[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Reaction of Ferric Chloride with Alkylbenzenes[1,2]

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A study was made of the interaction of anhydrous ferric chloride with benzene and alkylbenzenes (toluene, *p*-chlorotoluene, ethylbenzene, cumene and *t*-butylbenzene). Evidence was obtained for these several modes of reaction: nuclear chlorination, formation of diphenylmethane-type hydrocarbons, disproportionation and polymerization involving the alkyl side chains. The chemistry of the various processes is discussed.

Introduction

Previous reports on anhydrous ferric chloride as a chlorinating agent for aromatic compounds have been made by Thomas,[3] Dangyan[4] and more recently by Kovacic and Brace.[5] In an extension[6] of the inquiry to alkanes, reaction was found to occur under surprisingly mild conditions.

The purpose of the present work was to investigate the competing reactions involving the aromatic nucleus and the aliphatic side chain of alkylbenzenes, and to elucidate the reaction mechanisms. Benzene, toluene, *p*-chlorotoluene, ethylbenzene, cumene and *t*-butylbenzene were selected for this study.

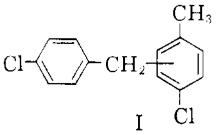
Results

Benzene.—As previously reported,[5] ferric chloride and benzene interacted very sluggishly. Reaction was apparent at the reflux temperature and after 9 hours yielded 9% of chlorobenzene, coal-like black solid, and 118% of the theoretical amount of hydrogen chloride. In all cases, yields of the aryl chloride and hydrogen chloride were calculated on the basis of the equation

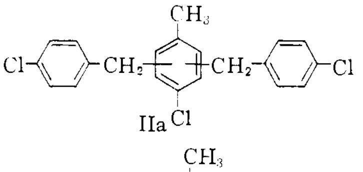
$$\mathrm{ArH} + 2\mathrm{FeCl_3} \longrightarrow \mathrm{ArCl} + 2\mathrm{FeCl_2} + \mathrm{HCl}$$

Toluene.—The presence of a methyl group on the benzene ring facilitated chlorination by ferric chloride. The reaction began at 45° and a 40% yield of chlorotoluene ($o/m/p$ = 13/< 1/87) was obtained along with black solid material. In addition, a liquid was isolated in very low yield, which is believed to contain a mixture of 2-, 3- and 4-methyldiphenylmethane from consideration of the physical constants, infrared spectrum and oxidative conversion to benzoylbenzoic acids.

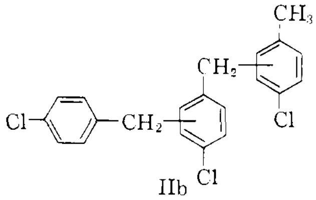
***p*-Chlorotoluene.**—From *p*-chlorotoluene and ferric chloride, there resulted, in addition to a mixture of dichlorotoluenes and polymeric solid, a liquid and a solid product which apparently are formed through involvement of the alkyl substituent. The liquid product is designated as a mixture of 2- and 3-(*p*-chlorobenzyl)-4-chlorotoluene (I) on the basis of the analysis, physical properties, infrared spectrum, dechlorination studies, and by comparison with authentic material prepared from *p*-chlorotoluene and α,*p*-dichlorotoluene by a Friedel–Crafts synthesis.



I



IIa

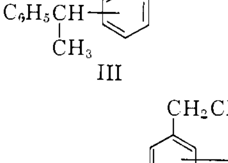


IIb

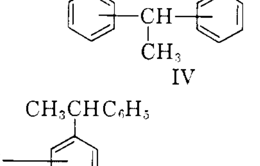
The infrared spectrum of I showed peaks at 12.4 μ characteristic of a 1,4-substituted benzene, and at 11.35 and 12.50 μ indicating 1,2,4-substitution. Catalytic dechlorination of I proceeded part way to completion yielding a crude product which exhibited infrared peaks characteristic of 2- and 3-methyldiphenylmethane. The product from the ferric chloride-catalyzed reaction of α,*p*-dichlorotoluene with *p*-chlorotoluene was found to have the same physical properties as I and a similar infrared spectrum. Dechlorination with sodium gave a mixture of 2- and 3-methyldiphenylmethane.

The solid product (II), m.p. 130.5–131°, has not been identified completely. Both structure IIa and IIb are consistent with the analysis, molecular weight and boiling point. Other isomers should also be considered, *e.g.*, those possibly arising through participation of the methylene group of I.

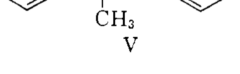
Ethylbenzene.—Compared with toluene, ethylbenzene possesses labile secondary hydrogens which are more susceptible to attack. As a result, nuclear chlorination diminished with apparent increase in side-chain participation (Table I). Evidence was obtained for formation of the products: benzene, *p*-chloroethylbenzene, diethylbenzene and 1,1-diphenylethane, in addition to 1-(ethylphenyl)-1-phenylethane (III), and possibly 1-(ethylphenyl)-1-(1′-phenyl-(ethylphenyl)-ethane (V) and 1,1-di-(ethylphenyl)-ethane (IV).



III



IV



V

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[1] Part III of a series on "Reactions of Metal Halides with Organic Compounds."

[2] From the forthcoming Ph.D. thesis of C. Wu and M.S. thesis, 1957, of R. W. Stewart, Case Institute of Technology. This paper was presented in part at the 131st Meeting of the American Chemical Society in Miami, Fla., April, 1957, Abstracts of Papers, p. 71-O.

[3] V. Thomas, *Compt. rend.*, **126**, 1211 (1898); **127**, 184 (1898); **128**, 1576 (1899); *Bull. soc. chim.*, [3] **21**, 286 (1899).

[4] M. Dangyan, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1780 (1938); *C. A.*, **33**, 4957 (1939).

[5] P. Kovacic and N. O. Brace, THIS JOURNAL, **76**, 5491 (1954).

[6] P. Kovacic and H. C. Volz, *ibid.*, **81**, 3261 (1959).

Isolation of benzene from the reaction mixture indicated disproportionation of ethylbenzene. The other disproportionation product, diethylbenzene, was present with chloroethylbenzene in a mixture which distilled at 178–179°, with the chloro compound comprising 58% of this fraction on the basis of elemental analysis. The infrared spectrum showed *o*-, *m*- and *p*-substitution peaks. Oxidation yielded a mixture of acids from which only *p*-chlorobenzoic acid and terephthalic acid were isolated and characterized. Since ferric chloride is a chlorinating agent of low "activity,"[7] the *meta* bands may reasonably be attributed for the most part to *m*-diethylbenzene. All absorbances characteristic of *m*-diethylbenzene were present in the spectrum of the 178–179° fraction.

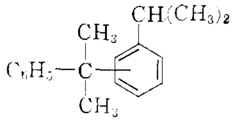
1,1-Diphenylethane was identified by comparison of the infrared spectrum with that of authentic material and by oxidative conversion to benzophenone.

The major product, b.p. 171–172° (23 mm.), was assigned structure III on the basis of the analysis, physical properties, infrared spectrum, and degradation to *p*-benzoylbenzoic acid and terephthalic acid by chromic acid oxidation. These acids would be formed from 1-(*p*-ethylphenyl)-1-phenylethane (III *para*). From consideration of the infrared spectrum, this hydrocarbon fraction was designated an isomeric mixture consisting mainly of the *p*-isomer. An authentic sample of III for comparison was synthesized by alkylation of ethylbenzene with styrene in the presence of ferric chloride catalyst. The liquid boiling at 174° (21 mm.) analyzed correctly for the desired product and possessed an infrared spectrum essentially identical with that of III except that the characteristic *meta* bands were virtually absent. In addition, the spectrum was a very close replica of that reported[8] for 1-(*p*-ethylphenyl)-1-phenylethane.

The fifth fraction from distillation, b.p. 182–183° (16.5 mm.), apparently not quite analytically pure, has been tentatively assigned structure IV, mainly from evidence provided by the infrared spectrum and molecular weight determination.

The subsequent fraction from distillation consisted of a yellow oil, b.p. 197–200° (0.7 mm.), whose infrared spectrum was strikingly similar to that of III. Analysis, molecular weight and physical properties are in accord with structure V. Oxidation yielded *p*-benzoylbenzoic acid and terephthalic acid. Hence the yellow oil is regarded as a mixture of the *p,p'*-isomer together with other isomers, *meta* bands being evident in the infrared spectrum along with *para* bands. Material for comparison was obtained in the form of a yellow oil, b.p. 171° (0.4 mm.), from the Friedel–Crafts reaction of styrene with ethylbenzene. The analysis and molecular weight were in agreement with the theoretical values, and the *para,para'* structural assignment for this product is in keeping with the formation of *p*-benzoylbenzoic acid and terephthalic acid from chromic acid oxidation. Except for the almost complete absence of *meta* bands, the infrared spectrum was a close duplication of that for the corresponding ethylbenzene–ferric chloride product.

Cumene.—The products in this case were similar in type to those obtained from the ethylbenzene–ferric chloride system. Accumulated evidence pointed to formation of the compounds: benzene, diisopropylbenzene, 2,2-diphenylpropane, 2-(isopropylphenyl)-2-phenylpropane (VI) and chlorocumene in extremely low yield.



VI

Apparently, the side chain of cumene is so susceptible to attack that nuclear chlorination is essentially eliminated as a competing reaction, less than 1% yield of chlorocumene being present in the fraction boiling at 196–198°. The remaining portion of this fraction consisted of diisopropylbenzene isomers as indicated by analysis, boiling point, infrared spectrum and oxidation to terephthalic acid.

Structure VI is in agreement with analytical and molecular weight data for the product which distilled at 118° (0.3 mm.). *Meta* and *para* bands were evident in the infrared spectrum. Oxidation of VI by various methods gave at best an oily, acidic fraction in very low yield. This unexpected result might be explained by the findings[9] of Brandenberger and Dvoretzky who reported an increase in nuclear oxidation with chromic acid as the number and complexity of side chains increased. Authentic 2-(isopropylphenyl)-2-phenylpropane was synthesized[10] by an alternative route from α-methylstyrene and cumene with aluminum chloride catalyst. The infrared spectrum of the product was very similar to that of VI except for differences in isomer distribution; VI was also obtained in a related investigation[10] and further characterized.

Both the ferric chloride reaction and the α-methylstyrene reaction with cumene gave unidentified, higher-boiling products.

***t*-Butylbenzene.**—From *t*-butylbenzene and ferric chloride, these products, formed by chlorination and disproportionation, were isolated and identified: benzene, chlorobenzene, chloro-*t*-butylbenzene, *m*- and *p*-di-*t*-butylbenzene.

Discussion

Chlorination.—Yields from the chlorination reaction in the alkylbenzene series varied from about 40% for toluene to less than 1% for cumene, contrasted with yields[5] in excess of 85% for chloro- and bromobenzene. Isomer distribution,[5] order of reactivity,[5] and solvent and catalytic effects[5,11] indicate that aromatic chlorination with ferric chloride proceeds by electrophilic substitution. The extremely high *para/ortho* ratio suggests that halogenation is effected by a reagent other than free

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(7) K. L. Nelson and H. C. Brown in "The Chemistry of Petroleum Hydrocarbons," Vol. 3, Reinhold Publishing Corp., New York, N. Y., 1955, p. 465.

(8) B. B. Corson, J. Dorsky, J. E. Nickels, W. M. Kutz and H. I. Thayer, *J. Org. Chem.*, **19**, 17 (1954).

(9) S. G. Brandenberger and I. Dvoretzky, Abstracts of Papers, 135th Meeting of the American Chemical Society, April, 1959, p. 93-O.

(10) P. Kovacic and A. K. Sparks, unpublished work.

(11) P. Kovacic and C. Wu, forthcoming publication.

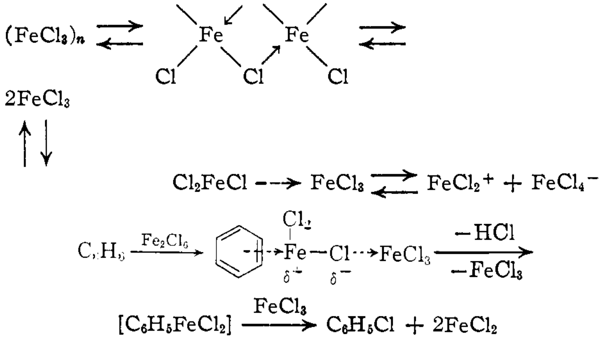
TABLE I

FERRIC CHLORIDE AND ALKYLBENZENES

Aromatic[a] cmpd.	Temp., °C.	HCl, mole	ArCl, mole	Disprop. prod. C_6H_6, mole	Disprop. prod. Dialkylbenzene, mole	"Dimer,"[b] mole	"Trimer,"[c] mole	Polymer, g.
Benzene	80	0.59	0.043	...	...	...	...	11.3
Toluene	45–68	.70	.198	...	...	0.005	...	10
p-Chlorotoluene[d]	104–109	.70	.046	...	...	.04	0.008	36
Ethylbenzene	37–38	.68	.041	0.026	0.031	.149	.013	15.1
Cumene	30–35	.64	.002	.026	.053	.157	.013	15.3
t-Butylbenzene	53–73	.59	.066	.295	.398	...	...	26.5

[a] Two moles of aromatic compound and one mole of ferric chloride. [b] Refers to the hydrocarbon product derived from two molecules of the starting aromatic. [c] Refers to the hydrocarbon product derived from three molecules of the starting aromatic. [d] Actual run made at half scale.

chlorine. Furthermore, no dissociation of ferric chloride to chlorine would be expected under the mild conditions of reaction. A plausible mechanism is suggested



The attacking species is considered to possess a rather large steric factor on the basis of the high *para/ortho* ratio, and only weak "activity"[7] as indicated by the low *meta* isomer content. The form in which ferric chloride participates is not known, nor whether the reaction is homogeneous or heterogeneous. Ferric chloride is reported[12] to exist as a dimer in non-polar solvents and as a solvated monomer in more polar media such as ether. The transition state for the electrophilic substitution is visualized as involving the dimer partly dissociated by the action of the basic aromatic nucleus. In this activated complex, one molecule of ferric chloride is considered to act as a Friedel–Crafts catalyst upon another in a situation analogous to the concerted displacement reaction proposed[7] for Friedel–Crafts alkylation by primary-alkyl halides.

Similarities are evident between individual steps of the hypothesis and the reported chemistry of organometallic compounds. Analogy for the postulated formation[13] of the unstable organo-iron compound may be found in the various reports concerning the processes of mercuration[14–16] and telluration.[17] The labile intermediate, $C_6H_5FeCl_2$, has also been invoked[18] in connection with the reaction of ferric chloride and diphenyldichlorosilane leading to phenyltrichlorosilane, chlorobenzene and ferrous chloride. In addition, the similarity is apparent between the last step and the reaction[18] of ferric chloride with phenylmagnesium bromide resulting in the formation of chlorobenzene.

Formation of Diphenylmethane-type Hydrocarbons.—Conversion of alkylbenzenes to diphenylmethane-type hydrocarbons indicates involvement of the aliphatic side chain in the reaction with ferric chloride. A reasonable interpretation of this result is illustrated for the ethylbenzene–ferric chloride system.

$$C_6H_5CH_2CH_3 \xrightarrow{3FeCl_3} C_6H_5\overset{+}{C}HCH_3{\cdot}FeCl_4^- + 2FeCl_2 + HCl$$

$$C_6H_5\overset{+}{C}HCH_3{\cdot}FeCl_4^- + C_6H_5CH_2CH_3 \longrightarrow \text{III} + HCl + FeCl_3$$

Direct side-chain attack by ferric chloride is consistent with the reported[6] interaction of ferric chloride with simple alkanes under comparatively mild conditions. Since investigation[6] of the ferric chloride–alkane reaction is only in the initial stages, little can be said concerning the mode of generation of the proposed carbonium ion.

In comparison with toluene, the formation of appreciably larger quantities of diphenylmethane-type product from *p*-chlorotoluene is quite interesting. It is conceivable that side-chain attack is enhanced by the *p*-chloro substituent through resonance stabilization in the transition state, as well as through inhibition of nuclear chlorination.

The yields of diphenylmethane derivatives increased in the order $C_6H_5CH_3 < p\text{-}ClC_6H_4CH_3 < C_6H_5C_2H_5 < C_6H_5CH(CH_3)_2$.

Polymerization.—In all of the ferric chloride–alkylbenzene reactions, considerable amounts of black or dark brown polymer-like solid or tar were obtained. Since side-chain attack is known to occur with resultant increase in molecular weight, it is logical to expect a continuation of this type of reaction leading to high molecular weight diphenylmethane derivatives. In fact, lower molecular weight hydrocarbons of this class, embodying two and three aromatic units, were isolated.

Since benzene yields mainly polymeric product, apparently polymerization can occur by an alternative route. In the case of *t*-butylbenzene, any isobutylene formed by acid-catalyzed degradation would be subject to conditions suitable for polar polymerization.

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[12] A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, London, 1950, p. 110.

[13] The term ferration is suggested for the proposed transformation.

[14] H. Gilman and G. F. Wright, THIS JOURNAL, **55**, 3302 (1933).

[15] W. J. Klapproth and F. H. Westheimer, *ibid.*, **72**, 4461 (1950).

[16] R. M. Schramm, W. Klapproth and F. H. Westheimer, *J. Phys. and Colloid Chem.*, **55**, 843 (1951).

[17] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, London, 1950, p. 992.

[18] A. Y. Yakubovich and G. V. Motsarev, *Zhur. Obshchei Khim.*, **23**, 1059 (1953); *C. A.*, **48**, 8187 (1954).

Disproportionation.—Ethylbenzene, cumene and *t*-butylbenzene were found to undergo disproportionation into benzene and dialkylbenzenes under the reaction conditions. The extent of disproportionation was in the expected order, $(CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2- > CH_3-$. Disproportionation and rearrangement of alkylbenzenes in acidic systems have been studied and interpreted[19a] by Lien and McCaulay.

Formation of 1,1-diphenylethane in the ethylbenzene–ferric chloride reaction might arise by (a) disproportionation of III or (b) interaction of $C_6H_5C^+HCH_3$ with benzene formed *in situ*. Similar considerations would apply to the formation of 2,2-diphenylpropane from cumene. In the *t*-butylbenzene case, chlorobenzene could arise either from reaction of ferric chloride with benzene formed in the reaction mixture, or from disproportionation of *t*-butylchlorobenzene. Theoretical considerations relevant to the formation of IV may be found in previous publications.[19b,20]

Acknowledgment.—We wish to express appreciation for support by the National Science Foundation and the Case Research Fund. We are grateful to Dr. Louis Schmerling for a sample of the dinitro derivative of bis-(*p*-chlorotolyl)-methane.

Experimental[21]

Materials.—Highest purity commercial products were used directly. Benzene, toluene, *p*-chlorotoluene and *α,p*-dichlorotoluene were from Eastman Kodak Co. Ethylbenzene, cumene and *t*-butylbenzene were 99 mole % minimum purity from Phillips Petroleum Co. Ferric chloride and *α*-methylstyrene were from The Matheson Co.

Ferric Chloride and Benzene. General Procedure.—Two moles (156 g.) of benzene and 1 mole (162 g.) of anhydrous ferric chloride were placed in a flask fitted with a nitrogen gas inlet, paddle stirrer, thermometer and a reflux condenser which was connected through a safety trap to a gas dispersion tube immersed in a phenolphthalein indicator solution (which was titrated with 2 *N* sodium hydroxide as hydrogen chloride was evolved). The black slurry was stirred at a rapid rate while dry nitrogen was introduced, and heated during 20 min. to reflux whereupon evolution of hydrogen chloride began. The hydrogen chloride produced during 9 hr. at 80° amounted to 0.59 mole (118%).

After steam distillation of the reaction mixture, the organic portion of the distillate was salted out, extracted with ether, dried, and distilled through a 12-in., helix-packed column with a variable take-off head, yielding 122 g. (1.6 moles) of benzene, b.p. 78–80°, and 5.2 g. (9.3%) of chlorobenzene, b.p. 131–133°, identical with authentic chlorobenzene by comparison of the infrared spectra. The black, solid residue in the steam distillation flask amounted to 11.3 g. (benzene-insoluble) after trituration with hot hydrochloric acid.

Anal. Found: (1) C, 77.89; H, 2.24; Cl, 17.89. (2) C, 77.73; H, 2.84; Cl, 18.74; Fe, 1.16.

Ferric Chloride and Toluene. (a).—Two moles of toluene was allowed to react with 1 mole of ferric chloride at 45–68° for 4 hr. as described in the general procedure. The reaction mixture yielded: recovered toluene, 1 mole, b.p. 108–111°; chlorotoluene, 25 g. (40%), b.p. 158–160°, n^{20}_D 1.5196; black solid, 13 g.; hydrogen chloride, 0.7 mole. The chlorotoluene was found by quantitative infrared analysis to consist of 13% *ortho-*, 87% *para-* and less than 1% *meta* isomer.

(b).—In a similar experiment at 105–110° for 0.5 hr., the product from 1 mole of toluene and 0.5 mole of ferric chloride was filtered, and the solid washed repeatedly with ether and then with water. Fractionation of the organic solution gave a 25% yield of chlorotoluene ($o/m/p$ = 14.5/1/84.5) and 0.5 g. of residue. Distillation of the residue gave a liquid, b.p. 279–280° (test-tube), which possessed absorption bands in the infrared region characteristic of 2-, 3- and 4-methyldiphenylmethane.[22]

The reaction mixture also yielded 10 g. of ether-insoluble black solid. An analytical sample was prepared by agitation with dimethylformamide, and dilution with water.

Anal. Found: C, 79.93; H, 4.37; Cl, 10.16; Fe, 3.75.

(c).—From toluene (6 moles) and ferric chloride (3 moles) at 60–70° for 3 hr., there was obtained, in addition to chlorotoluene and polymer, 1.5 g. of liquid, b.p. 272° (742 mm.) (test-tube), n^{21}_D 1.5700; reported[22] for the methyldiphenylmethanes: 2-isomer, b.p. 280.5° (760 mm.), n^{20}_D 1.5763; 3-isomer, b.p. 279° (760 mm.), n^{20}_D 1.5712; 4-isomer b.p. 282° (760 mm.), n^{20}_D 1.5692. The infrared spectrum indicated that the sample was a mixture of the three isomers.

Anal. Calcd. for $C_{14}H_{14}$: mol. wt., 182. Found: mol. wt., 180.

Oxidation with chromic acid yielded *p*-benzoylbenzoic acid,[23a] m.p. 194–195°, leaflets from aqueous alcohol; the mixture melting point with an authentic sample showed no depression. Addition of water to the mother liquor yielded, after 3 days at room temperature, a small amount of needle-like crystals, m.p. 93°, which melted at 126–127° after being freed of water; reported[23b] for *o*-benzoylbenzoic acid, m.p. 93° (hydrate), 127° (anhydrous). The mixture melting point with an authentic anhydrous sample (Eastman Kodak Co.) was not depressed. Crystals melting at 138–142° were also obtained.

Nitration with 2:1 sulfuric acid–nitric acid yielded a yellow, viscous mass which could not be crystallized.

Ferric Chloride and *p*-Chlorotoluene.[5]—Ferric chloride (81 g., 0.5 mole) was added in one portion to *p*-chlorotoluene (127 g., 1 mole) at 104°. Hydrogen chloride was evolved vigorously, and the reaction mixture turned to a thick, black mass. A total of 0.7 mole of hydrogen chloride was generated during 30 min. at 104–109°. Steam distillation left a red, soft tar, 30 g., which was soluble in organic solvents. The distillate yielded 97 g. (0.86 mole) of unreacted *p*-chlorotoluene, b.p. 160–162°, and 3.6 g. (9%) of a colorless liquid, b.p. 113° (33 mm.), which was identified by infrared analysis as a mixture of 2,4-dichlorotoluene [9.07(s), 9.14(s), 9.55(s), 12.04(s), 14.17(s) μ] and 3,4-dichlorotoluene [8.28(m), 8.77(m), 8.88(s), 9.73(s), 10.6(w) μ] by comparison with the spectrum of an authentic mixture.

The red tar was distilled *in vacuo* yielding 5 g. of slightly yellow oil, 1.5 g. of brown crystals and 18 g. of brown, solid residue.

The yellow oil was redistilled to give a colorless liquid (I), b.p. 123° (0.16 mm.), n^{20}_D 1.5916, d^{27} 1.202. The infrared spectrum showed peaks at 8.83(m), 9.22(s), 9.60(s), 9.88(s), 11.0(m), 11.22(w), 11.36(m), 12.40(vs), 12.50(m), 13.26(m), 14.02(w), 15.26(m) μ.

Anal. Calcd. for $C_{14}H_{12}Cl_2$: C, 66.95; H, 4.82; Cl, 28.23; mol. wt., 251. Found: C, 66.66; H, 4.77; Cl, 28.5; mol. wt., 250.

The brown crystals were recrystallized from absolute alcohol as colorless crystals (II?), m.p. 130.5–131°. The following infrared bands were present in the 11–15 μ region: 11.25(w), 11.35(w), 11.83(m), 12.1(m), 12.37(vs), 12.8(w), 13.05(w), 13.72(w), 14.2(w), 14.7(w) and 15.13(w). The 2–11 μ region was essentially identical with that of I.

Anal. Calcd. for $C_{21}H_{17}Cl_3$: C, 67.13; H, 4.56; Cl, 28.31; mol. wt., 376. Found: C, 67.12; H, 4.69; Cl, 28.55; mol. wt., 374.

Dechlorination of I by Catalytic Hydrogenation.—A 2.5-g. (0.01 mole) quantity of I, b.p. 123° (0.16 mm.), was dissolved in 50 ml. of 10% alcoholic potassium hydroxide solution containing 220 mg. of palladium oxide catalyst. The hydrogenation was carried out at room temperature under 1

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[19] (a) A. P. Lien and D. A. McCaulay, THIS JOURNAL, **74**, 6246 (1952); **75**, 2407 (1953); (b) D. A. McCaulay, M. C. Hoff, N. Stein, A. S. Couper and A. P. Lien, *ibid.*, **79**, 5808 (1957).

[20] L. Schmerling, J. P. Luvisi and R. W. Welch, *ibid.*, **81**, 2718 (1959).

[21] Boiling points and melting points are uncorrected. Elemental analyses were made by Weiler and Strauss, Oxford, England.

[22] J. H. Lamneck, Jr., H. F. Hipsher and V. O. Fenn, Natl. Advisory Comm. Aeronaut., Tech. Note No. 3154 (1954), p. 9.

[23] (a) M. E. Smith, THIS JOURNAL, **43**, 1920 (1921); (b) W. Hemilian, *Ber.*, **11**, 837 (1878); (c) P. Senff, *Ann.*, **220**, 225 (1883).

atm. pressure. After 3 hr. the hydrogen uptake was 30% of theory, and a test for chloride ion was positive. The reaction mixture was washed with water, extracted with ether, dried and freed of solvent. The residue was distilled; the infrared spectrum of the first fraction, b.p. 105° (1 mm.), showed new strong bands at 13.05, 13.48, 13.82 and 14.40 μ. The spectrum was compared with the published spectra of methyldiphenylmethanes, and was found to correspond to a mixture of 2- and 3-methyldiphenylmethane, except for bands which could be attributed to either starting material or partially dechlorinated product.

Authentic *p*-(Chlorobenzyl)-4-Chlorotoluene. 1. Synthesis.—To a mixture of α,*p*-chlorotoluene (40.3 g., 0.25 mole) and *p*-chlorotoluene (143 g., 1.13 moles), which was continuously shaken in an ice-bath, was added portionwise 12 g. (0.07 mole) of ferric chloride catalyst. After evolution of hydrogen chloride had subsided, the reaction mixture was allowed to stand at room temperature for 1.5 hr., poured into water, and worked up by ether extraction and distillation of the combined extracts. These various fractions resulted: recovered *p*-chlorotoluene, 90.7 g., b.p. 160–162°; a colorless liquid, 40 g. (64%), b.p. 137–138° (0.5 mm.), $n^{20}D$ 1.5915, d^{27} 1.201. Except for differences in band intensities, the infrared spectrum of the high-boiling product was essentially identical with the corresponding liquid (I) obtained from the *p*-chlorotoluene–ferric chloride reaction.

Anal. Calcd. for $C_{14}H_{12}Cl_2$: C, 66.95; H, 4.82; Cl, 28.23. Found: C, 66.65; H, 4.74; Cl, 28.5.

The distillation residue consisted of brown, viscous material (19 g.).

Nitration of authentic I with 2:1 sulfuric acid–nitric acid afforded a dinitro derivative, pale yellow crystals, m.p. 142.5–143.5° (from glacial acetic acid); a mixture melting point with the dinitro derivative of bis-(*p*-chlorotolyl)-methane[20] (m.p. 145–151°; reported 144°) was depressed to 120–142°. The infrared spectra of the two nitro derivatives were similar but not identical.

Anal. Calcd. for $C_{14}H_{10}Cl_2N_2O_4$: N, 8.21. Found: N, 8.48.

2. Dechlorination. (a) With Sodium.—A 5–10 μ sodium dispersion was prepared by stirring vigorously (at 20,000 r.p.m. for 10 min.) 3 g. of sodium in 50 ml. of mesitylene at 150°. After the addition of 6 g. of authentic I, the mixture was stirred at 150–160° for 4 hr. Work-up yielded a crude product which on distillation through an 18 in. by 6 mm. spinning band column gave 3 g. (70%) of a colorless liquid, b.p. 149° (30 mm.), b.p. 273° (744 mm.) (test-tube), $n^{20.5}D$ 1.5708. The infrared spectrum revealed it to be a mixture of 2- and 3-methyldiphenylmethane.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74; mol. wt., 182. Found: C, 92.30; H, 7.99; mol. wt., 181.

Oxidation with chromic acid afforded acidic material which upon crystallization from 2:1 water–methanol gave *m*-benzoylbenzoic acid as the first crop, m.p. 162–163° from toluene; methyl ester, m.p. 62°; reported[23a] m.p. 161°; methyl ester, m.p. 62°. Addition of water to the mother liquor yielded *o*-benzoylbenzoic acid in small amount, m.p. 129–130° from toluene.

Nitration yielded a yellow, viscous mass that resisted crystallization.

(b) Attempted with Magnesium.—Iodine-activated magnesium powder (0.73 g.) and authentic I (3.14 g.) were sealed in an evacuated tube and heated at 260° for 3 days. The reaction mixture underwent no apparent change and a test for chloride ion was weak. Distillation of the organic material yielded only recovered starting material.

Ferric Chloride and Ethylbenzene.—A mixture of ethylbenzene (212 g., 2 moles) and ferric chloride (1 mole) evolved hydrogen chloride rapidly at 37°. Since the temperature rose quickly to 46°, cooling was applied in order to maintain the temperature at 37–38°. During 2 hr., 0.68 mole of hydrogen chloride was evolved.

The reaction mixture was poured over ice, and organic materials were extracted with ether leaving 1.1 g. of ether- and water-insoluble black solid. The black ethereal extract was washed repeatedly with water, dried and fractionated. A colorless liquid, wt. 2 g., b.p. 78–81°, was collected and identified as benzene by the infrared spectrum. After 1.3 moles of ethylbenzene, b.p. 130–135°, was recovered, the residue was distilled under vacuum through a 12-in. helix-packed column. The distillate (10 g.), fraction A, was a slightly green liquid with a strong characteristic odor, b.p. 69° (11 mm.), b.p. 178–179° (750 mm.), $n^{20}D$ 1.5061, which appeared to be a mixture of chloroethylbenzene (58%) and diethylbenzene (42%) (lit.: *p*-chloroethylbenzene,[24] b.p. 179–180°, $n^{18}D$ 1.5223; *p*-diethylbenzene,[25] b.p. 183°, $n^{20}D$ 1.4973). The infrared spectrum showed *ortho, meta* and *para* bands; comparison with the reported[26a] spectra of diethylbenzenes indicated the presence of *p*-diethylbenzene (8.93, 9.80, 12.07 μ) and the *m*-isomer (11.28, 11.58, 12.54, 14.0, 14.27 μ).

Anal. Calcd. for C_8H_9Cl: C, 68.33; H, 6.45; Cl, 25.22. Calcd. for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 75.08; H, 7.73; Cl, 14.7.

Oxidation of A with chromic acid in acetic acid gave ether-soluble *p*-chlorobenzoic acid, m.p. 243–244°, reported[27] m.p. 243°; and ether-insoluble acid which was separated into two parts by fractional precipitation of the sodium derivative in an attempt to concentrate isophthalic acid in the mother liquor. After acidification of the precipitated salt, the acid was converted to the methyl ester, m.p. 139–140°, which possessed an infrared spectrum identical with that of an authentic sample of dimethyl terephthalate, m.p. 140°. The mother liquor was acidified, and the methyl ester of the acid was prepared; the infrared spectrum showed that this ester was also dimethyl terephthalate.

The viscous residue from distillation of A was distilled through a 3-in. Vigreux column, yielding 36.3 g. of a yellow liquid, b.p. 96–220° (1 mm.), and 15.1 g. of black, solid residue. The liquid was redistilled through a 12-in. helix-packed column, and separated into four fractions: B, 2.5 g. of a colorless liquid, b.p. 100° (1 mm.); C, 19 g. of a colorless liquid, b.p. 113–123° (1 mm.); D, 9.9 g. of a colorless liquid, b.p. 135–140° (1 mm.); E, 3.6 g. of a yellow, viscous, residual oil.

Fraction B was purified by redistillation, b.p. 267–268° (746.6 mm.), $n^{20}D$ 1.5699, d^{20} 0.9928; reported[28] for 1,1-diphenylethane: b.p. 272.6° (760 mm.), $n^{20}D$ 1.5725, d^{20} 0.9995. The infrared spectrum was identical with that reported[26b,29a] for 1,1-diphenylethane.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.89; H, 8.03.

Oxidation of B with chromic acid in acetic acid gave a viscous, yellow oil which did not crystallize. The crude product was treated directly with 2,4-dinitrophenylhydrazine reagent, giving orange crystals, m.p. 239° (from ethanol–ethyl acetate). A mixture m.p. with an authentic sample of the 2,4-dinitrophenylhydrazone of benzophenone, m.p. 239°, exhibited no depression.

On redistillation, fraction C gave a liquid (III), b.p. 171–172° (23 mm.), $n^{20}D$ 1.5595, d^{20} 0.9742; reported[8] for 1-(*p*-ethylphenyl)-1-phenylethane: b.p. 170° (20 mm.), $n^{20}D$ 1.5605, d^{20} 0.9746. The infrared spectrum was very similar to that reported[8] except for the presence of *m*-substitution bands at 5.36, 5.63, 11.26, 11.50, 12.51 μ.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.32; H, 8.38.

Oxidation of C with chromic acid in acetic acid gave terephthalic acid (dimethyl ester, m.p. 140°) and *p*-benzoylbenzoic acid (m.p. 194°; methyl ester, m.p. 106.5–107°).

Anal. Calcd. for $C_{14}H_{10}O_3$: neut. equiv., 226. Found: neut. equiv., 227.

Fraction D was redistilled into two parts. The first part, b.p. 175–177° (20 mm.), appeared to be rich in III according to the infrared spectrum. The second part (IV?), b.p. 182–183° (16.5 mm.), b.p. 122–123° (0.3 mm.), $n^{20}D$ 1.5536, d^{20} 0.9734, weighed 4.2 g.; infrared bands characteristic of monosubstituted benzenes (5.16, 5.36, 5.56, 5.73, 13.2 and 14.35 μ) had disappeared, and bands characteristic of *p*- and *m*-substitution (5.28, 12.04 and 5.18, 5.38, 5.64, 11.27, 12.6, 14.25 μ, respectively) had increased in intensity.

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(26) F. D. Rossini, K. Li and R. B. Ries, Infrared Spectral Data, Am. Petr. Inst. Res. Proj. 44, 1956; (a) Ser. No. 1419, 1588 and 1589; (b) Ser. No. 410.

(27) H. Gelissen and P. H. Hermans, *Ber.*, **58**, 285 (1925).

(28) K. T. Serijan, I. A. Goodman and W. J. Yankauskas, *Natl. Advisory Comm. Aeronaut.*, Tech. Note No. **2557** (1951), p. 4.

(29) *Ibid.*, (a) p. 8; (b) p. 11.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.70; H, 9.30; mol. wt., 238. Found: C, 90.08; H, 9.10; mol. wt., 234.

Fraction E was redistilled to give a yellow, viscous oil (V?), b.p. 197–200° (0.7 mm.), n^{20}_{D} 1.5828, d^{20} 1.0177. The infrared spectrum was strikingly similar to that of fraction C; it was also very similar to that of the corresponding product from styrene and ethylbenzene except for *meta* bands which were either absent or very weak in the latter sample.

Anal. Calcd. for $C_{24}H_{26}$: C, 91.66; H, 8.33; mol. wt., 314. Found: C, 91.46; H, 8.44; mol. wt., 319.

Authentic 1-(Ethylphenyl)-1-phenylethane and 1-(Ethylphenyl)-1-(1′-phenyl-(ethylphenyl)-ethane)(?).—Freshly distilled styrene (26 g., 0.25 mole) was added with stirring during 40 min. to a mixture of ethylbenzene (126.5 g., 1.125 moles) and ferric chloride catalyst (12.15 g., 0.075 mole) at 5°. Stirring was continued for 3 hr. while the temperature was increased to room temperature. The reaction mixture was washed thoroughly with water, dried and distilled. There resulted 100 g. of recovered ethylbenzene, b.p. 135–136°; 20.6 g. (53% based on unrecovered ethylbenzene) of a liquid product, b.p. 174° (21 mm.), n^{20}_{D} 1.5603, d^{20} 0.9752; and a jelly-like residue. The infrared spectrum of the liquid was identical with that reported[8] for 1-(*p*-ethylphenyl)-1-phenylethane.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.37; H, 8.42.

The viscous residue was distilled *in vacuo* yielding 4 g. of a colorless liquid, 6.5 g. of a yellow viscous oil, and 10.8 g. of brown, tarry residue.

The colorless liquid, b.p. 53–54° (30 mm.), n^{20}_{D} 1.5429, possessed an infrared spectrum identical with that of styrene.[30]

The yellow oil was redistilled through a short Vigreux column, b.p. 171° (0.4 mm.), n^{20}_{D} 1.5807, d^{20} 1.023. The infrared spectrum was strikingly similar to that[8] of 1-(*p*-ethylphenyl)-1-phenylethane.

Anal. Calcd. for $C_{24}H_{26}$: C, 91.66; H, 8.33; mol. wt., 314. Found: C, 91.40; H, 8.47; mol. wt., 312.

Oxidation of the yellow oil with chromic acid in acetic acid gave an ether-soluble acid and an ether-insoluble acid. A mixture melting point of the ether-soluble acid (m.p. 195°; methyl ester, m.p. 106–107°) with *p*-benzoylbenzoic acid, obtained from oxidation of C, was undepressed. The methyl ester of the ether-insoluble acid melted at 139–140°, and was shown to be identical with dimethyl terephthalate by a mixture melting point with an authentic sample.

Ferric Chloride and Cumene.—The exothermic reaction of cumene (240 g., 2 moles) with ferric chloride (1 mole) was maintained at 30–35° by cooling. After 2 hr., 0.64 mole of hydrogen chloride was generated. An ethereal solution of the organic material from the reaction mixture was washed with water, freed of solvent, and distilled to give 2 g. of benzene, b.p. 78–80° (identified by the infrared spectrum); 163 g. (1.35 moles) of cumene, b.p. 151–152°; and a black, viscous residue. Distillation of the residue at the aspirator gave 52 g. of a yellow liquid and 15.3 g. of black solid. The yellow liquid was fractionated into five parts: A, 9 g., b.p. 45° (0.6 mm.); B, 10 g., b.p. 90–110° (0.8 mm.); C, 17 g., b.p. 120° (0.6 mm.); D, 10 g., b.p. 120–130° (0.5 mm.); E, 4.5 g. of yellow residue.

Fraction A was a slightly green liquid with a characteristic odor, b.p. 196–198° (756 mm.), n^{20}_{D} 1.4944, which appeared to be a mixture of chlorocumene (4%) and diisopropylbenzene (96%), (lit.: *p*-chlorocumene,[31] b.p. 195–197° (730 mm.), n^{25}_{D} 1.514; *p*-diisopropylbenzene,[32] b.p. 202–204°, n^{20}_{D} 1.4907). The infrared spectrum had peaks at 12.04 (*para*), 12.59 (*meta*) and 13.17 μ (*ortho*).

Anal. Calcd. for $C_9H_{11}Cl$: C, 69.90; H, 7.17; Cl, 22.93. Calcd. for $C_{12}H_{18}$: C, 88.89; H, 11.11. Found: C, 87.88; H, 10.44; Cl, 0.90.

Chromic acid oxidation of A gave a colorless acidic fraction which was separated into two parts by extraction with ethanol in an attempt to concentrate isophthalic acid in the ethanolic solution. Both parts were found to be terephthalic acid by comparison of the infrared spectra of their dimethyl esters with that of dimethyl terephthalate [5.8(s), 7.85(s), 8.95(s), 9.75(m) and 13.65(s) μ].

Fraction B was redistilled through a short Vigreux column over a temperature range of 90 to 117° at 0.35 mm. The analytical sample, b.p. 92–93° (0.35 mm.), n^{20}_{D} 1.5579, had a spectrum identical with that[29b] of 2,2-diphenylpropane (lit.[28]: b.p. 281.2°, n^{20}_{D} 1.5703) except for weak *para* and *meta* bands at 12.05 and 12.62 μ, respectively.

Anal. Calcd. for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.61; H, 8.57.

A sample which was collected at 107–108° (0.25 mm.), n^{20}_{D} 1.5565, showed increased intensity in the *para* and *meta* regions.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.97; H, 9.04.

Fraction C was found to be uniform by redistillation. The sample (VI) taken for analysis boiled at 116° (0.6 mm.), n^{20}_{D} 1.5546, d^{26} 0.9682. The infrared spectrum, which possessed strong *para* and *meta* bands, was very similar to that of the product[10] from isopropylation of 2,2-diphenylpropane.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.40; H, 9.37.

Oxidation of C with various agents including chromic acid and nitric acid yielded only trace amounts of oily acidic material.

Fraction D was distilled twice into several fractions, and each was analyzed by the infrared method. The last fraction was found to be richest in the *p*-isomer of VI with only a weak *meta* band at 12.6 μ, b.p. 120° (0.3 mm.), n^{20}_{D} 1.5536, d^{36} 0.9682. Infrared bands were present at the following positions (μ): 7.12(m), 7.26(s), 7.37(s), 8.43(w), 8.76(w), 9.2(m), 9.34(m), 9.52(m), 9.73(s), 9.85(s), 12.07(s), 12.60-(w), 13.12(s), 14.35(s).

Anal. Calcd. for $C_{18}H_{22}$: C, 90.70; H, 9.30; mol. wt., 238. Found: C, 90.46; H, 9.51; mol. wt., 242.

Fraction E was redistilled to give a yellow, viscous oil, b.p. 173° (0.3 mm.), n^{20}_{D} 1.5689, d^{26} 1.008. The infrared spectrum was essentially identical with that of VI.

Anal. Calcd. for $C_{27}H_{32}$: C, 92.00; H, 8.00; mol. wt., 352.5. Found: C, 91.04; H, 8.49; mol. wt., 332.

Authentic 2-(Isopropylphenyl)-2-phenylpropane.[10]—α-Methylstyrene (60 g., 0.5 mole) was added slowly at 0° to a mixture of cumene (2 moles) and anhydrous aluminum chloride (0.05 mole). The desired product, 14 g., boiled at 149–151° (5 mm.), n^{20}_{D} 1.5582. The infrared spectrum corresponded to that of VI except for differences in isomer distribution.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.77; H, 9.14.

Repeated distillation was required to separate an accompanying product, presumably 2,2-diphenylpropane, from the 2-(isopropylphenyl)-2-phenylpropane.

Ferric Chloride and *t*-Butylbenzene.[33]—*t*-Butylbenzene (268 g., 2 moles) and ferric chloride (1 mole) reacted exothermically at 73°. During 4 hr. at a controlled temperature of 53–59°, 0.69 mole of hydrogen chloride was obtained. After steam distillation, the dried organic distillate was fractionated in a Todd column at a reflux ratio of 10 to 1. Before the recovery of 0.88 mole of *t*-butylbenzene, b.p. 167°, n^{20}_{D} 1.4926, d^{20} 0.8665, there resulted 23 g. of benzene, b.p. 78.8–79°, n^{20}_{D} 1.4998, d^{20} 0.8790 and 5 g. of chlorobenzene, b.p. 130–131°, n^{20}_{D} 1.5250, d^{20} 1.1068 (each identified by the infrared spectrum).

A colorless oil with the odor of licorice, 11.2 g., was obtained at 209–217°, with center cut, b.p. 214–215°, n^{20}_{D} 1.5053; reported[34] for *p*-chloro-*t*-butylbenzene, b.p. 214–216°, n^{20}_{D} 1.509. A chlorine test was positive. The infrared spectrum showed the sample to be mainly *p*-chloro-*t*-butylbenzene, and, except for differences in isomer distribution, was essentially the same as that previously reported.[8]

A colorless oil with a faint odor, 37.4 g., distilled at 223–226°, with center cut, b.p. 223°, n^{20}_{D} 1.4885; reported[35]

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(30) Believed to arise from the pyrolysis of styrene polymer. Dimer was isolated in a similar reaction reported[8] by Corson, *et al.*

(31) I. P. Tsukervanik, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1512 (1938); *C. A.*, **33**, 4587 (1939).

(32) V. N. Ipatieff and H. Pines, THIS JOURNAL, **59**, 56 (1937).

(33) Performed by F. J. Donat who also assisted with other aspects of the experimental work.

(34) W. H. C. Rueggeberg, M. L. Cushing and W. A. Cook, THIS JOURNAL, **68**, 191 (1946).

(35) H. Pines, G. J. Czajkowski and V. N. Ipatieff, *ibid.*, **71**, 3798 (1949).

for *m*-di-*t*-butylbenzene, b.p. 101° (11.2 mm.), n^{20}_D 1.4879. The infrared spectrum was identical in every detail with the reported spectrum.[35]

Anal. Calcd. for $C_{14}H_{22}$: C, 88.33; H, 11.67. Found: C, 88.42; H, 11.66.

The residue consisted of 38 g. of brown, oily solid which, on washing with ethanol, yielded 36 g. of colorless crystals, m.p. 80–80.2° (crystallized twice from cyclohexane), b.p. 237°; a mixture melting point with authentic *p*-di-*t*-butylbenzene (Eastman Kodak Co.), m.p. 76.8–78°, b.p. 237°, showed no depression. In addition, the infrared spectra were identical.

The black solid left from steam distillation of the reaction mixture was dissolved in toluene, extracted with water, and evaporated to dryness yielding 26.5 g. of black, glassy solid.

Analytical Methods.—Analysis of the mixtures of chlorotoluene isomers was effected by use of a plot of the known concentration in cyclohexane solution *versus* the absorbance according to the base line method.[36] *Meta* isomer determinations were made by the differential method. The absorbance was measured at the indicated wave length (μ): *o*-chlorotoluene (13.40), *p*-chlorotoluene (12.45) and *m*-chlorotoluene (13.0). Comparison with known mixtures showed a deviation of no more than ±1% for the *p*-isomer. Infrared spectra were obtained with a Perkin–Elmer model 21 infrared spectrophotometer. Molecular weights were determined by the Rast method.

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[36] R. L. Bohon, R. Isaac, H. Hoftiezer and R. J. Zellner, *Anal. Chem.*, **30**, 245 (1958).

CLEVELAND, OHIO

[CONTRIBUTION FROM THE DOW CHEMICAL CO., WESTERN DIVISION]

Physical and Chemical Effects of Substituent Groups on Multiple Bonds. II. Thiolesters[1]

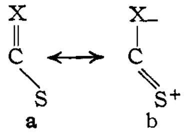
BY A. W. BAKER AND G. H. HARRIS

RECEIVED SEPTEMBER 11, 1959

Correlations of carbonyl frequencies and basicities have shown that sulfur in thiolesters participates in resonance interaction in the ground state through 3d-orbitals. The ν_{CO} values of thiolesters are 40–60 cm.$^{-1}$ lower than those of esters (almost the same as those of amides), but the carbonyl basicities are much lower. This precludes amide-type resonance.

The electronic structure of the chemical bonds in certain types of sulfur compounds has been unexpectedly variable and difficult to characterize. This is particularly evident in functional groups where sulfur can form multiple bonds to a single ligand, either by formal, non-charged structures or by conjugative interaction with an adjacent unsaturated group. While the former double bond structures have been the subject of many recent papers,[2–5] the latter have received relatively little attention and are not well understood.

One question of particular interest in compounds containing sulfur attached directly to a π-electron system pertains to the nature of the conjugative interaction and the type of orbitals used by sulfur in the consequent π-bond formation. Infrared spectra of vinyl sulfides or aliphatic and aromatic thiolesters show that the sulfur atom causes a surprisingly large perturbation on the adjacent double bond. For an ethylenic C═C group, this is much larger than the effect shown by oxygen and, for the carbonyl group, is in the opposite direction and nearly equivalent to the effect of nitrogen. It can be measured indirectly by the shift to lower frequencies of the characteristic double bond stretching vibrations, a shift which unquestionably is not due to mechanical coupling or physical mass effects. The cause of this perturbation has been described previously[6] as a reduction in the force constant of the double bond due to a conjugative shift of electrons away from the sulfur orbitals according to valence bond structures Ia and Ib. These involve the use of 3p-orbitals by sulfur. However, it is now well known[7] that the 3p π-bonds of sulfur are much less stable than the 2p π-bonds of oxygen and that the electron release of divalent sulfur (–SR) is less than that of oxygen (–OR). It has also been shown conclusively that sulfur can expand its valence shell to 10 or more electrons under conditions which indicate that the energies required for d-orbital utilization are not exorbitantly high.[8] Therefore, despite the fact that atom X may have a higher electronegativity than sulfur, it is much more probable that the drift of electrons is in the opposite direction due to conjugative coupling of the type shown in structures IIa and IIb.



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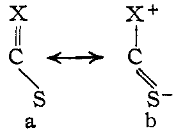

II

These two different types of resonance interaction, discussed below from the standpoint of orbital overlap, have opposite effects on the electron charge or bond hybridization of atom X. Consequently, when X is an atom having lone pair electrons (N,O), the availability or basicity of these electrons will be quite different according to the type of interaction. The conjugation shown in structure I will obviously increase the basicity of the lone pair electrons since the amount of p-character in these orbitals increases, but the conju-

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[1] Presented before an open scientific meeting June, 1958, at the Western Regional Research Laboratories, Bureau of Agriculture and Industrial Chemistry, Albany, Calif.

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[3] H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

[4] Hans Siebert, *Z. anorg. u. allgem. Chem.*, **275**, 210 (1954).

[5] W. Moffitt, *Proc. Roy. Soc.* (*London*), **200A**, 409 (1950).

[6] R. B. Barnes, R. C. Gore, V. Liddel and V. Z. Williams, "Infrared Spectroscopy," Reinhold Publishing Corp., New York, N. Y., 1944.

[7] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapt. II.

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