(54.5 g., 0.2 mole) and benzene (78 g., 1 mole) was heated at 80° for 1 hr., and stirred with 100 ml. of 3 *N* hydrochloric acid under nitrogen. After removal of the polymer by filtration under nitrogen, the aqueous phase was separated and kept under nitrogen. The dark red-brown solution (5 ml.) was added to 50 ml. of 3 *N* hydrochloric acid and titrated potentiometrically with 0.1 *N* ceric ammonium nitrate (Beckman pH meter, saturated calomel reference, and platinum indicator electrode). The curve obtained matched closely that of a known mixture of molybdenum trichloride and molybdenum pentachloride in 3 *N* hydrochloric acid. Three points of inflection were obtained, the first two corresponding to the oxidation of Mo^{+3} to Mo^{+5}, and Mo^{+5} to Mo^{+6}, respectively. The third inflection corresponded to the potential derived from the presence of Ce^{+3} and excess Ce^{+4} in solution.

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Reaction of Antimony Pentachloride with Monoalkylbenzenes[1]

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The products formed from antimony pentachloride and monoalkylbenzenes included chloroalkylbenzenes, diarylmethane type hydrocarbons, disproportionation products, and polymeric material. Ethylbenzene yielded chloroethylbenzene, 1-(ethylphenyl)-1-phenylethane, and polymer. Cumene gave chlorocumene, benzene, diisopropylbenzene, 2-(isopropylphenyl)-2-phenylpropane, and polymer. Evidence was found for a cocatalytic effect in the cumene–antimony pentachloride reaction involving side-chain attack.

The major portion of the previous work concerning the behavior of antimony pentachloride toward aromatic compounds has dealt with nuclear chlorination.[3] We have recently reported evidence indicating that the halogenation proceeds by electrophilic substitution effected by an attacking species of low activity.[4] Furthermore, preliminary dissociation of the metal halide was deemed unlikely. In the present study, our aim was to elucidate the nature of the antimony pentachloride–monoalkylbenzene reaction by product identification and by an investigation of cocatalysis.

The products formed were found to include chloroalkylbenzenes, diarylmethane type hydrocarbons, disproportionation products, and polymeric material (Table I). Bear in mind that the reactions proceed with evolution of hydrogen chloride and reduction of Sb^{+5} to Sb^{+3}. These results then closely parallel those published a few years ago for the ferric chloride–alkylbenzene systems.[5,6]

TABLE I

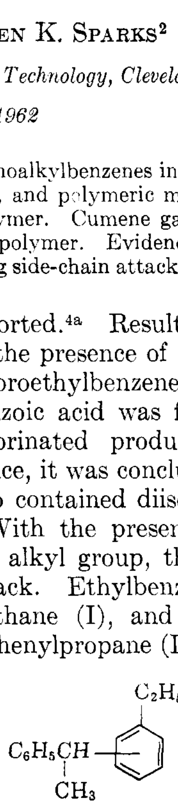
ANTIMONY PENTACHLORIDE AND MONOALKYLBENZENES[a]

			Products		
C_6H_5R, R =	Time, hr.	Temp., °C	ClC_6H_4R, %	Diarylmethane type, %	Polymer, g.
CH_3[b]	2.5	18–31	87	..	..
CH_3CH_2	2.1	17–33	78	2	3.7
$(CH_3)_2CH$	3	8–40	14	20	20.6

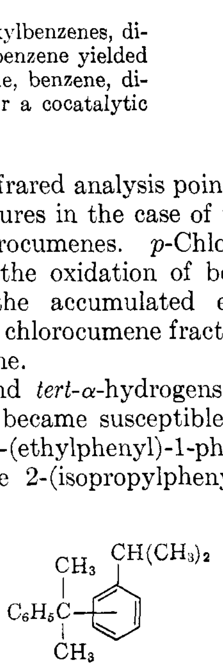
[a] Monoalkylbenzene (2 moles), antimony pentachloride (0.5 mole). [b] Ref. 4a.

Nuclear chlorination occurred with all of the alkylbenzenes, decreasing in the order, $C_6H_5CH_3 > C_6H_5C_2H_5 > C_6H_5CH(CH_3)_2$. Quantitative data for the isomer distribution of the chlorotoluene have already been reported.[4a] Results from the infrared analysis pointed to the presence of isomeric mixtures in the case of the chloroethylbenzenes and chlorocumenes. *p*-Chlorobenzoic acid was formed from the oxidation of both chlorinated products. From the accumulated evidence, it was concluded that the chlorocumene fraction also contained diisopropylbenzene.

With the presence of *sec*- and *tert*-α-hydrogens in the alkyl group, the side-chain became susceptible to attack. Ethylbenzene yielded 1-(ethylphenyl)-1-phenylethane (I), and cumene gave 2-(isopropylphenyl)-2-phenylpropane (II).



I



II

The evidence in support of the structural assignment for I is quite convincing, based partly upon elemental analysis, molecular weight, and chromic acid oxidation to *p*-benzoylbenzoic acid. The infrared spectrum indicated the presence of isomeric 1-(ethylphenyl)-1-phenylethanes, and was very similar, except for the relative intensities of various bands, to that of material prepared from ethylbenzene and styrene by the Friedel–Crafts method. I has also been reported as a product of the ethylbenzene–ferric chloride reaction.[5] Supporting evidence was provided by the studies of Corson and co-workers[7] on the dimerization of styrene in ethylbenzene. They demonstrated the presence of 1-(*p*-ethylphenyl)-1-phenylethane spectrometrically and also by oxidation to *p*-acetylbenzophenone and *p*-benzoylbenzoic acid. In addition, these investigators synthesized the authentic 1-(*o*- and *p*-ethylphenyl)-1-phenylethanes by unequivocal methods. All bands present in the infrared spectra of the authentic ortho and para isomers were also observed in the spectrum of the ethylbenzene–antimony pentachloride product.

Identification of the corresponding hydrocarbon (II) from cumene proved to be a more arduous task, since

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[1] Part XI in the series on "Reactions of Metal Halides with Organic Compounds," from the Ph.D. thesis of A. K. Sparks, Case Institute of Technology, 1960.

[2] Allied Chemical Corp. Fellow, 1958–1960.

[3] For a review, see A. K. Sparks, Ph.D. thesis, Case Institute of Technology, 1960.

[4] (a) P. Kovacic and A. K. Sparks, *J. Am. Chem. Soc.*, **82**, 5740 (1960); (b) *J. Org. Chem.*, **26**, 1310 (1961); (c) 2541 (1961).

[5] P. Kovacic, C. Wu, and R. W. Stewart, *J. Am. Chem. Soc.*, **82**, 1917 (1960).

[6] P. Kovacic and C. Wu, *J. Org. Chem.*, **26**, 762 (1961).

[7] B. B. Corson, J. Dorsky, J. E. Nickels, W. M. Kutz, and H. I. Thayer *ibid.*, **19**, 17 (1954).

oxidation yielded only a small amount of oily acidic material which resisted crystallization. Elemental analysis and molecular weight determination provided the formula $C_{18}H_{22}$. In the presence of aluminum chloride–hydrogen chloride, the diarylmethane type product underwent degradation with formation of cumene. Many analogous dealkylations are recorded in the literature, *e.g.*, the conversion of triphenylmethane to diphenylmethane on treatment with aluminum chloride.[8] Comparison with authentic 2-(isopropylphenyl)-2-phenylpropane was made possible through two independent syntheses: isopropylation of 2,2-diphenylpropane and the Friedel–Crafts alkylation of cumene with α-methylstyrene. The infrared spectra of the products from both reactions were in excellent agreement with that of the corresponding material from the cumene–antimony pentachloride reaction. IV was also characterized as a product from the cumene–ferric chloride reaction.[5] Evidence for the presence of benzene and diisopropylbenzene pointed to the occurrence of disproportionation in the cumene reaction.

Table I shows the effect of alteration in the alkyl group on nuclear chlorination and side-chain attack. It is apparent that nuclear halogenation decreases with increasing complexity of the substituent group, whereas the yield of polymer and diarylmethane product increases. This is reasonable since the ease of the side-chain attack is known to vary in the order, $(CH_3)_2CH > CH_3CH_2 > CH_3$.

In this series the close correspondence of the change in polymer yield with the change in diarylmethane yield suggests that the two are formed by similar reactions. One would logically expect continued side-chain participation from the diarylmethanes resulting in higher molecular weight products. Additional support is provided by the alkylbenzene–ferric chloride investigations[5,6] in which tri[5,6]- and tetraarylmethanes[9] have been isolated.

An investigation was made of the possible involvement of cocatalysis in the side-chain reaction (Table II). The evidence indicated that such an effect was indeed present. As compared with the unpurified commercial material, cumene which was distilled from sodium gave a drastically higher yield of chlorocumene and a decreased amount of polymer. Addition of a small quantity of either cumene hydroperoxide or phenol decreased the yield of chlorocumene from purified cumene, whereas the yields of 2-(isopropylphenyl)-2-phenylpropane and polymer were enhanced. A pronounced temperature effect was revealed by the increase in nuclear chlorination and decrease in side-chain attack by a decrease in reaction temperature.

A plausible interpretation of the side-chain attack involves hydride abstraction[10,11] in which a Brönsted acid functions as a cocatalyst, with accompanying reduction of Sb^{+5}. On the other hand, benzyl type radicals may be generated through initial formation of radical species from cumene hydroperoxide or phenol. The limited evidence does not justify a more detailed discussion at this time.

TABLE II

ANTIMONY PENTACHLORIDE–CUMENE–COCATALYST

Cocatalyst	Mole	Temp., °C	Chlorocumene, %	2-(Isopropylphenyl)-2-(phenylpropane), %	Polymer g.
		15–20	81	2	0.4
		44–47	62	10	2
[a]		41–44	19	11	7.9
Cumene hydroperoxide	0.005	40–44	27	18	5.3
Phenol	.006	42–44	25	18	6

[a] Commercial cumene was used directly without purification.

Interaction of antimony pentachloride with the alkyl side-chain is not surprising in view of the reports concerning reaction of the metal halide with simple alkanes.[12] However, little assistance is provided by the previous work since the organic products were not isolated and characterized.

Experimental[13]

Materials.—Cumene, Fisher Scientific Co., and ethylbenzene, Phillips Petroleum Co., were dried over anhydrous sodium sulfate. Cumene, Phillips Petroleum Co., used in the cocatalyst studies was distilled, b.p. 150.5°, from sodium through a 12-in. helix-packed column. Other materials were antimony pentachloride, Baker Chemical Co.; cumene hydroperoxide, Matheson Coleman and Bell; phenol, reagent grade, Merck.

Antimony Pentachloride and Ethylbenzene.—Ethylbenzene (2 moles) and antimony pentachloride (0.5 mole) were allowed to react according to the general procedure.[4a] A total of 109% of hydrogen chloride was evolved during 2 hr. The steam-volatile material yielded chloroethylbenzenes, 46.3 g. (73%), b.p. 178–180°, n^{20}_{D} 1.5180, infrared absorption maxima at 12.2 (*para*), 12.8 (*meta*) and 13.4 (*ortho*) μ; lit.,[14] for *para*-isomer, b.p 179–180°.

Anal. Calcd. for C_8H_9Cl: C, 68.33; H, 6.45; Cl, 25.22. Found: C, 68.49; H, 6.73; Cl, 24.95.

A portion (9 g.) on oxidation with chromic acid in acetic acid yielded *p*-chlorobenzoic acid, 5.1 g., m.p. 239–241°, from benzene; mixture melting point with authentic material, 238–239°.

The residue from steam distillation of the original reaction mixture was filtered, and the solid was washed repeatedly with 6 *N* hydrochloric acid and then with ether. The aqueous filtrate was also extracted with ether. A brown residue, 3.7 g., remained after this treatment. The ether solutions were combined with the residue from distillation of the steam-volatile material, and on distillation gave 1-(ethylphenyl)-1-phenylethane (I), 1.8 g., b.p. 169–176° at 21 mm., n^{20}_{D} 1.5629, infrared absorption maxima at 11.3, 12.1, 12.5, 13.1, and 14.4 μ; lit.,[7] for the *para*-isomer, b.p. 170° at 20 mm., n^{20}_{D} 1.5605.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.38; H, 8.62; mol. wt., 210. Found: C, 91.24; 91.58; H, 8.73, 8.43; mol. wt., 214 (in benzene).

Oxidation with chromic acid gave *p*-benzoylbenzoic acid, m.p. 190–190.5° (lit.,[15] m.p. 194°); methyl ester, m.p. 103–104° (lit.,[15] m.p. 106–107°).

Authentic 1-(Ethylphenyl)-1-phenylethane.—A mixture of ethylbenzene (2 moles), styrene (0.5 mole), and anhydrous aluminum chloride (0.05 mole) was heated for 1 hr. at 3–6°, and then briefly at 40°. After extraction with hydrochloric acid and then with water, distillation of the dried organic solution yielded two fractions, b.p. 142–149° at 5 mm., n^{20}_{D} 1.5611, and b.p. 149–154° at 5 mm., n^{20}_{D} 1.5609, total wt., 16.7 g. (16%).

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(13) Melting points and boiling points are uncorrected. Elemental analyses were performed by Drs. Weiler and Strauss, Oxford, England, and by Geller Laboratories, Bardonia, N. Y.

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The infrared spectra of the two fractions were essentially identical with that of the corresponding material obtained from the ethylbenzene–antimony pentachloride reaction, except for relative intensities of the substitution bands. Both fractions were analyzed.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.38; H, 8.62. Found: C, 91.19, 91.29; H, 8.43, 8.55.

Antimony Pentachloride and Cumene.—Cumene (2 moles) and antimony pentachloride (0.5 mole) were allowed to react at 8–40° for 3 hr. The steam-volatile material yielded a fraction, b.p. 110–122° at 62 mm., 17.2 g., apparently a mixture of chlorocumene, 63%, and diisopropylbenzene, 37% infrared absorption maxima at 12.2, 12.6, and 13.3 μ; lit.,[16] for *p*-chlorocumene, b.p. 79–81° at 15 mm.; lit.,[17] for *p*-diisopropylbenzene, b.p. 85–86° at 14 mm.

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, 76.59; H, 8.50; Cl, 14.4.

Oxidation of a portion, 10 g., with chromic acid afforded a mixture of acids, 3 g., which was separated by extraction with ether; ether soluble acid, m.p. 236–237°, mixture melting point with authentic *p*-chlorobenzoic acid, 237–239°. The ether-insoluble acid gave a methyl ester, m.p. 139–140.5°; lit.,[18] m.p. for dimethyl tetephthalate, 140°.

Anal. Calcd. for $C_8H_6O_4$: neut. equiv., 83.1. Found: neut. equiv., 82.8, 85.2.

The solid residue from steam distillation of the original reaction mixture was treated with hydrochloric acid after filtration, and after extraction with ether consisted of a black solid, 20.6 g. The aqueous filtrate was also extracted with ether, and the ether solutions were combined with the residue from vacuum distillation of the steam-volatile material. Distillation yielded three fractions, wt. 25 g., which were collected between 152.5–164° at 7 mm., with the largest fraction (II) boiling at 153–157° at 7 mm., n^{20}D 1.5578, wt. 12.5 g.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.70; H, 9.30; mol. wt., 238. Found: C, 90.55; H, 9.12; mol. wt., 238 (in benzene).

The infrared spectra of the three fractions were identical except for small differences in the relative intensity of bands attributed to *meta*- and *para*-isomers. Attempted oxidation with alkaline permanganate, nitric acid, or chromic acid was unsuccessful; only a small amount of oily acidic product, which resisted crystallization, was obtained from chromic acid. The hydrocarbon was inert to permanganate at room temperature, and reacted with bromine with evolution of hydrogen bromide.

In a similar experiment involving cumene (3 moles) and antimony pentachloride (0.75 mole), benzene, 6.7 g., was also isolated and characterized by the infrared spectrum and physical constants, b.p. 78–81°, n^{20}D 1.5013.

Degradation of 2-(Isopropylphenyl)-2-phenylpropane.—After dry hydrogen chloride was bubbled for 3 min. through a mixture of 2-(isopropylphenyl)-2-phenylpropane, b.p. 153–158° at 7 mm., (5 g.), benzene (60 g.), and aluminum chloride (5 g.), the reaction mixture was heated at the reflux temperature for 5 hr. Following washes with hydrochloric acid and with water, the mixture was distilled. The fraction, b.p. 72–76° at 56 mm., 2.4 g., was identified as cumene by the infrared spectrum and refractive index, n^{20}D 1.4912. A complex mixture of higher boiling materials, 1.6 g., was also obtained, in addition to 0.2 g. of yellow tar.

Authentic 2-(Isopropylphenyl)-2-phenylpropane. A. From 2,2-Diphenylpropane and Isopropyl Chloride. (a) 2,2-Diphenylpropane.—A mixture of benzene (350 g., 4.5 moles), 2,2-dichloropropane[19] (63 g., 0.56 mole), and anhydrous aluminum chloride (7.5 g.) was stirred at 0–13° for 30 min., at room temperature for 90 min., and finally at 45–55° for 60 min. After the reaction mixture was poured onto ice, the organic layer was separated, washed first with 3 *N* hydrochloric acid and then with water, dried, and distilled. 2,2-Diphenylpropane, 39 g., was collected at 127–129° at 2 mm., n^{20}D 1.5684 (lit.,[20] b.p. 281.2°, n^{20}D 1.5703). The infrared spectrum was in excellent agreement with that reported in the literature.[20]

(b) Isopropylation of 2,2-Diphenylpropane.—A mixture of isopropyl chloride (2 g., 0.025 mole), 2,2-diphenylpropane (15 g., 0.075 mole), and anhydrous aluminum chloride (0.13 g.) was stirred at 0° for 2 hr., at 40° for 30 min., and at room temperature for 4 hr. After treatment with ice and extraction first with hydrochloric acid and then with water, distillation yielded a fraction, b.p. 145–147° at 3 mm., n^{20}D 1.5576, 1 g., whose infrared spectrum was essentially identical with that of the $C_{18}H_{22}$ hydrocarbon obtained from cumene–antimony pentachloride.

B. From Cumene and α-Methylstyrene.—By a similar procedure 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). Work-up gave a product, b.p. 149–151° at 5 mm., n^{20}D 1.5582 ,14 g., whose infrared spectrum was essentially identical with that of the corresponding material from the cumene–antimony pentachloride reaction.

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.

Antimony Pentachloride–Cumene-Cocatalyst. General Procedure.—Cumene (1 mole), freshly distilled from sodium, was mixed with the catalyst and brought to the desired reaction temperature. Antimony pentachloride (0.25 mole) was added slowly (about 0.5 ml./min.) during 1 hr., and the reaction was then allowed to proceed for 3 hr. from the time of initial addition of the metal chloride. After the reaction mixture had been washed thoroughly with dilute hydrochloric acid and with water, and any insoluble polymer removed by filtration, the organic solution was carefully fractionated to remove benzene (from disproportionation) and unchanged cumene. The residue was then distilled through an 18 in. by 5 mm. spinning band column. The fraction boiling at 188–194° was analyzed for chlorine so that the yield of chlorocumene could be calculated. The 2-(isopropylphenyl)-2-phenylpropane was separated by vacuum distillation and its identity confirmed by comparison of the infrared spectrum with that of the synthetic material. The data are recorded in Table II.

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