Free-Radical Reactions of Iodobenzene Dichloride with Hydrocarbons

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A previous study in this laboratory[1] showed that iodine trichloride reacted with cyclohexane in a light-induced reaction to give cyclohexyl chloride, cyclohexyl iodide, and hydrogen chloride as the major products. Determination of the relative amounts of the various products indicated that the following free-radical chain sequence was operative. In view of the

$$R\cdot + ICl_3 \longrightarrow RCl + ICl_2\cdot \tag{1}$$

$$ICl_2\cdot + RH \longrightarrow ICl + HCl + R\cdot \tag{2}$$

$$R\cdot + ICl \longrightarrow RI + Cl\cdot \tag{3}$$

$$Cl\cdot + RH \longrightarrow R\cdot + HCl \tag{4}$$

necessity for considering $ICl_2\cdot$ as a chain-carrying species, we undertook an investigation of the light-induced reactions of iodobenzene dichloride, $C_6H_5ICl_2$, with hydrocarbons to ascertain whether these reactions required the $C_6H_5ICl\cdot$ species as a chain-carrying entity. The existence of this latter radical has been postulated by Bloomfield[2] as an intermediate in the additive chlorination of the unsaturated linkages in rubber by iodobenzene dichloride. Substitution reactions between iodobenzene dichloride and saturated hydrocarbons, however, do not appear to have been investigated.

We have found that light-induced reactions of iodobenzene dichloride with saturated hydrocarbons produce chlorinated hydrocarbons, hydrogen chloride, and iodobenzene. Table I lists the products and their distribution found in typical light-induced reactions with cyclohexane and toluene.

TABLE I

LIGHT-INDUCED REACTIONS OF IODOBENZENE DICHLORIDE WITH CYCLOHEXANE AND TOLUENE AT 15°

Hydrocarbon, mmoles	Iodobenzene dichloride, mmoles	Products, mmoles
Cyclohexane,[a] 835	10.15	Hydrogen chloride, 9.64 Cyclohexyl chloride, 8.90 Iodobenzene, 9.86
Toluene, 471	8.88	Hydrogen chloride, 8.36 Benzyl chloride, 7.44 Iodobenzene, 8.39

[a] In a reaction between cyclohexane (835 mmoles) and iodobenzene dichloride (11.3 mmoles) induced by benzoyl peroxide at 81°, the following quantities of products were found: hydrogen chloride, 9.4 mmoles; cyclohexyl chloride, 6.8 mmoles; and odobenzene, 9.2 mmoles.

The products and their distribution conceivably could be accounted for by any one of the following free-radical chain mechanisms.

Mechanism A

$$C_6H_5ICl_2 \longrightarrow C_6H_5I + Cl_2$$

This was followed by the chain sequence

$$Cl\cdot + RH \longrightarrow HCl + R\cdot$$

$$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot$$

Mechanism B

$$C_6H_5ICl_2 + R\cdot \longrightarrow RCl + C_6H_5I + Cl\cdot$$

$$Cl\cdot + RH \longrightarrow HCl + R\cdot$$

Mechanism C

$$C_6H_5ICl_2 + R\cdot \longrightarrow RCl + C_6H_5ICl\cdot$$

$$C_6H_5ICl\cdot + RH \longrightarrow R\cdot + C_6H_5I + HCl$$

The chain sequence in mechanism A could also be initiated by the photolysis of molecular chlorine arising from the thermal decomposition of iodobenzene dichloride.

All three sequences could be initiated by the photolytic decomposition of iodobenzene dichloride.

$$C_6H_5ICl_2 \longrightarrow C_6H_5ICl\cdot + Cl\cdot$$

A significant difference between mechanism C and mechanisms A and B is the process whereby hydrogen is abstracted from the hydrocarbon. In mechanisms A and B, a chlorine atom functions as the hydrogen abstracter, whereas the corresponding agent in mechanism C is the $C_6H_5ICl\cdot$ radical. Support for mechanism C comes from the determination of the distribution of isomeric alkyl chlorides formed when iodobenzene dichloride reacts with 2,3-dimethylbutane. Thus, with 2,3-dimethylbutane as substrate, the products at both 15 and 40° included 2-chloro-2,3-dimethylbutane and its dehydrohalogenation product, 2,3-dimethylbutene-2, iodobenzene, and hydrogen chloride, but *no* 1-chloro-2,3-dimethylbutane, the predominant isomer formed by chlorination of 2,3-dimethylbutane with molecular chlorine.[3] The high degree of selectivity found for the chlorinations with iodobenzene dichloride would appear definitely to eliminate mechanisms A and B.

Our proposal that the hydrogen abstracter in chlorinations with iodobenzene dichloride is solely the $C_6H_5ICl\cdot$ radical must be examined in the light of Russell's results[3] on the chlorination of 2,3-dimethylbutane in iodobenzene as solvent. The latter investigator proposed that, in addition to chlorine atoms, there existed in the system $C_6H_5ICl\cdot$ radicals formed by the union of these atoms with solvent.[4] In such a system both kinds of radicals function as hydrogen-abstracting agents, the $C_6H_5ICl\cdot$ radicals abstracting only tertiary hydrogens and the chlorine atoms abstracting both primary and tertiary hydrogens. The formation of 1-chloro-2,3-dimethylbutane in Russell's system and its absence in the iodobenzene dichloride–2,3-dimethylbutane system is thus reasonable.

In view of the results obtained with iodobenzene dichloride, the light-induced reaction of iodine trichloride with 2,3-dimethylbutane was also studied, to see whether additional support could be obtained for the $ICl_2\cdot$ radical postulated previously.[1] It was found that, at 10–15°, 2-chloro-2,3-dimethylbutane and 1-chloro-2,3-dimethylbutane were formed in a ratio of 12.5 to 1. Russell[3] observed that in the chlorination of 2,3-dimethylbutane with molecular chlorine at 25° the ratio of 2-isomer to 1-isomer was 0.7 to 1. The high

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(1) W. W. Hess, E. S. Huyser, and J. Kleinberg, *J. Org. Chem.*, **29**, 1106 (1964).

(2) G. Bloomfield, *J. Chem. Soc.*, 114 (1944).

(3) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958).

(4) G. A. Russell, private communication relative to ref. 3.

degree of selectivity with iodine trichloride compared with molecular chlorine is consistent with our previous proposal that $ICl_2\cdot$ is involved in hydrogen abstraction reactions when iodine trichloride is used in chlorination reactions. The formation of a small amount of the 1-isomer indicates that there is some hydrogen abstraction by chlorine atoms and is therefore also consistent with the previously proposed mechanism (reactions 1–4 for light-induced reactions of iodine trichloride with hydrocarbons).

Experimental

Materials and Equipment.—Cyclohexane and toluene (Matheson Coleman and Bell) were Spectroquality reagents and were used without further purification. The 2,3-dimethylbutane (Phillips Petroleum Co., pure grade) was also used as obtained.

Iodobenzene dichloride was prepared by reaction of chlorine (Matheson Co., Inc.) with iodobenzene (Eastman, practical grade) in chloroform in the manner described previously.[5] Prior to use, the compound was recrystallized from a chloroform–petroleum ether mixture and dried in a vacuum desiccator, m.p. 110–112° (uncor.).

Iodine trichloride was obtained by the union of iodine and chlorine according to the method of Booth and Morris.[6]

2-Chloro-2,3-dimethylbutane was made by the light-induced reaction of trichloromethanesulfonyl chloride with 2,3-dimethylbutane at 80°[7]: b.p. 117–119°. Gas chromatographic analysis of the material on the columns a, d, and e described below showed only one peak.

Chlorination of 2,3-dimethylbutane with molecular chlorine at 0° gave a mixture of monochloro derivatives, b.p. 115–130°. Gas chromatographic analysis showed two peaks, the first of which had a retention time identical with that of 2-chloro-2,3-dimethylbutane; the other peak was assumed to be due to 1-chloro-2,3-dimethylbutane. In all quantitative determination of these isomers, the peak area ratios and the mole ratios were assumed to be identical. Russell[8] reported a 2% difference between the peak area ratio and mole ratio for these two isomers when a thermal conductivity detector was employed.

Gas chromatographic analyses were performed on an Aerograph A-90P equipped with a thermal conductivity detector and a Sargent (Model SR) recorder. The following columns were used: (a) a 4.5 ft. × 0.5 in. column packed with 2% by weight GE-SE-30 silicone rubber on Chromosorb W; (b) a 4 ft. × 0.25 in. column packed with 10% by weight E-600 polyglycol (The Dow Chemical Co.) on Chromsorb W; (c) a 10 ft. × 0.25 in. column packed with 10% by weight diethylene glycol succinate on Chromosorb W; (d) a 5 ft. × 0.25 in. column packed with 20% by weight Carbowax 20M on Chromosorb W; and (e) a 7 ft. × 0.25 in. column packed with 15% by weight *sec*-octyl sebacate on Chromosorb W.

Reaction of Iodobenzene Dichloride with Cyclohexane.—In a typical reaction, a known quantity of iodobenzene dichloride in a large excess of cyclohexane was illuminated with a 275-w. General Electric sunlamp at 15° for about 2 hr. During the course of illumination a stream of nitrogen was passed through the reaction mixture at a rate of 3 ml./min. into a known volume of standard sodium hydroxide solution. The hydrogen chloride produced was determined by titration of unconsumed sodium hydroxide.

The reaction mixture was distilled and the fractions containing the cyclohexyl chloride and iodobenzene formed were collected. These compounds were identified from their retention times on three different columns a, b, and c by comparison with authentic samples. The amounts of these two compounds were determined from their peak areas using bromobenzene as an internal standard. The correction factor relating the peak area ratio to mole ratio for each product with respect to bromobenzene was determined from known mixtures of these materials.

In a benzoyl peroxide induced reaction (see footnote to Table I), the products were identified and their quantities were determined as described above for the light-induced reaction.

Reaction of Iodobenzene Dichloride with Toluene.—In a typical reaction, a known quantity of iodobenzene dichloride in a large excess of toluene was illuminated at 15° in the manner described for the reaction with cyclohexane. The hydrogen chloride produced was determined by its reaction with standard sodium hydroxide solution, and the benzyl chloride and iodobenzene by gas chromatography (on columns a, c, and e) in a manner analogous to that described for mixtures of cyclohexyl chloride and iodobenzene.

Reaction of Iodobenzene Dichloride with 2,3-Dimethylbutane.—In a typical experiment, approximately 3 mmoles of iodobenzene dichloride in about 77 mmoles of 2,3-dimethylbutane was illuminated at 15° until all the iodobenzene dichloride had been consumed. The hydrogen chloride produced in the reaction was removed as it formed by means of a stream of nitrogen. Samples (30 μl.) of the reaction solution were subjected to gas chromatographic analysis on three different columns (a, d, and e). A large chromatographic peak corresponding in retention time to that of an authentic sample of 2-chloro-2,3-dimethylbutane was observed in each sample. A small peak with a retention time identical with that of an authentic sample of 2,3-dimethylbutene-2 (Phillips Petroleum Co., pure grade) was also found. There was no peak with a retention time the same as that of 1-chloro-2,3-dimethylbutane. Experiment showed that a quantity of the 1-chloro isomer up to 1% of the 2-chloro isomer could be detected readily.

Essentially identical results were obtained when no attempt was made to remove the hydrogen chloride formed in the reaction.

Reaction of Iodine Trichloride with 2,3-Dimethylbutane.—A mixture of 2 mmoles of iodine trichloride in 100 mmoles of 2,3-dimethylbutane was illuminated at 10–15° until all of the solid iodine trichloride had disappeared. Gas chromatographic examination of 10–30-μl. aliquots of the reaction solution on columns a, d, and e showed the presence of both monochloro isomers of 2,3-dimethylbutane, as well as a small amount of 2,3-dimethylbutene-2. The sum of the areas of the peaks corresponding in retention time to the times of authentic samples of 2-chloro-2,3-dimethylbutane and 2,3-dimethylbutene-2 was 12.5 times greater than the peak area attributed to 1-chloro-2,3-dimethylbutane.

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[5] H. J. Lucas and E. R. Kennedy, *Org. Syn.*, **22**, 69 (1942).

[6] H. S. Booth and W. C. Morris, *Inorg. Syn.*, **1**, 167 (1939).

[7] E. S. Huyser and B. Giddings, *J. Org. Chem.*, **27**, 3391 (1962).

Lithium–Methylamine Reduction of Certain 9-Substituted Fluorenes[1]

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The reduction of fluorene to 1,2,3,4-tetrahydrofluorene with lithium metal and low molecular weight amines has been reported by Benkeser.[3] In an attempt to prepare 1,2,3,4-tetrahydro-9-hydroxyfluorene-9-carboxylic acid (1), the method of Benkeser was applied to 9-hydroxyfluorene-9-carboxylic acid. An infrared spectrum of the resulting acidic product and of its methyl ester showed the presence of a double bond, but failed to reveal an alcoholic hydroxyl. An n.m.r. spectrum (in chloroform-*d*) of the free acid showed peaks at 7.2 (4 protons), 4.18 (1 proton), 2.4 (4 protons), and a poorly resolved peak at 1.8 p.p.m. (4 protons). The failure of the spectrum to reveal vinyl protons limited the structure to 2 or 3. The paramagnetic shift associated

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[3] R. A. Benkeser, Advances in Chemistry Series, Vol. 23, American Chemical Society, Washington, D. C., 1959, p. 58.