitric acid for 18 hours. A 77% yield of phthalic acid was obtained. After recrystallization from hot water and drying, the acid sublimed without melting above 300°, indicating terephthalic acid. This acid was heated with absolute methanol in the presence of hydrogen chloride. On cooling, a mass of white crystals separated in the form of thin plates. The crystals melted at 141–2°, indicating the dimethyl ester of terephthalic acid. There was no indication of isophthalic ester. A separate sample of the acid was tested for orthophthalic acid by conver-

sion to fluorescein (S. P. Mulliken, "The Identification of Pure Organic Compounds," vol. I, pp. 84–5). The test indicated the presence of the ortho isomer but in very small quantity. The strongest test was given by the phthalic acid derived from the diisopropyl compound. The structures of the di-t-butyl and dicyclohexyl compounds were determined by oxidation with chromic acid, and 86% and 72% of terephthalic acid was obtained. This was identified as before.

In Table 3 are presented data obtained in examples of the alkylation of benzene with isopropyl alcohol, characterized chiefly by the employment of relatively small proportions of PF_5, based on the alcohol, as compared with the examples of Table 1. The alkylations of Table 3 were carried out in glass apparatus at atmospheric pressure, employing PF_5 gas derived from the thermal decomposition of benzene-diazonium hexafluorophosphate in an autoclave at 120–125° C. The PF_5 and nitrogen gases which were formed were bubbled through the reaction mixture contained in a flask cooled in an ice bath. Upon absorption of PF_5 in the reaction mixture it changed from colorless to a canary yellow color and two liquid layers formed. The reaction mixture was refluxed thereafter for one hour. The reaction mixture was then cooled to room temperature, the lower aqueous layer was discarded and the upper hydrocarbon layer was washed twice with 10% aqueous sodium hydroxide and then with water. The hydrocarbon products were then dried over anhydrous calcium chloride and distilled from sodium.

TABLE 3

Alkylation of aromatic hydrocarbons with isopropanol using PF_5 *gas*

Ex.	Mol Ratio, Aromatic/Alcohol	Molar Ratio, Pf_5/Alclhol	Reaction Period, Hrs.	Alkylate, Percent Theor. Yield				Total Alkylate, Percent Theory
				C_6H_5R	$C_6H_4R_2$	$C_6H_3R_3$	$C_6H_2R_4$	
9	(C_6H_6) 5/1	0.45	6	35.7	17.3	12.2	15.6	80.8
10	(C_6H_6) 3/1	0.52	5	31.8	[a] 17.3	12.7	30.9	92.7
11	(C_6H_6) 2/1	0.59	3	25.5	14.5	[b] 53		93.0
12	(C_6H_6) 1/1	0.59	2	24.2	18.5	12.2	35.8	90.7
13	(Cumene) 5/1	0.45	2	----------	[a] 25.4	19.2	15.1	59.7
14	(Toluene) 5/1	0.45	2	----------	[c] 48.0	15.0	18.0	81.0

[a] Largely para-diisopropylbenzene.
[b] Based on triisopropylbenzene.
[c] Ortho:meta:para=2:1:1.

Examples 9 to 12 show that decreasing the ratio of benzene to alcohol has little effect on the yield of diisopropylbenzene. The yield of monoisopropylbenzene is reduced as the ratio is decreased and higher yields of the polyalkylated benzenes are attained. Alkylation of toluene and cumene with isopropanol in Examples 13 and 14, respectively, gave higher yields of the dialkylbenzene products.

The triisopropylbenzene of Example 10 was found to boil at 120° C. at 20 mm. Hg, n_D^{20}, 1.4910, indicating the 1,2,4-isomer. The tetraisopropylbenzene of Example 10 was found to melt at 117.5 to 118.5° C., indicating the 1,2,4,5-isomer.

In Table 4 are presented data obtained in examples in which PF_5 gas was employed as a catalyst under pressure with isopropanol, isopropyl chloride and propylene for the alkylation of benzene and toluene. In these examples the PF_5 was free of nitrogen.

The procedure employed in performing Example 15 is described in detail since it is typical of the procedure employed in the other examples of Table 4. The reactor was a 250 cc. stainless steel autoclave provided with a magnetically-actuated stirrup-type stirrer (a commercial Magne-Dash reactor). It was pressure-tested with nitrogen, then evacuated and 78 g. of reagent grade benzene and 20 g. of isopropanol were introduced. The autoclave was then heated to 150° C. and PF_5 from a weighed sausage bomb was added over a 2.5 hour period, more being added as the pressure dropped. A total of 19 g. of PF_5 was added and the maximum pressure was 500 p. s. i. g. at 150° C. Stirring of the reaction mixture was stopped after 2.5 hours and the autoclave was allowed to cool. The autoclave was opened and the product was transferred to a separatory funnel. The lower aqueous layer was separated and discarded. The upper hydrocarbon layer was washed twice with 50 cc. each of aqueous 10% NaOH solution and twice with water. The hydrocarbon product was dried over calcium chloride and weighed 71.2 g. The product was distilled from sodium using a 3-foot high, ⅜-inch diameter Stedman packed still. Distillation of products gave:

	Grams	B. P., ° C.	Pressure, mm. Hg
Benzene	43.6	80	750.2
Monoisopropylbenzene	18.3	151.5	750.2
Diisopropylbenzene	5.1	120–123	60.0
Polyisopropylbenzenes	1.7	147–173	60.0
Bottoms	1.5	semi-solid	----------

TABLE 4

Alkylation of aromatics under pressure using PF_5 *gas*

Ex.	Molar Ratio, Aromatic/Alkylating Agent	Molar Ratio, PF_5/Alkylating Agent	Temp., ° C.	Press., p. s. i. g.	Reaction Period, Hrs.	Alkylate, Percent Theor.			
						C_6H_5R	$C_6H_4R_2$	Polyalkylate	Total
15	(C_6H_6) 3/1 (Isopropanol)	0.45	150	500	2.5	45.8	18.9	[a] 15.6	80.3
16	(C_6H_6) 3/1 (Isopropanol)	0.5	24	350	24.0	71.4	21.5	----------	92.9
17	(C_6H_6) 3/1 (Isopropylchloride)	0.59	142	525	3.0	50.0	[b] 29.0	[a] 14.7	93.7
18	(Toluene) 5/1 (Propene)	0.05	24	200	1.0	----------	[c] 40.0	[d] 49.3	89.3

[a] Based on tetraisopropylbenzene.
[b] Largely para-.
[c] 60% ortho; 20% meta; 20% para.
[d] Based on diisopropyltoluene.

Alkylation of benzene with isopropanol using PF_5 gas in an autoclave at higher temperatures and higher pressures favored the formation of monoisopropylbenzene as indicated in Examples 15 and 16 of Table 4. The yield of the diisopropylbenzene was a little greater than that obtained in glass equipment at atmospheric pressure. A comparison of Example 15 with Example 16 shows that a much higher yield of isopropylbenzene was obtained at room temperature and a relatively long reaction period than at the conditions of high temperature and relatively short reaction period.

Substitution of isopropyl chloride for isopropyl alcohol in the alkylation of benzene in an autoclave at elevated temperature and pressure gave higher yields of mono and diisopropylbenzenes as shown by Example 17. This reaction may be effected with much smaller amounts of PF_5, but it was carried out with this much PF_5 to compare it with alkylations using alcohols. The para position was preferred in dialkylation, possibly because of steric as well as electronic effects.

In Example 18 the alkylation of toluene with propylene proceeded at room temperature (and 200 p. s. i. g.) using only a small amount of PF_5. Example 18 indicates that the steric effect of a methyl group in the aromatic feed stock is much smaller than that of an isopropyl group since the predominant dialkylbenzene was the ortho isomer.

In the alkylation of benzene by isopropanol in the presence of 0.5 to 1 mol of benzenediazonium hexafluorophosphate per mol of isopropanol, the formation of substantial yields of diphenyl, amounting to about one-third of the theoretical maximum, was noted in some instances. Apparently, decomposition of the hexafluorophosphate in the presence of benzene and PF_5 occurs to form nitrogen, HF and diphenyl.

Chemical and physical tests were used to determine the isomer distribution of the diisopropylbenzenes of Examples 10, 13 and 17. These were oxidized with 5 N nitric acid for 16–18 hours at reflux temperature. Oxidation yields of 75 to 82% were obtained. The phthalic acids sublimed above 300° C. Only a faint test for orthophthalic acid was obtained by means of the fluorescein test. The acids were converted to the dimethyl ester by reaction with absolute methanol and anhydrous HCl during one hour at reflux temperature. White plates of the dimethyl ester were obtained which melted at 139–140° C. indicating the para isomer, dimethyl terephthalate. Thus the structure of the original hydrocarbon was predominantly para-diisopropylbenzene.

Although the specific examples illustrate certain facets of our invention, it will be understood that it is more broadly applicable. The alkylation may be conducted at temperatures between about 0° C. and about 150° C., the most desirable temperature or temperature range employed in any specific instance being readily determined by simple small-scale experiment. The pressure can likewise be broadly varied as well as the molar ratios of the reactants and of catalyst to the reactants. The reaction can be carried out in the presence of inert solvents or reaction media, usually in the presence of non-reactive hydrocarbons such as liquid paraffins and/or cycloparaffins, which may be employed in proportions between about one-tenth and about two parts by weight per part by weight of the aromatic compound employed as a feed stock. In those instances in which polyalkylation products (resulting from the introduction of more than one alkyl group in the aromatic compound employed as charging stock) are not desired, the polyalkylation products formed in the reaction may be recycled, in continuous processes, or may be charged in proportions up to about the equilibrium proportion in batch alkylation procedures. The usual equipment and operating methods which are known in the alkylation art and in related arts of effecting chemical reactions and processes may be employed for the purposes of our invention and especially for its adaptation to large scale usage.

Having thus described our invention, what we claim is:

1. An alkylation process which comprises contacting an aromatic compound having at least one alkylatable nuclear carbon atom with an olefin-acting compound containing at least three carbon atoms in the alkylating group with PF_5 under alkylation reaction conditions.

2. The process of claim 1 wherein said aromatic compound is an aromatic hydrocarbon.

3. An alkylation process which comprises contacting an aromatic hydrocarbon having at least one alkylatable nuclear carbon atom with a monoolefinic hydrocarbon containing at least three carbon atoms per molecule and with PF_5 under alkylation reaction conditions.

4. The process of claim 3 wherein said monoolefinic hydrocarbon contains a terminal vinyl group.

5. The process of claim 3 wherein said aromatic hydrocarbon is benzene and said monoolefinic hydrocarbon is propylene.

6. The process of claim 3 wherein said aromatic hydrocarbon is toluene and said monoolefinic hydrocarbon is propylene.

7. The process of claim 3 wherein said aromatic hydrocarbon is cumene and said monoolefinic hydrocarbon is propylene.

8. The process of claim 3 wherein said aromatic hydrocarbon is t-butylbenzene and said monoolefinic hydrocarbon is isobutylene.

9. An alkylation process which comprises contacting an aromatic hydrocarbon having at least one alkylatable nuclear carbon atom with an alcohol having at least three carbon atoms per molecule and with PF_5 under alkylation reaction conditions.

10. An alkylation process which comprises contacting an aromatic hydrocarbon having at least one alkylatable nuclear carbon atom with a halohydrocarbon having at least three carbon atoms per molecule and with PF_5 under alkylation reaction conditions.

11. An alkylation process which comprises reacting a secondary alcohol containing at least three carbon atoms per molecule and at least an equimolar proportion of an aromatic compound having at least one alkylatable nuclear carbon atom with PF_5 in a proportion of at least about 30 mol percent, based on said alcohol, at a temperature sufficient to effect alkylation.

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