to stir for an additional 10 to 15 hours. The ratio of reactants, summary of conditions and yields are given in Table III. The reaction mixture was worked up by adding water,[8] in order to dissolve the potassium methanesulfonate, extracting the aqueous solution with several 10-ml. portions of hexane, washing the hexane layer with 5 ml. of 5% potassium hydroxide solution to remove any hydroperoxide, then washing the hexane layer with distilled water until the washings were neutral, and drying the hexane layer over anhydrous sodium sulfate. The solvent was then removed under a slight vacuum through an 8-inch column packed with glass helices and the residue distilled. In the case of the isomeric dibutyl peroxides, vacuum distillation through an 8-inch Vigreux column completely separated the peroxide from the unreacted, higher boiling alkyl methanesulfonate. Redistillation through the same Vigreux column was sufficient to obtain the purified di-*n*-amyl peroxide; but fractionation through a small column was better and was, in fact, necessary for purification of the diisoamyl peroxide. Di-*n*-hexyl peroxide was not completely separated from the *n*-hexyl methanesulfonate by careful fractionation through a 1.2 × 45 cm. column packed with $^1/_8$ inch glass helices, and it was therefore necessary to resort to another method of purification as indicated below in those cases with twelve or more carbon atoms.

TABLE III

PREPARATION OF DIALKYL PEROXIDES

	Alkyl methane-sulfonate g.	mole	Methanol, ml.	50% KOH soln., g.	Total "30%" H_2O_2, g.[c]	Time, hr.	Crude yield,[a] %
n-Butyl	30.4	0.20	70	22.4	13.6	15	44[b]
2-Butyl	106.4	.70	280	80	60.0	23	17
Isobutyl	15.2	.10	50	11.2	10.2	23	10
n-Amyl	16.6	.10	50	11.2	10.2	18	57
n-Amyl	49.8	.35	150	33.6	28.0	12	48
Isoamyl	16.6	.10	50	11.2	10.2	18	50
2-Pentyl	7.4	.045	20	5.0	4.5	24	20
n-Hexyl	9.0	.05	30	5.6	5.1	22	62
2-Hexyl	9.0	.05	30	5.6	5.1	18	28
n-Heptyl	9.7	.05	30	5.6	5.1	22	72

[a] Yield of the once-distilled peroxide fraction based upon the amount of the alkyl methanesulfonate taken. [b] If the amount of recovered *n*-butyl methanesulfonate is taken into account this yield would be 48%. [c] The hydrogen peroxide used in all of these experiments was 25.3% by titration.

The peroxides could be purified from contaminating alkyl methanesulfonate by refluxing with 5 g. of 40% sulfuric acid and 10 ml. of methanol per gram of peroxide. In the case of di-*n*-heptyl peroxide, isopropyl alcohol was used in place of methanol to make the mixture homogeneous. The time necessary for the hydrolysis of the contaminating heptyl and hexyl methanesulfonates was 11 to 12 hours. The course of the purification could be followed readily by the characteristic absorption band in the infrared at 8.5 μ possessed by the alkyl methanesulfonates but lacked by the dialkyl peroxides studied. The mixture was cooled, diluted with an equal volume of water and extracted with hexane. The hexane extracts were washed with potassium hydroxide solution, washed with water and dried over anhydrous sodium sulfate; and the purified product was recovered by distillation. If the infrared spectra of a test sample indicated the presence of carbonyl contaminants, resulting from decomposition of some of the dialkyl peroxide during the acid treatment, the hexane solution was stirred with alumina and filtered before distillation. The new dialkyl peroxides along with their properties are given in Table I.

Initial experiments on attempted purification of the dialkyl peroxides by basic hydrolysis of the contaminating alkyl methanesulfonate showed that these peroxides were attacked readily by base. Thus the decomposition of di-*n*-amyl peroxide was essentially complete upon refluxing for one hour in 25% aqueous potassium hydroxide in enough methanol to give a homogeneous solution. Di-*n*-heptyl peroxide was decomposed similarly by standing for 15 hours at room temperature in an aqueous potassium hydroxide–methanol solution. No noticeable decomposition as measured by infrared spectra had been observed for several of these dialkyl peroxides after storage for one year at approximately 0°.

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(8) In several experiments the potassium methanesulfonate was filtered and washed with methanol and hexane. The recovery amounted to 55 to 70% in these cases. The amount which was soluble in the aqueous methanol was, of course, not recovered.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Sodium Catalyzed Reactions. II.[1] Side-chain Ethylation of Alkyl Aromatic Hydrocarbons Catalyzed by Sodium

BY HERMAN PINES,[2a] J. A. VESELY AND V. N. IPATIEFF[2b]

RECEIVED JULY 16, 1954

It has been found that side-chain ethylation of alkylbenzenes or of related hydrocarbons, such as indan, can be accomplished by treating ethylene with alkylbenzenes in the presence of a catalyst consisting of sodium and a promoter. Promoters which were effective for the side chain ethylation usually consisted of organic compounds which presumably react with sodium to form organosodium compounds. The side-chain ethylation occurs with alkylbenzenes which have at least one hydrogen atom on the α-carbon atom attached to the aromatic ring. Toluene formed *n*-propylbenzene and 3-phenylpentane, cumene yielded *t*-amylbenzene, xylenes formed the corresponding *n*-propyltoluenes, indan produced 1-ethylindan, etc. A mechanism for the reaction is proposed.

The ring alkylation of aromatic hydrocarbons has been the subject of extensive studies in the literature. Catalysts which have been used for this reaction consist of acids or acid-acting compounds. The catalysts used most widely for the ethylation of benzene and of alkylbenzenes are aluminum chloride–hydrogen chloride,[3a] silicophosphoric acid[3b,c] and silica–alumina (cracking catalyst).[3d] None of these catalysts has been reported to cause any side-chain ethylation of the alkylbenzenes present or formed during the reaction.

The present work shows that side-chain ethylation of alkylbenzenes or of related hydrocarbons, such as indan, can be accomplished by treating ethylene with alkylbenzenes in the presence of a catalyst consisting of sodium and a promoter. The

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(1) For paper I of these series see H. Pines, J. A. Vesely and V. N. Ipatieff, THIS JOURNAL, **77**, 347 (1955).

(2) (a) The Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois; (b) Deceased, November 29, 1952.

(3) (a) C. C. Price, "Organic Reactions," Vol. III, Chapt. I, John Wiley and Sons, Inc., New York, N. Y., 1946; (b) V. N. Ipatieff and L. Schmerling, *Ind. Eng. Chem.*, **38**, 400 (1946); (c) W. J. Mattox, *Trans. Am. Inst. Chem. Eng.*, **41**, 463 (1945); (d) A. A. O'Kelly, J. Kellet and J. Plucker, *Ind. Eng. Chem.*, **39**, 154 (1947).

TABLE I

SIDE-CHAIN ETHYLATION OF MONOALKYLBENZENES AND OF RELATED HYDROCARBONS

The ethylation was carried out in a 850-ml. rotating autoclave at 200–225° for 4 hours. The initial ethylene pressure was 30 atmospheres. The yields of mono- and diethylated aromatic hydrocarbons are based on alkylbenzenes reacted.

Experiment	1	2	3	4	5	6	7	8
C_6H_5R, 1 mole, R	Methyl	Ethyl	Isopropyl	*s*-Butyl	*t*-Butyl	Cyclohexyl	Indan	Methylnaphthalene[h]
Sodium, g.	10	10	10	7	5	6	6	5
Anthracene, g.	4	4	4	2.5[j]	2	2	2	2
Aromatics reacted, mole %	65	68	37	41	2	18	14	39
Monoethylated arom., mole %	57[a]	75[c]	78[e]	90[d]		50[f]	26[g]	64[i]
Diethylated arom., mole %	22[b]	10[d]						

[a] *n*-Propylbenzene. [b] 3-Phenylpentane. [c] *s*-Butylbenzene. [d] 3-Methyl-3-phenylpentane. [e] *t*-Amylbenzene. [f] 1-Ethyl-1-phenylcyclohexane. [g] Ethylindan. [h] Mixture of α- and β-isomers. [i] Probably a mixture of α- and β-*n*-propylnaphthalene. [j] *o*-Chlorotoluene was used as a promoter.

TABLE II

SIDE-CHAIN ETHYLATION OF POLYALKYLATED BENZENES

The ethylation was made in a 850-ml. rotating autoclave at 200–225° for 4 hours. The initial ethylene pressure was 30 atmospheres. In each experiment 4–6 g. of sodium and 2 g. of anthracene was used.

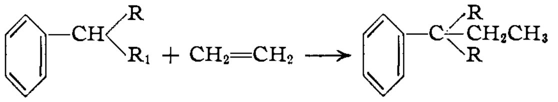
Experiment	1	2	3	4	5[h]
Aromatics (1 mole)	*o*-Xylene	*m*-Xylene	*p*-Xylene	Mesitylene	*p*-Cymene
Aromatics reacted, mole %	61	52	31	19	45
Monoethylated arom., mole %[j]	66[a]	66[c]	80[e]	79[g]	62[i]
Diethylated arom., mole %[j]	28[b]	29[d]	12[f]		

[a] *o*-*n*-Propyltoluene. [b] Contains about 50% of 3-*o*-tolylpentane. [c] *m*-*n*-Propyltoluene. [d] Contains about 75% of 3-*m*-tolylpentane. [e] *p*-*n*-Propyltoluene. [f] 3-*p*-Tolylpentane. [g] 1,3-Dimethyl-5-*n*-propylbenzene. [h] *o*-Chlorotoluene, 2 g., was used as a promoter. [i] *p*-*t*-Amy toluene. [j] The yields are based on the reacted aromatic hydrocarbons.

reaction usually is carried out in a rotating autoclave under 30 atmospheres initial ethylene pressure and at about 200–225°.

Promoters found to be effective for the side-chain ethylation consisted of organic compounds such as anthracene, *o*-chlorotoluene, *o*-toluic acid, pyridine organic peroxides, etc., which, under experimental conditions used for ethylation, presumably reacted with sodium to form organosodium compounds.

Side-chain Ethylation of Monoalkylbenzenes and of Related Hydrocarbons.—Side-chain ethylation occurs with alkylbenzenes which have at least one hydrogen atom on the α-carbon atom attached to the aromatic ring. The reaction proceeds according to the general formula (R and R_1 may be hydrogen or a saturated hydrocarbon group).



t-Butylbenzene, which does not have a hydrogen on the carbon atom attached to the ring, does not react with ethylene.

Alkylbenzenes containing a methyl group or a primary alkyl group can react with more than one ethylene molecule; the reaction proceeds stepwise and in each case the carbon atom attached to the aromatic ring is involved in the reaction. In the case of ethylation of toluene, 3-ethyl-3-phenylpentane is produced.

n-Propylbenzene is the primary product of the reaction between toluene and ethylene. On further ethylation 3-phenylpentane and 3-ethyl-3-phenylpentane are produced. It was found that in the ethylation of toluene, 3-phenylpentane was always formed in addition to *n*-propylbenzene. This indicates the ease which which *n*-propylbenzene reacts with ethylene.

Ethylbenzene reacts with ethylene to form *s*-butylbenzene and some 3-methyl-3-phenylpentane.

Isopropylbenzene reacts with ethylene in the presence of sodium and a promoter to form *t*-amylbenzene.

In a few instances it was noticed that the ethylated alkylbenzene fractions contained, according to the permanganate test,[4] small amounts of unsaturated hydrocarbons, probably alkenylbenzenes. By selective hydrogenation, using copper chromite as a catalyst, these compounds were converted to the corresponding alkylbenzenes.

The ethylation of monoalkylbenzenes is usually a clean-cut reaction and the various ethylated products obtained by this procedure, even without an extensive purification, are spectroscopically pure.

The gaseous products recovered from the side-chain alkylation contained, besides unreacted ethylene, small amounts of ethane and still much smaller amounts of hydrogen. The yield of ethane produced, in experiments made in a rotating autoclave, was from 0.8 to 2 liters per mole of toluene reacted. There was a larger amount of ethane produced when the reaction was carried out in a turbomixer.

The ethylation of aromatic hydrocarbons is not limited to alkylbenzenes. Cyclohexylbenzene likewise undergoes ethylation and the monoethylated product formed by this reaction was found to be 1-ethyl-1-phenylcyclohexane.

Indan reacted with ethylene in the presence of sodium and a promoter and the main product of the reaction was 1-ethylindan.

The experimental conditions used and results obtained are summarized in Table I.

Side-chain Ethylation of Polyalkylated Benzenes.—The ethylation of xylenes, of *p*-cymene and of mesitylene was investigated and the results obtained are represented in Table II.

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[4] V. N. Ipatieff, W. W. Thompson and H. Pines, THIS JOURNAL, 70, 1658 (1948).

TABLE III

THE EFFECT OF PROMOTERS UPON THE SIDE-CHAIN ETHYLATION OF TOLUENE

The experiments were made in a 850-ml. rotating autoclave. In each experiment 92 g. (1 mole) of toluene, 7–10 g. of sodium and 2–4 g. of promoter was used. The reaction was carried out at 200–225° for 4 hours.

Experiment	1	2	3	4	5	6	7
Promotor	None	Anthracene	Fluorene	Dihydroanthracene	*o*-Chlorotoluene	*o*-Bromotoluene	Benzyl chloride
Toluene reac., %	2[a]	65	26	18	51	42	9
Yield, mole %							
n-Propylbenzene		57	67	56	63	70	48
3-Phenylpentane		22	8	6	16	17	

Experiment	8	9	10	11	12	13	14
Promoter	Allyl chloride	*s*-Butyl chloride	*o*-Toluic acid	Benzonitrile	Pyridine	*m*-Cresol	Di-*t*-butyl peroxide
Toluene reacted, %	36	23	53	42	28	23	36[b]
Yield, mole %							
n-Propylbenzene	73	80	60	67	64	61	61
3-Phenylpentane	16	11	21	14	7	8	17

[a] Temperature of the reaction was 325°. [b] In the absence of sodium less than 10% of toluene reacted and *n*-propylbenzene was not formed.

o-Xylene seems to react with ethylene more readily then *m*-xylene and the latter more readily than *p*-xylene. Whether the difference in ease of reaction is real or due to the inherent experimental variations will have to be evaluated further. The monoethylated xylenes consisted of the corresponding *o*-, *m*- and *p*-*n*-propyltoluene, the yield of which amounted, based on the reacted toluene, to from 66 to 80%. The diethylated xylenes were composed mainly of the corresponding 3-tolylpentanes; these results indicate that the *n*-propyl ethylates more readily than the methyl group.

p-Cymene on monoethylation yields almost exclusively *p*-*t*-amyltoluene; very little, if any, *p*-*n*-propylcumene was produced. It is very probable that *p*-tolyl group activates the isopropyl group in the ethylation reaction. The study of competing reactions which involve the ethylation of dialkylbenzenes containing two different alkyl groups is contemplated.

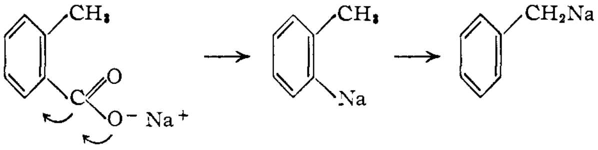
Mesitylene reacts with ethylene under experimental conditions similar to that of xylenes. The main reaction product is presumably 1,3-dimethyl-5-*n*-propylbenzene.

Effect of Promoters upon the Side-chain Ethylation of Toluene.—The relative effectiveness of various promoters was determined by treating toluene with ethylene in a rotating autoclave in the presence of sodium and a promoter. The reaction was made at 200–225° for 4 hours, using in each experiment 92 g. of toluene, 7–10 g. of sodium and 2–4 g. of the promoter. Table III summarizes the results obtained with some of the more active promoters.

It was found that hydrocarbons which react readily with sodium are efficient promoters for side-chain ethylation. Thus anthracene and fluorene caused the reaction of 65 and 26%, respectively, of the toluene charged. The reacted toluene yielded about 60% of *n*-propylbenzene and 8–22% of 3-phenylpentane. The reaction of sodium with various hydrocarbons has been reported in the literature.[5]

o-Chlorotoluene and *o*-bromotoluene were found to be excellent promoters for the ethylation of toluene, much better than benzyl chloride. The halotoluenes probably formed at first *o*-tolylsodium which on heating isomerizes to benzylsodium[6]; in the case of benzyl chloride it seems likely that the benzylsodium formed at first, reacts with another molecule of benzyl chloride to produce dibenzyl.[7] This competing reaction may be responsible for the lower yields of the side-chain ethylated product.

o-Toluic acid was found to be a very good promoter for the side-chain ethylation of toluene. It is possible that under the experimental conditions used it decomposes to produce benzylsodium, according to the scheme



The isomerization of tolylsodium to benzylsodium has been reported previously.[6]

It was found that aromatic compounds are usually better promoters than the corresponding aliphatic compounds: *e.g.*, *o*-chlorotoluene, *p*-toluic acid and benzonitrile are excellent alkylation promoters while butyl chlorides, isovaleric acid and acrylonitrile show smaller effect upon ethylation of toluene.

Peroxides, such as *t*-butyl peroxide, act also as promoters for the side chain ethylation of aromatic hydrocarbons. When applied to toluene it caused 36% of the toluene to react to form 61% *n*-propylbenzene and 17% of 3-phenylpentane. In the absence of sodium only about 10% of the toluene reacted; the product of the reaction did not contain, however, any of the above indicated alkylbenzenes. It is likely that, in the presence of sodium, the methyl free radical formed from the decomposition of *t*-butyl peroxide, or the benzyl free radical which might have been formed from

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[5] For general literature survey see Franz Runge, "Organometallverbindungen," Wissenschaftliche Verlagsgesellschaft, Stuttgart, 1944.

[6] H. Gilman and H. A. Pacevitz, THIS JOURNAL, **62**, 673 (1940).

[7] S. Cannizzaro and A. Rossi, *Ann.*, **121**, 250 (1862); A. Stelling and R. Fittig, *Ann.*, **137**, 258, (1866); A. M. Comey, *Ber.*, **23**, 1115 (1890).

TABLE IV

EFFECT OF CONCENTRATION OF SODIUM AND ANTHRACENE UPON THE ETHYLATION OF BENZENE

The ethylation was carried out in a 850-ml. autoclave using 1 mole of toluene and 30 atm. of ethylene pressure in each experiment. The reaction was made at 200–225° for 4 hours.

Experiment	1	2	3	4	5
Sodium, g. (mole)	10(0.44)[a]	5(0.22)[a]	5(0.22)[b]	5(0.22)[b]	10[a]
Anthracene, g. (mole)	4(0.02)	4(0.02)	2(0.011)	0.8(0.004)	0
Toluene reacted, mole %	65	41	48	35	2
n-Propylbenzene, mole %	57	71	71	71	
3-Phenylpentane, mole %	22	15	17	11	

[a] Sodium was used in the form of chunks. [b] Sodium was pressed as shiny ribbon into the glass autoclave liner.

the reaction of toluene with the methyl free radical, reacted with the sodium to produce an organosodium compound, which acted as a chain initiator in the ethylation of toluene.

Effect of the Concentration of Catalysts upon the Side-chain Ethylation.—The effect of the concentration of sodium and of anthracene, used as promoter, was investigated upon the side-chain ethylation of toluene. The experimental results obtained are given in Table IV.

It seems that the ratio of toluene to sodium to anthracene used plays an important role. The amount of toluene reacted and the respective yields of *n*-propylbenzene and of 3-phenylpentane are relatively high when the ratio of 1 mole of toluene, 0.22 g. atom of sodium and 0.01 mole of anthracene were used. When the amount of anthracene added was decreased to 0.004 mole, the yield of toluene reacted decreased from 48 to 35%. No reaction occurred when anthracene was omitted from the reaction.

It is preferred always to use a larger amount of sodium for a more rapid reaction; the major part of the sodium used is, however, usually recovered from the reaction.

Side-chain Ethylation of Toluene in a Turbomixer.—In all the experiments discussed previously the ethylations were made in a glass liner inserted in a 850-ml. rotating autoclave. Since this procedure did not permit a very intimate contact between the catalyst and the organic reactants, it was decided to make a few experiments in a Turbomixer which is a stirring type pressure reactor, described below under section Apparatus and Procedure. Furthermore it was possible in this apparatus to add the ethylene intermittently. The reaction was started at about 150–160° and the temperature was raised slowly to about 205–215°. The experimental conditions used and results obtained are summarized in Table V.

The results obtained in the Turbomixer apparatus are in general agreement with those obtained in the rotating autoclave, although the distribution of products formed is somewhat different. As in the previously described experiments the main products of the reaction were *n*-propylbenzene and 3-phenylpentane.

The major part of the sodium was recovered. A sludge remained after filtering off the reactants under atmosphere of nitrogen. The dark material which remained on the filter contained organosodium compounds, according to its behavior toward the decomposition with alcohol and to exposure to air. When free of solvents this organosodium residue was pyrophoric.

TABLE V

ETHYLATION OF TOLUENE IN A TURBOMIXER

In each experiment 184 g. (2 moles) of toluene, 7.7 g. (0.33 g. at.) of sodium and 2.5 g. (0.02 mole) of *o*-chlorotoluene was used.

Experiment	1	2
Ethylene charged, moles	2.0	1.4
Temperature, °C.	150–205	160–215
Duration, hours	25	19
Gaseous prod. recovd., mole	0.67	0.28
Ethylene, mole	.40	.06
Ethane, mole	.23	.19
Ethylene reacted, moles	1.6	1.35
Toluene reacted, mole %	53	59
Yield based on toluene reacted		
n-Propylbenzene, mole %	51	46
3-Phenylbenzene, mole %	24	26
Yield based on ethylene reacted		
Ethane, mole %	14	9
n-Propylbenzene	34	40
3-Phenylpentane	33	44
Higher boiling products formed,[a] g.	45	12

[a] The product contained 3-ethyl-3-phenylpentane and some still higher boiling hydrocarbons.

Probable Mechanism of Side-chain Ethylation.—A more thorough investigation of the problem is required in order to understand the mechanism of the ethylation of alkylaromatic hydrocarbons in the presence of sodium and a promoter. This will necessitate carrying out the investigation with highly purified materials under strictly controlled conditions and preferably with more intimate contact between the reactants and the catalyst. Based, however, on present data it seems reasonable to assume that the side-chain ethylation is a chain reaction. The function of the promoter apparently is to initiate the chain reaction. This probably is achieved by the interaction of the promoter with the sodium to form an organosodium compound which metalates the alkylaromatic hydrocarbons; the hydrogen on the carbon atom attached to the aromatic ring is replaced by sodium. The sodium alkylaromatic hydrocarbon thus formed adds to the ethylene to form new organosodium compounds, which then again metalate the original aromatic hydrocarbon or an ethylated aromatic hydrocarbon, which possesses a hydrogen on alkyl group attached to the benzene ring. The reaction can be represented by the following scheme, using as an example an organic halide as a chain initiator, and toluene as the aromatic hydrocarbon.

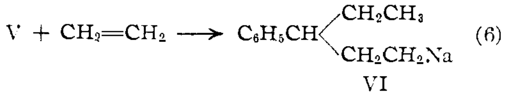
$$RX + 2Na \longrightarrow RNa + NaX \quad (1)$$

$$\underset{I}{C_6H_5CH_3} + RNa \longrightarrow \underset{II}{C_6H_5CH_2Na} + RH \quad (2)$$

$$\text{II} + CH_2{=}CH_2 \longrightarrow \underset{\text{III}}{C_6H_5CH_2CH_2CH_2Na} \qquad (3)$$

$$\text{III} + \text{I} \longrightarrow \underset{\text{IV}}{C_6H_5CH_2CH_2CH_3} + \text{II} \qquad (4)$$

$$\text{II} + \text{IV} \longrightarrow \text{I} + \underset{\text{V}}{C_6H_5CH(Na)CH_2CH_3} \qquad (5)$$



$$\text{V} + CH_2{=}CH_2 \longrightarrow \underset{\text{VI}}{C_6H_5CH\begin{matrix}\diagup CH_2CH_3 \\ \diagdown CH_2CH_2Na\end{matrix}} \qquad (6)$$

$$\text{VI} + \text{I} \longrightarrow C_6H_5CH(C_2H_5)_2 + \text{II etc.} \qquad (7)$$

The reaction product, as was indicated already, contained small amounts of ethane and some higher boiling hydrocarbons, probably products of polymerization or condensation. It is very probable that some of the sodium alkylaromatic hydrocarbons decompose to form sodium hydride, which most probably adds to ethylene to form sodium ethyl. The latter through the metalation of alkylaromatic hydrocarbons then forms ethane and sodium alkylaromatic compounds. It is very probable that the unsaturated alkylaromatic hydrocarbon, formed from the decomposition of the organosodium compounds, may react with metallic sodium to form an addition compound. Such addition reactions have been reported previously.[8]

The purpose of using an excess of sodium over that required for the formation of the original chain initiator is to maintain the chain reactions by the continuous generation of organosodium compounds. This is accomplished by the interaction of sodium with aromatic olefins obtained by the decomposition of the original organosodium compounds. The excess of sodium also may prevent the decomposition of sodium hydride to sodium and hydrogen by shifting the equilibrium toward the sodium hydride side. It has been shown previously that sodium hydride can act as a catalyst in hydrocarbon reactions.[1]

Experimental

Apparatus and Procedure. Rotating Autoclaves.—The reagents were placed in a tared Pyrex glass liner provided with a capillary. The sodium, in the form of shining ribbon, was added directly from the sodium press into the liner which contained the aromatic hydrocarbon and the promoter. It was found that sodium could be added in chunk form. In some cases the addition of glass helices along with the chunk form sodium resulted in greater reaction than obtained in their absence. The liner was then inserted into a rotating stainless steel autoclave of 850-ml. capacity. The autoclave was sealed and flushed out with nitrogen; ethylene then was added. The autoclave now was heated slowly till the break in pressure was observed, which usually occurred at about 200°. The duration of heating at this temperature or at about 25° higher was continued in most cases for about four hours. The autoclave then was allowed to cool to room temperature overnight. The gases were collected and in many cases analyzed by mass spectrograph. The product in the liner was weighed and filtered. The sodium and the sludge was washed with *n*-pentane and the wash added to the filtrate. The latter was distilled on a column of about 20-plate efficiency. Various fractions were collected and analyzed, predominantly by means of infrared spectroscopy.

In many instances syntheses of hydrocarbons were made in order to be able to compare the products obtained with those having a known structure.

Turbomixer Type Autoclave.—This autoclave uses an induction field to drive an armature contained within a high pressure zone.[9] To a lower end of the armature is attached a shaft which extends into a stainless steel autoclave. A turbine impeller, 6 cm. in diameter, is connected to the shaft. A stator ring which breaks the swirling movement of the stirred liquid and produces proper interchange of material from top to bottom is situated around the impeller. The impeller rotates at about 1500–1600 r.p.m. The autoclave can be utilized for continuous flow reactions. For the present investigation a reactor of 1000-ml. capacity was used.

The reactor was charged with toluene, sodium and *o*-chlorotoluene. It was then sealed and ethylene was introduced to a pressure of 28 atmospheres. The autoclave was heated slowly and at 195° the pressure reached 39 atmospheres. When the pressure dropped to 27 atmospheres, ethylene was added to a pressure of 44 atmospheres. This was repeated several times. The amount of total ethylene added was determined by recording the pressure drop of a calibrated 3-liter storage vessel placed in a constant temperature bath.

The general procedure for working up the reaction product was the same as for the experiments made in a rotating autoclave.

Preparation of Hydrocarbon. *o*-Tolylpropane, *p*-*n*-Propylisopropylbenzene and 1-ethylindan were prepared according to conventional procedures. The boiling points and indices of refraction of these hydrocarbons were in agreement with the data reported in the literature.[10]

***p*-*t*-Amyltoluene.**—*p*-*t*-Amylphenol was hydrogenated to 4-*t*-amylcyclohexanol and then oxidized to 4-*t*-amylcyclohexanone, according to the methods described previously.[11] The 4-*t*-amylcyclohexanone then was treated with methylmagnesium iodide to form 1-methyl-4-*t*-amylcyclohexanol. The latter then was dehydrated to the olefin and dehydrogenated to the *p*-*t*-amyltoluene, using platinized alumina as the catalyst. The amyltoluene distilled at 216°, $n^{20}D$ 1.4970; literature[12] b.p. 86° at 12 min., $n^{20}D$ 1.4965.

3-Tolylpentanes.—The tolylpentanes were prepared by treating the respective tolylmagnesium bromides with 3-pentanone. The 3-tolylpentanols thus produced were dehydrated by means of oxalic acid and hydrogenated in the presence of copper chromite catalyst at 75° under 100 atmospheres of hydrogen pressure. The following are the distillation temperatures and indices of refraction of the tolylpentanes

	B.p., °C.	$n^{20}D$
3-*o*-Tolylpentane	201–202	1.4900
3-*m*-Tolylpentane	200–201	1.4918
3-*p*-Tolylpentane	205	1.4928

These compounds were not reported in the literature.

1-Ethyl-1-phenylcyclohexane was prepared by treating ethylcyclohexene with benzene in the presence of hydrogen fluoride as a catalyst, according to the procedure described previously.[13] The ethylcyclohexene was made by the dehydration of 4-ethylcyclohexanol using alumina as a catalyst.

The structure of 1-ethyl-1-phenylcyclohexane was determined by dehydrogenation over chromia–alumina catalyst.[14] Only biphenyl was produced, which indicates that the ethyl group was attached to a quaternary carbon atom.

1-Ethyl-1-phenylcyclohexane distilled at 257–258°, $n^{20}D$ 1.5282.

Infrared Spectral Analysis.—The ethylated aromatic hydrocarbons obtained from the reaction of ethylene with alkylaromatic or related hydrocarbons were identified and their concentrations determined by means of infrared

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[8] For the summary of the literature see reference 5, pages 88–98.

[9] G. L. Hervert, U. S. Patent No. 2,377,937 (June 12, 1945) to Universal Oil Products Co.

[10] G. Egloff, "Physical Constants of Hydrocarbons," Volumes 3 and 4, Reinhold Publ. Corp., New York, N. Y., 1946, 1947.

[11] H. Pines, G. J. Czajkowski and V. N. Ipatieff, THIS JOURNAL, **71**, 3798 (1949).

[12] J. Colonge and L. Pichat, *Bull. soc. chim. France*, 177 (1949).

[13] V. N. Ipatieff, E. E. Meisinger and H. Pines, THIS JOURNAL, **72**, 2772 (1950).

[14] Catalogue of Infrared Spectra, American Petroleum Institute, Project 44.

TABLE VI

MAIN CHARACTERISTIC BANDS IN MICRONS OF SOME AROMATIC HYDROCARBONS

Toluene				Pentane					
o-n-Propyl-	*m-n*-Propyl-	*p-n*-Propyl-[a]	*p-t*-Amyl-	3-*o*-Tolyl-	3-*m*-Tolyl-	3-*p*-Tolyl-	*p-n*-Propylcumene	1-Phenyl-1-ethylcyclohexane	1-Ethylindan
8.88	8.52	7.21	7.61	7.56	8.57	7.61	7.20	7.36	7.69
9.17	9.06	7.50	8.06	7.70	8.70	8.03	7.30	8.30	7.91
9.39	9.61	8.92	8.33	8.00	9.36	8.23	7.42	9.23	8.32
9.71	11.10	9.59	8.52	9.11	9.62	8.39	7.75	9.71	8.61
10.12	11.33	9.75	8.90	9.22	11.20	8.75	8.26	10.02	9.19
10.68	11.45	12.45	9.41	9.70	11.36	9.00	8.93	11.37	9.78
13.47	12.83	13.35	9.52	10.33	12.81	9.63	9.35	11.70	10.73
	13.02		9.76	10.64	12.98	9.80	9.49	12.34	13.16
			9.88	10.90	14.24	10.96	9.77	13.27	13.33
			12.28	11.27		11.27	11.89		13.51
			12.88	13.28		12.27	12.39		
			13.82	13.76			14.18		

[a] The synthesis of the compound is described by H. Pines, D. R. Strehlau and V. N. Ipatieff, THIS JOURNAL, 71, 3534 (1949).

spectral analysis. In the following cases, where infrared spectra were not available, it was necessary to synthesize the compounds which were expected to be formed in the ethylation reaction. The infrared spectra of the synthetic aromatic hydrocarbons are given in Table VI.

The infrared spectra of *n*-propyl-, isopropyl- and *sec*-butylbenzene were catalogued by the American Petroleum Institute.[14]

The spectra of 3-phenylpentane, *t*-amylbenzene and 3-methyl-3-phenylpentane were reported previously.[15]

Acknowledgment.—The authors wish to thank Mr. Ed Baclawski of U. O. P., Riverside, Ill., for the infrared spectral analyses.

(15) H. Pines, W. D. Huntsman and V. N. Ipatieff, THIS JOURNAL, **73**, 4343 (1951); **75**, 2311 (1953).

RIVERSIDE, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Absorption Spectra of Halogenated Cyclopentenones[1]

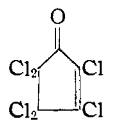
BY E. T. MCBEE, D. K. SMITH AND H. E. UNGNADE

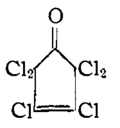
RECEIVED AUGUST 2, 1954

Infrared and ultraviolet absorption spectra have been determined for a series of chlorocyclopentenones. The spectral characteristics of the compounds are in agreement with the conjugated structure for 2,3,4-trichloro-2-cyclopentenone, 2,3,-4,4,5-pentachloro-2-cyclopentenone and the lower melting isomer of hexachlorocyclopentenone. The higher melting isomer of hexachlorocyclopentenone is not conjugated.

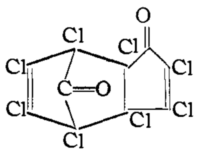
Introduction

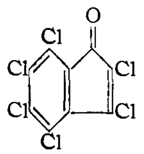
The structures of the two isomeric hexachlorocyclopentenones I and II have been investigated extensively[2,3,4] and although both chemical[2,4] and physical methods[5] have been applied to this problem, the structural assignments have been tentative. On purely chemical evidence, the lower melting isomer (m.p. 28°) was assigned the conjugated structure I and the higher melting isomer (m.p. 88°) the unconjugated structure II.[4]


I


II

The structures of the related 2,3,4,4,5-pentachloro-2-cyclopentenone (III)[3] and 2,3,4-trichloro-2-cyclopentenone (IV)[6] are subject to similar uncertainties, while the diketone V[3,4] can be regarded as structurally certain because of its method of formation by dehydrohalogenation of III and its conversion to perchloroindone (VI) by thermal degradation.


V


VI

Inasmuch as conjugated ketones, such as I, have characteristic absorption in the ultraviolet[7] and in the infrared,[8] the absorption spectra of the chlorocyclopentenones I–V have been determined for the purpose of structure identification.

Experimental[9]

Materials and Methods.—Hexachloro-2-cyclopentenone (I), prepared by the action of sulfuric acid on octachlorocy-

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(1) Abstracted from a portion of a thesis submitted by Delmont K. Smith to the Graduate School of Purdue University in partial fulfillment of the requirements for the Ph.D. degree.

(2) T. Zincke and F. Küster, *Ber.*, **22**, 486 (1899); **23**, 820, 2200 (1890); **26**, 2104 (1893).

(3) T. Zincke and K. H. Meyer, *Ann.*, **367**, 1 (1909).

(4) J. S. Newcomer and E. T. McBee, THIS JOURNAL, **71**, 946 (1949).

(5) H. Van Brederode, H. Gerding and H. J. Prins, *Rec. trav. chim.*, **65**, 174 (1946).

(6) R. K. Meyers, Ph.D. Thesis, Purdue University, 1950.

(7) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy," Edward Arnold, London, 1954, p. 90.

(8) J. F. Grove and H. A. Willis, *J. Chem. Soc.*, 486 (1942).

(9) All temperatures are uncorrected.