Conjugate Addition of the Wittig Reagent[1]

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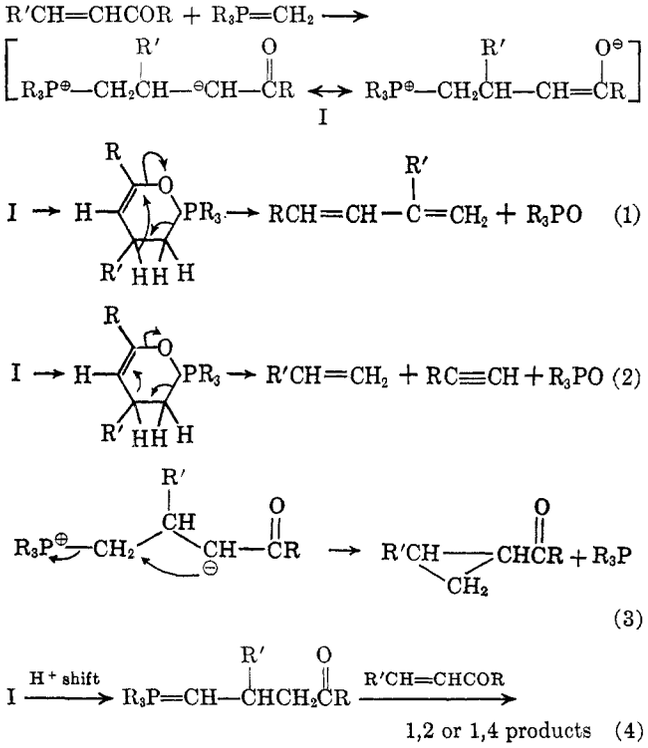
A cyclopropyl ketone is formed in the reaction of benzalacetomesitylene with the Wittig reagent. Benzalacetophenone underwent the normal addition. Some reactions of the cyclopropyl ketone and its independent synthesis are described.

1,4 addition of the Wittig reagent to an α,β-unsaturated carbonyl compound leads to a zwitterionic intermediate (I) which potentially can react further by several processes. Reactions which have been

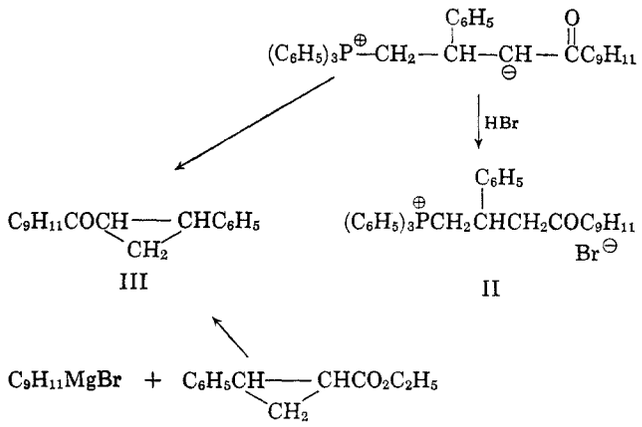


proposed to proceed by routes 1,[2] 2,[3] and 4[4] have been described. This paper is concerned with the amplification of a preliminary report[5] of a reaction proceeding by route 3.

Treatment of benzalacetophenone with methylenetriphenylphosphorane[6] produced the dimer[7] of 1,3-diphenylbutadiene in 40% yield. A very small amount of a ketone, $C_{31}H_{26}O$, was obtained but was not investigated further.[8] It is presumed that the diphenylbutadiene dimer was produced by 1,2 addition of the Wittig reagent, although it is possible that it arose from a 1,4 addition proceeding by route 1.

It is expected that hindrance about the carbonyl group of an α,β-unsaturated ketone would prevent reaction there and favor conjugate addition as it does with many organometallic reagents. It was found that the Wittig reagent did not attack acetomesitylene. When benzalacetomesitylene was treated with methylenetriphenylphosphorane in ether, an insoluble white solid was produced immediately. Ethyl acetate extraction of this solid yielded the phosphonium salt II (Chart I). The structure of this salt is based on its elemental analysis, infrared spectrum (saturated mesityl ketone, $\nu_{C=O}$ 1685 cm^{-1}), and its further decomposition product, which is discussed below. The source of the proton which is necessary for the production of this material is unknown. It was originally thought[5] to be water, which was used during some of the work-ups, but the salt also was obtained when water was not used.

CHART I



When the reaction was run in the same way, except that the ether was replaced by xylene before the heating period and the mixture was heated at 115–125° for 4 hr, the solid originally present slowly decomposed and upon work-up of the mixture a new ketone, 2-phenylcyclopropyl mesityl ketone (III), was obtained. The structure of this ketone is based upon its elemental analysis and infrared spectrum and by its identity with the product of the reaction of mesitylmagnesium bromide with ethyl 2-phenylcyclopropanecarboxylate. This latter reaction was of

(1) This research was carried out in part under Army Ordnance Contract No. D-01-021-ORD-11878.

(2) H. H. Inhoffen, K. Brückner, G. Domagk, and H. Erdmann, *Chem. Ber.*, **88**, 1415 (1955).

(3) F. Bohlmann, *ibid.*, **89**, 2191 (1956). A different mechanism has been suggested for this reaction: J. Levisailles, *Bull. Soc. Chim. France*, 1021 (1958).

(4) H. J. Bestman and F. Seng, *Angew. Chem.*, **74**, 154 (1962).

(5) J. P. Freeman, *Chem. Ind.* (London), 1254 (1959). Reference 4 also contains a preliminary report of a route-3 reaction.

(6) Dr. E. Lewis, Florida State University, carried out some exploratory experiments on this reaction but did not characterize the products; his experiments were run at 65° in ether–tetrahydrofuran. We are indebted to Dr. Lewis for this information.

(7) W. Herz and E. Lewis, *J. Org. Chem.*, **23**, 1646 (1958); T. L. Jacobs and M. H. Goodrow, *ibid.*, **23**, 1653 (1958). We are indebted to these authors for generous samples of their products.

(8) This ketone appeared to be a saturated mesityl ketone ($\nu_{C=O}$ 1680 cm^{-1}). It was not 4-benzoyl-1,3,5-triphenyl-1,3-hexadiene,[7] as shown by its different infrared spectrum and depression of its melting point when admixed with authentic material. It is possible that it is 6-benzoyl-1,3,5-triphenyl-1,3-hexadiene, formed by a 1,2 addition as the last stage of a route-4 process.

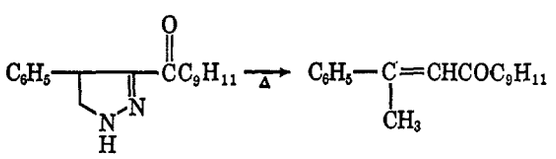
some interest and will be discussed later in this article. The reactions are summarized in Chart I.

The reaction between benzalacetomesitylene and methylenetriphenylphosphorane is the only Wittig reaction from which a cyclopropyl ketone has been reported. However, the reaction of fluorenone with alkylidenetriphenylphosphoranes produced dialkylfluorenylcyclopropanes, apparently through the intermediate formation of an alkylidenefluorene.[9] The formation of cyclopropanes from epoxides and the Wittig reagent has also been reported.[10] A similar reaction of epoxides with phosphonate anions also produces cyclopropanes.[11] Triethyl phosphonoacetate anion failed to react with benzalacetomesitylene. Some α,β-unsaturated esters react with the Wittig reagent to produce cyclopropanes.[4]

It is probable that the formation of cyclopropyl ketones from the Wittig reagent is a reaction of narrow scope. Since the advent of the use of dimethyloxosulfonium methylide for this purpose,[12] no further efforts were expended to define all the parameters. It appears that a Wittig reagent will preferentially attack the carbonyl group of an α,β-unsaturated ketone unless the carbonyl group is sterically hindered.

Some other routes to ketone III were investigated. Benzalacetomesitylene reacted with diazomethane to produce 3-mesitoyl-4-phenylpyrazoline (IV). When this compound was decomposed thermally, β-methylbenzalacetomesitylene (V)[13] was produced rather than the cyclopropyl ketone. This mode of decomposition is similar to that of the pyrazoline from benzalacetophenone.[14]

$$C_6H_5-CH=CHCOC_9H_{11} + CH_2N_2 \rightarrow$$



IV V

Since mesityl cyclopropyl ketone has been prepared by the Friedel–Crafts reaction between cyclopropanecarbonyl chloride and mesitylene,[15] the reaction between 2-phenylcyclopropanecarbonyl chloride and mesitylene was examined. None of the cyclopropyl ketone III was obtained but rather an unsaturated ketone isomeric with III. When ketone III was warmed in carbon disulfide with aluminum chloride, the same ketone was produced. Based on its infrared spectrum, which indicates the presence of a conjugated mesityl ketone ($\nu_{C=O}$ 1640 cm^{-1}), this ketone is believed to be 3-phenylpropenyl mesityl ketone (VI). Catalytic hydrogenation of ketone VI converted it to 3-phenylpropyl mesityl ketone identical with an authentic sample.[16,17]

$$\text{III} \xrightarrow{AlCl_3}$$

$$C_6H_5CH_2CH=CHCOC_9H_{11} \xleftarrow{AlCl_3} C_9H_{12} + C_6H_5-\underset{\displaystyle CH_2}{\overset{\displaystyle CH_2}{\diagup\diagdown}}CHCOCl$$

VI

Based on the known acid-catalyzed ring openings of cyclopropane rings,[18] the expected product would have been cinnamyl mesityl ketone (VII). Depending

$$C_6H_5CH-\underset{\displaystyle CH_2}{\overset{\displaystyle CH}{\diagup\diagdown}}CHCOC_9H_{11} \xrightarrow{H^+} C_6H_5\overset{+}{C}HCH_2CH_2COC_9H_{11} \xrightarrow{-H^+}$$

$$C_6H_5CH=CHCH_2COC_9H_{11}$$

VII

upon the amount of catalyst, the temperature, and the time allowed for the ring-opening reaction, ketone VI was occasionally contaminated with an unconjugated ketone, presumably VII. A pure sample of VII was never obtained, but the reaction of 4-phenyl-3-butenoyl chloride[19] and mesitylene in the presence of aluminum chloride produced a similar mixture in which the β,γ-unsaturated isomer predominated. Similarly, addition of acetomesitylene enolate to phenylacetaldehyde produced a mixture of VI and VII.

$$C_6H_5CH=CHCH_2COCl + C_9H_{12} \xrightarrow{AlCl_3}$$

$$\text{VI} + \text{VII} \xleftarrow{} \overset{\ominus}{C}H_2COC_9H_{11} + C_6H_5CH_2CHO$$

Although the equilibrium VI $\rightleftarrows$ VII was not studied intensively, the formation of ketone VI appears to be favored.

The reaction of mesitylmagnesium bromide with ethyl 2-phenylcyclopropanecarboxylate yielded the desired ketone III, but in every preparation unreacted ester was recovered. The recovered ester, however, proved to be exclusively the *cis* isomer. This was proved by comparison of infrared spectra and gas chromatographic retention times with those of an authentic sample.[20] The original ester prepared by the action of ethyl diazoacetate on styrene[21] was found to be 1:1 mixture of the *cis* and *trans* isomers. The mesityl Grignard reagent thus selectively reacted with the less hindered isomer, the *trans* ester, and the product of this reaction is most probably *trans*-2-phenyl-1-mesitoylcyclopropane. Since this product was identical with that produced in the Wittig reaction, the latter product (III) would also have the *trans* configuration. Although base-catalyzed epimerization is possible in both these reactions, it seems more likely that the more stable isomer, the *trans* isomer, would survive. Because of the superposition of the strong methyl signals on the cyclopropane-ring hydrogen signals, it was not possible to use nmr coupling-constant data to determine the configuration of this ketone.

(9) R. Mechoulam and F. Sondheimer, *J. Am. Chem. Soc.*, **80**, 4386 (1958).
(10) D. B. Denney and M. J. Boskin, *ibid.*, **81**, 6330 (1959).
(11) W. S. Wadsworth, Jr., and W. D. Emmons, *ibid.*, **83**, 1733 (1961).
(12) E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 867 (1962); **87**, 1353 (1965).
(13) E. P. Kohler and C. E. Barnes, *ibid.*, **55**, 960 (1937).
(14) L. I. Smith and W. B. Pings, *J. Org. Chem.*, **2**, 23 (1937).
(15) R. C. Fuson and F. N. Baumgartner, *J. Am. Chem. Soc.*, **70**, 3255 (1948).
(16) During the preparation of an authentic sample of 3-phenylpropyl mesityl ketone from the reaction of mesityl cyclopropyl ketone with benzene in the presence of aluminum chloride,[15] a small amount of 1-tetralone was isolated. It was found that extended heating of the desired mesityl ketone with aluminum chloride produced 1-tetralone in good yield. This reaction is another example of the use of hindered ketones as acylating agents.[17]
(17) R. C. Fuson, W. A. Hills, and B. Vittimberga, *J. Am. Chem. Soc.*, **82**, 2559 (1960).
(18) G. Büchi and D. M. White, *ibid.*, **79**, 750 (1957).
(19) R. P. Linstead and L. T. D. Williams, *J. Chem. Soc.*, 2735 (1926).
(20) R. Fuchs and J. J. Bloomfield, *J. Am. Chem. Soc.*, **81**, 3158 (1959). We are indebted to Dr. Fuchs for samples of both the *cis* and *trans* esters.
(21) W. L. Yost and A. Burger, *ibid.*, **70**, 2198 (1948).

Experimental Section

2-Phenylcyclopropyl Mesityl Ketone. A. Wittig Reaction.—The Wittig reagent was prepared by the addition of 14.3 g (0.04 mole) of triphenylmethylphosphonium bromide to a solution of phenyllithium prepared from the reaction of 0.6 g (0.08 g-atom) of lithium, 6.3 g (0.04 mole) of bromobenzene, and 150 ml of ether. The resulting mixture was stirred for 2 hr, and then 10 g (0.04 mole) of benzalacetomesitylene[13] in 100 ml of ether was added slowly. The golden color of the Wittig reagent was discharged immediately and a cream-colored precipitate formed. The ether was removed by distillation while 250 ml of xylene was added. The resultant mixture was heated at 115–125° for 4 hr. The mixture was cooled and poured onto ice, and the organic material was separated and dried. Upon removal of the solvent *in vacuo*, an orange gum was obtained. This was dissolved in pentane containing a small amount of methylene chloride and chromatographed on silica. Elution with 3:1–1:1 pentane–methylene chloride yielded an orange oil, 5.2 g (50%). Distillation gave 2-phenylcyclopropyl mesityl ketone as a yellow viscous oil, bp 150–155° (0.1 mm), $n^{20}D$ 1.5754, yield 4.3 g (41%).

Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.45; H, 7.88.

B. Grignard Reaction.—To the Grignard reagent prepared from 40 g (0.20 mole) of bromomesitylene and 5 g (0.21 g-atom) of magnesium in 250 ml of ether was added 9.5 g (0.05 mole) of ethyl 2-phenylcyclopropanecarboxylate[21] in 100 ml of ether. The resulting solution was heated under reflux overnight and worked up in the usual manner. Distillation of the organic product yielded mesitylene, ethyl *cis*-2-phenylcyclopropanecarboxylate, bp 76–80° (0.25 mm), and *trans*-2-phenylcyclopropyl mesityl ketone, bp 150–152° (0.1 mm), $n^{20}D$ 1.5755, yield 7.4 g (56%).

The identity of the ester was established by comparison of its infrared spectrum with that of an authentic sample[20] and its retention time on a Carbowax column at 200°, using a Perkin-Elmer 154C vapor fractometer, which was also identical with that of authentic material and different from that of the *trans* ester.

C. Oxosulfonium Ylide Reaction.[22]—To a solution of 0.03 mole of dimethyloxosulfonium methylide in 50 ml of dimethyl sulfoxide prepared from 6.6 g of dimethyloxosulfonium iodide and 1.5 g of 50% sodium hydride–mineral oil dispersion[12] was added 6.3 g (0.025 mole) of benzalacetomesitylene in 15 ml of dimethyl sulfoxide at 0°. The mixture was stirred at room temperature for 2 hr and at 50° for 1 hr. After the standard work-up, the residual oil was chromatographed on silica gel and the desired product was eluted with 3:1 hexane–methylene chloride: yield 2.0 g (32%). The infrared spectrum of the product was identical with the spectra of products prepared in the other reactions.

(2-Phenyl-3-mesitoylpropyl)triphenylphosphonium Bromide (II).—To a solution of *ca.* 0.01 mole of triphenylmethylenephosphorane, prepared as described above, in 50 ml of anhydrous ether was added 2.5 g (0.01 mole) of benzalacetomesitylene in 25 ml of anhydrous ether. A white precipitate formed immediately. This solid was filtered and recrystallized from ethyl acetate: mp 210–220° dec.

Anal. Calcd for $C_{37}H_{36}BrOP$: C, 73.14; H, 5.97, Br, 13.15; P, 5.10. Found: C, 72.06; H, 5.87; Br, 13.54; P, 5.50.

The structure of compound II was inferred from its elementary analysis, the presence of a saturated mesitylene ketone band at 1685 cm^{-1} (Nujol mull), and the absence of olefinic hydrogen atoms (nmr spectrum in acetone-d_6).

Benzalacetophenone and the Wittig Reagent.—The Wittig reagent was prepared as described from 200 ml of 1 *M* butyllithium in pentane and 17.9 g (0.05 mole) of methyltriphenylphosphonium bromide. The pentane was replaced with tetrahydrofuran, and 10.4 g (0.05 mole) of benzalacetophenone in 100 ml of tetrahydrofuran was added. The resultant mixture was heated under reflux overnight. The solid material that formed was filtered; it proved to be a mixture of triphenylphosphine oxide and lithium bromide. The ether-soluble material was washed with water, dried, and concentrated. The residue was chromatographed on silica; 5:1 petroleum ether (bp 30–60°)–methylene chloride eluted 6.2 g (40%) of **1,3,4-triphenyl-4-styrylcyclohexene,** mp 136–138°, identical with authentic material.[7] Petroleum ether–methylene chloride (3:1) eluted a small amount (0.2 g) of a ketone ($\nu_{C=O}$ 1680 cm^{-1}), mp 176–177° (from ethanol).

Anal. Calcd for $C_{31}H_{26}O$: C, 89.85; H, 6.28. Found: C, 89.61; H, 6.02.

Petroleum ether–methylene chloride (1:1) eluted 2.5 g of unchanged benzalacetophenone. An unidentified residue was eluted with ethyl acetate.

Reaction of Benzalacetomesitylene with Diazomethane.—An ethereal solution of diazomethane (*ca.* 1 g) was added to 150 ml of ether containing 5 g of benzalacetomesitylene at 0 to −5°. This solution was allowed to stand overnight at room temperature. The solvent was evaporated to yield a yellow oil which crystallized when petroleum ether was added to its benzene solution. Recrystallization from ethanol yielded white crystals of 4-phenyl-3-mesitoylpyrazoline, mp 160–162°. Its infrared spectrum showed sharp NH absorption at 3320 cm^{-1} and hindered carbonyl absorption at 1640 cm^{-1}.

Anal. Calcd for $C_{19}H_{20}N_2O$: C, 78.05; H, 6.90; N, 9.58. Found: C, 78.00; H, 7.03; N, 9.36.

When the pyrazoline was heated at 200–220° (0.1 mm) for 2 hr, a yellow oil gradually distilled and solidified. Recrystallization from ethanol yielded yellow needles, mp 85–87°; β-methylbenzalacetomesitylene melts at 84°.[14]

Isomerization of 2-Phenylcyclopropyl Mesityl Ketone.—To 2 g of the ketone in 50 ml of carbon disulfide was added 0.7 g of aluminum chloride. It was necessary to cool the mixture with ice to control the exotherm. Stirring was continued at room temperature for 2 hr., during which time the mixture became dark red. It was poured on ice and hydrochloric acid, and the organic material was isolated in the usual manner. Removal of the solvent and distillation yielded a yellow oil, bp 136–140° (0.05 mm), $n^{20}D$ 1.5696.

Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.59, H, 7.74.

Its infrared spectrum showed carbonyl absorption at 1652 cm^{-1} similar to that in β-methylbenzalacetomesitylene. Its structure is assumed to be that of **3-phenylpropenyl mesityl ketone.** Upon treatment of 0.9 g of this ketone in 25 ml of ethanol with hydrogen at atmospheric pressure in the presence of 0.1 g of Pd–C catalyst, a new ketone, whose infrared spectrum was identical with that of **3-phenylpropyl mesityl ketone,**[15] was produced.

Reaction of Mesitylene and 2-Phenylcyclopropanecarbonyl Chloride.—To a suspension of 2.5 g (0.019 mole) of aluminum chloride in 50 ml of carbon disulfide was added a mixture of 3 g (0.0166 mole) of 2-phenylcyclopropanecarbonyl chloride[21] and 6 g (0.05 mole) of mesitylene in 20 ml of carbon disulfide at 0°. The mixture was allowed to warm to room temperature and stirred there for 2 hr. Work-up in the usual manner furnished 2.4 g (63%) of a yellow oil whose infrared spectrum was indistinguishable from that of 3-phenylpropenyl mesityl ketone.

Reaction of Acetomesitylene Enolate with Phenylacetaldehyde.—To a solution of 0.1 mole of ethylmagnesium bromide in 100 ml of ether was added 15.8 g (0.09 mole) of acetomesitylene in 50 ml of ether. This mixture was stirred for 1 hr, and then a solution of 12 g (0.1 mole) of phenylacetaldehyde in 50 ml of ether was added. This mixture was heated under reflux for 1 hr and then poured on ice and hydrochloric acid. The organic extracts were washed with water and sodium carbonate, dried, and concentrated. As infrared examination of the residue indicated the presence of a hydroxy ketone, it was dissolved in 50 ml of acetic acid containing 2 drops of concentrated sulfuric acid. This solution was heated on the steam bath for 2 hr, poured on ice, and extracted with ether. The ether extracts were washed with sodium carbonate solution and water, dried, and concentrated to yield a dark oil that was chromatographed on silica to yield 6.6 g (32%) of an oil, whose infrared spectrum was similar to that of 3-phenylpropenyl mesityl ketone but which showed a second carbonyl group of slightly lower intensity at 1690 cm^{-1}, indicating the presence of the unconjugated isomer.

Reaction of 4-Phenyl-3-butenoyl Chloride and Mesitylene.—A mixture of 5.5 g (0.03 mole) of 4-phenyl-3-butenoyl chloride[19] and 7.2 g (0.06 mole) of mesitylene in 50 ml of carbon disulfide was added with stirring at 0° to a suspension of 4.6 g (0.034 mole) of aluminum chloride in 50 ml of carbon disulfide. The mixture was allowed to warm to room temperature and stirred there for 2 hr. It was then poured on ice and hydrochloric acid.

(22) We are indebted to Mr. James Plonka for carrying out this experiment.

The organic extracts yielded a yellow oil, bp 140–145° (0.1 mm), whose infrared spectrum indicated it to be a mixture of 3-phenylpropenyl and 3-phenylallyl mesityl ketones.

Preparation of α-Tetralone from 3-Phenylpropyl Mesityl Ketone.—A mixture of 5 g (0.02 mole) of 3-phenylpropyl mesityl ketone[15] and 3 g of aluminum chloride was heated under reflux in carbon disulfide for 12 hr. The mixture was then poured on ice and hydrochloric acid, and the organic material was extracted with ether, washed with water, dried, concentrated, and chromatographed on silica to remove the mesitylene. α-Tetralone was eluted with 1:1 petroleum ether–methylene chloride and identified by its infrared spectrum and preparation of its 2,4-dinitrophenylhydrazone derivative, mp 260° (lit.[23] mp 262°), yield 2.3 g (80%).

α-Tetralone was similarly obtained, along with mesitylene, in the reaction of mesityl cyclopropyl ketone with benzene in the presence of aluminum chloride.[15] Less tetralone was produced in this latter reaction if the mixture was stirred at room temperature overnight after mixing of the reagents and then heated under reflux for only 1 hr.

(23) G. D. Johnson, *J. Am. Chem. Soc.*, **73**, 5888 (1951).

Iodine Formation in the Reaction of Polymethylbenzenes with Iodine Monochloride

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In acetic acid, hexamethylbenzene and pentamethylbenzene react with iodine monochloride by a process which is first order with respect to the aromatic hydrocarbon and second order in the halogen. In the reaction of hexamethylbenzene, iodine is produced and substitution of chlorine occurs at the aromatic side chain. The reaction of pentamethylbenzene appears to result mainly in ring iodination, although a small amount of free iodine is also formed. It is concluded that side-chain as well as ring substitution of the polymethylbenzenes is polar in nature and that, in the former reaction, a methylenecyclohexadiene serves as an intermediate. Some acetylated material, presumed to result from solvolysis of the initially formed haloaromatic substance, has been detected in the products of the hexamethylbenzene reaction. Side-chain chlorination of hexamethylbenzene by iodine monochloride also occurs in nitromethane solution. Unlike the corresponding reaction in acetic acid, halogenation in this solvent is self-inhibiting. Apparently, hydrogen chloride generated in the reaction forms a complex with iodine monochloride which is much less reactive than the free halogen.

It has been established previously[1] that hexamethylbenzene reacts with iodine monochloride in carbon tetrachloride to form pentamethylbenzyl chloride (eq 1). The reaction of pentamethylbenzene and

$$C_6(CH_3)_6 + 2ICl \longrightarrow C_6(CH_3)_5CH_2Cl + I_2 + HCl \quad (1)$$

iodine monochloride in carbon tetrachloride results mainly in the formation of pentamethyliodobenzene $C_6(CH_3)_5I$, a fact which suggests that halogenation occurs by a polar rather than a homolytic process. Since the rate laws for the halogenation of the two polymethylbenzenes are both of the form[1,2]

$$-d[ICl]/dt = k[ArH][ICl]^3 \quad (2)$$

it has been concluded that side-chain chlorination of hexamethylbenzene by iodine monochloride also occurs by a polar process which is mechanistically similar in character to the pentamethylbenzene reaction. The ring iodination of pentamethylbenzene by ICl is accompanied by the formation of some molecular iodine.

The investigation of iodine monochloride as a halogenating agent for penta- and hexamethylbenzene has now been extended mainly to determine the influence on the course of the reactions of shifting from carbon tetrachloride to more polar solvents. This brief report is concerned largely with the reactions in acetic acid and in nitromethane. Confirming evidence is also presented that, as has previously been assumed, the iodine formed in the pentamethylbenzene reaction in carbon tetrachloride is produced (eq 3) simultaneously with side-chain-chlorinated pentamethylbenzene (see Experimental Section).

$$C_6H(CH_3)_5 + 2ICl \longrightarrow C_6H(CH_3)_4CH_2Cl + I_2 + HCl \quad (3)$$

(1) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **86**, 4158 (1964).
(2) L. J. Andrews and R. M. Keefer, *ibid.*, **79**, 1412 (1957).

Experimental Section

Kinetics of Reaction of the Polymethylbenzenes and ICl.—Acetic acid[3] and nitromethane[4] were purified for solvent use as described previously. Iodine monochloride was prepared from the elemental halogens.[5] Eastman Organic Chemicals penta- and hexamethylbenzenes were used without further purification. The methods employed in preparing rate samples and in following the course of the reactions by spectrophotometric methods (using 1-cm absorption cells as reaction vessels) were closely similar to those applied in earlier rate work on the polyalkylbenzene–ICl reaction with carbon tetrachloride as the solvent.[1,2] Stock solutions of iodine monochloride and iodine (the latter prepared from the reagent grade halogen) were standardized by iodometric methods.

In the runs with pentamethylbenzene as the reacting hydrocarbon, the quantities of iodine monochloride consumed and of iodine formed were calculated (eq 4 and 5) from optical densities, d, of the solutions which were measured from time to time at two different wavelengths (λ_1 and λ_2). For reactions in acetic acid, wavelengths of 500 mμ and either 370, 420, or 430 mμ were used. For reactions in nitromethane, the two wavelengths were 500 and 420 mμ. The extinction coefficients, ϵ and ϵ' were determined separately for each reaction mixture since they vary with changes in the aromatic hydrocarbon concentration of the medium. The reactions were generally followed to high percentages (75% or more) of completion.

$$d_{\lambda_1} = \epsilon_{ICl}[ICl] + \epsilon_{I_2}[I_2] \quad (4)$$

$$d_{\lambda_2} = \epsilon'_{ICl}[ICl] + \epsilon'_{I_2}[I_2] \quad (5)$$

In investigating the reactions of hexamethylbenzene, a single wavelength, either 550 or 580 mμ, was employed in individual rate runs. The ICl concentrations during the course of the runs were calculated[1] from these readings and initial ICl concentrations on the assumption that 2 moles of the reacting halogen were consumed in forming 1 mole of iodine.

In the runs with both penta- and hexamethylbenzene, hydrogen chloride was produced in appreciable quantity. It was established by separate experiment that in acetic acid the extinction

(3) K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 983 (1927).
(4) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **81**, 1063 (1959).
(5) A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p 846.