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.

Acknowledgment.—The authors express their appreciation to the National Science Foundation for support of this work.

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(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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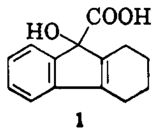
(1) Abstracted from a portion of a thesis submitted by R. J. A. in partial fulfillment of the requirements for the degree of Doctor of Philosophy, State University of Iowa, 1964. The investigation was supported in part by Fellowship Grant GPM-12680, National Institutes of Health.

(2) To whom correspondence should be addressed.

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

with a proton adjacent to a carboxyl group[4] would shift the benzilic proton downfield from its normal position at 3.3 p.p.m., thus suggesting that structure **2** is the correct one. A small amount of a hexahydrofluorenecarboxylic acid was also isolated from the reaction mixture.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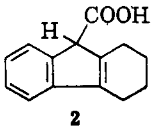
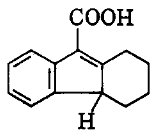
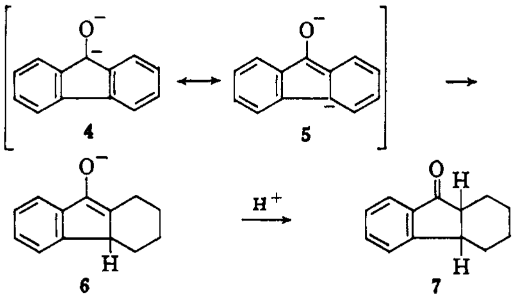

2


3

An attempt was made to reduce fluoren-9-one to 1,2,3,4-tetrahydrofluoren-9-ol. This reaction resulted in the formation of 1,1a,2,3,4,4a-hexahydrofluoren-9-one (**7**), and a considerable amount of fluoren-9-ol. The formation of **7** is explainable on the basis of an initial formation of a dianion **4**.[5] Reduction of its resonance form **5** would result in the enolate **6** which is converted to **7** on addition of acid.



When fluoren-9-ol was treated with the reducing mixture, the only product isolated was **7**. This suggests initial formation of an alkoxide ion, followed by loss of the acidic proton at position 9, resulting in the dianion **4**. The formation in this sequence of the *cis*-fused ring isomer of **7** was shown by comparison of the n.m.r. and infrared spectra of the product with those of authentic samples of *cis*- and *trans*-1,1a,2,3,4,4a-hexahydrofluoren-9-ones, prepared by the method of House and coworkers.[6] The n.m.r. spectrum of the *cis* isomer (in carbon tetrachloride) showed a series of peaks at 7.6 (4 protons), a quartet spaced at 7 c.p.s. centered at 3.35 (1 proton), a quartet centered at 2.65 (1 proton), and two broad peaks at 2.1 and 1.5 p.p.m. (8 protons) which were insufficiently resolved to determine splitting patterns. The *trans* isomer had a spectrum showing a series of peaks at 7.4 (4 protons) and very broad overlapping signals centered at 3.0 (2 protons) and at 1.7 p.p.m. (8 protons). These observations are in agreement with the findings of Moniz and Dixon,[7] that the spectrum of a rigid *trans*-fused cyclohexane ring has broad and overlapping signals, while the flexible *cis*-fused ring has sharp and narrow signals.

The quartet centered at 3.35 p.p.m. in the spectrum of *cis*-1,1a,2,3,4,4a-hexahydrofluoren-9-one has been assigned to the proton at position 4a, based on assignments by House and Carlson[8] in 1,1a,4,4a-tetrahydrofluoren-9-one systems. In the spectrum for *cis*-**7**, coupling between the proton at 4a and each of the protons at 4, as well as the proton at 1a, is 6–7 c.p.s. in each case; these data coincide with the findings of House and Carlson[8] relative to 1,1a,4,4a-tetrahydrofluoren-9-ones. These data suggest that the dihedral angle between $H{-}C_{(4a)}{-}C_{(1a)}{-}H$ and $H{-}C_{(4a)}{-}C_4{-}H$ (for each C-4 proton) is approximately 30 or 150°.[9] The main distortion of the six-membered ring in the *cis* isomer is a deformation of the chair conformation toward that of a boat.[10] Dreiding models of *cis*-1,1a,2,3,4,4a-hexahydrofluoren-9-one show that the twisted boat conformation would be consistent with the n.m.r. data. House and Carlson[8] have suggested the possibility of a twisted boat conformation in 1,1a,4,4a-tetrahydrofluoren-9-one systems.

Experimental[11]

1,2,3,4-Tetrahydrofluorene-9-carboxylic Acid (2).—Anhydrous methylamine (30 ml.) was added and condensed in a 50-ml. flask equipped with a Dry Ice–acetone cold finger condenser and containing 10 g. (0.044 mole) of 9-hydroxyfluorene-9-carboxylic acid[12] and 2 g. (0.261 g.-atom) of lithium wire. The mixture was stirred for 3 hr.; then solid ammonium chloride was added until the brown reaction mixture turned a deep red. The methylamine was allowed to evaporate at room temperature; the reaction flask was cooled in an ice bath, and 20 ml. of water was added. The acid products were precipitated with an excess of dilute hydrochloric acid and were collected on a filter. This material was dissolved in hot benzene, and, on cooling, 3.6 g. (63%) of 1,2,3,4-tetrahydrofluorene-9-carboxylic acid separated, m.p. 174–175°. The infrared spectrum ($CHCl_3$) showed peaks at 5.9 (C=O) and 6.1 μ (C=C stretching).

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.40; H, 6.55. Found: C, 78.18; H, 6.55.

The mother liquor from the crystallization of **2** yielded 0.4 g. of a solid, m.p. 133–135°, believed to be a hexahydrofluorene-9-carboxylic acid. Several recrystallizations from benzene–Skellysolve B resulted in a pale yellow solid, m.p. 160–161°. An infrared spectrum ($CHCl_3$) showed peaks at 5.9 (C=O) and at 3.7 μ (associated OH), but no C=C stretching peak was detected.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.78; H, 7.44. Found: C, 78.06; H, 7.11.

Methyl 1,2,3,4-Tetrahydrofluorene-9-carboxylate.—This derivative was prepared from **2** with diazomethane: b.p. 102–104° (0.03 mm.), $n^{25}D$ 1.5747. An infrared spectrum ($CHCl_3$) showed peaks at 5.85 (C=O) and at 6.1 μ (C=C stretching).

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.90; H, 6.89.

***cis*-1,1a,2,3,4,4a-Hexahydrofluoren-9-one (7). A. From Fluoren-9-one.**—Anhydrous methylamine (30 ml.) was condensed in an apparatus described above, which contained 10 g. (0.055 mole) of fluoren-9-one and 2.2 g. (0.3 g.-atom) of lithium wire. The mixture was stirred 1.5 hr. and the reaction was quenched by addition of solid ammonium chloride, the end point being accompanied by a color change from dark violet to yellow. The methylamine was allowed to evaporate from the reaction mixture at room temperature, the total volume being maintained by addition of acetone. Dilution of this acetone solution with water caused separation of 2.0 g. (20%) of fluoren-9-ol, m.p. 150–151°

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[4] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 57; J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 285.

(5) R. A. Benkeser, ref. 3, p. 59, suggested a dianionic intermediate in reductions of aromatic systems with lithium and low molecular weight amines.

(6) H. O. House, V. Paragamian, R. S. Ro, and D. J. Wluka, *J. Am. Chem. Soc.*, **82**, 1457 (1960).

(7) W. B. Moniz and J. A. Dixon, *ibid.*, **83**, 1671 (1961).

(8) H. O. House and R. G. Carlson, *J. Org. Chem.*, **29**, 74 (1964).

(9) See ref. 4, p. 87.

(10) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 276.

(11) Melting points are corrected and boiling points are uncorrected. Analyses were by Huffman Microanalytical Laboratories, Wheatridge, Colo. N.m.r. spectra were determined at 60 Mc. with a Varian Associates A-60 instrument. Infrared spectra were determined by use of a Perkin-Elmer Infracord or a Beckman IR-5A spectrophotometer.

(12) H. Klinger, *Ann.*, **389**, 237 (1912).

(lit.[13] m.p. 148–150°). The mother liquor was evaporated to dryness, affording 5.6 g. of a dark oil which was distilled at 96–102° (0.1 mm.) to produce 2.93 g. (27%) of an oil which did not crystallize (lit.[6] m.p. 40–41°). An infrared spectrum of this material ($CHCl_3$) was identical with one of an authentic sample of *cis*-1,1a,2,3,4,4a-hexahydrofluoren-9-one.[6] The compound formed a 2,4-dinitrophenylhydrazone, m.p. 195–197° (lit.[6] m.p. 195–196.5°).

B. From Fluoren-9-ol.—Fluoren-9-ol[13] (5.2 g., 0.03 mole) was reduced by the procedure described in A. After evaporation of the methylamine at room temperature, 25 ml. of water was added, and the resulting mixture was extracted with ether. On evaporation of the ether, 3.56 g. (64%) of a liquid remained, which crystallized to a soft yellow solid and which formed a 2,4-dinitrophenylhydrazone, m.p. 195–197°. An infrared spectrum of the product of the reaction was identical with that of the product of A.

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(13) A. A. R. Sayigh, *J. Org. Chem.*, **25**, 1707 (1960).

Homolytic Aromatic Substitution. IV.[1] Synthesis of 9-Aryl-10-nitrophenylanthracenes

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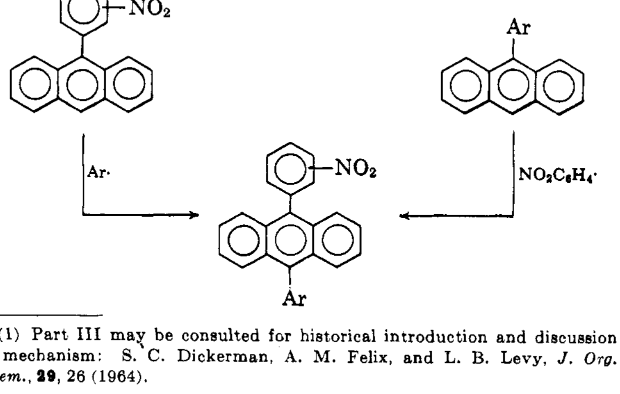
In an earlier paper of this series Meerwein arylation of anthracene was shown to afford a general route to 9-aryl- and 9,10-diarylanthracenes and, more importantly, to otherwise inaccessible nitrophenyl- and dinitrophenylanthracenes.[1] This reaction has now been employed to prepare previously unknown 9-aryl-10-nitrophenylanthracenes. All of these compounds are unsymmetrically substituted derivatives of 9,10-diphenylanthracene and possess a common structural feature, a nitrophenyl group. Obviously, it is possible to envisage alternative routes to such compounds as indicated in the accompanying equations. For example, 9-phenyl-10-*o*-nitrophenylanthracene is the major product expected from homolytic phenylation of 9-*o*-nitrophenylanthracene as well as by *o*-nitrophenylation of 9-phenylanthracene. Preparation of a compound by the two methods establishes constitution provided that the identities of the starting materials are known. 9-Nitrophenylanthracenes (*ortho*, *meta*, and *para*) were available by Meerwein arylation of anthracene[1] and the additional 9-arylanthracenes were synthesized by unequivocal methods.



The 9-aryl-10-nitrophenylanthracenes described here are listed in Table I which also includes yields, melting points, and elemental analyses. Several of these derivatives of 9,10-diphenylanthracene (**3**, **4**, **7**, and **9**) have been reported in the previous paper[1] and are included in Table I to facilitate comparison. The present study completes three sets of constitutional isomers: the 9-phenyl-10-nitrophenylanthracenes (**1**–**3**), the 9-nitrophenyl-10-nitrophenylanthracenes (**4**–**9**), and the 9-methoxyphenyl-10-nitrophenylanthracenes (**10**–**18**). Comparison of infrared spectra and mixture melting points served to establish the identity of samples prepared by alternative routes. Six of the 9-methoxyphenyl-10-nitrophenylanthracenes were synthesized from 9-methoxyphenylanthracenes only and the assignment of constitution to these compounds was made on the basis of spectra and by analogy.

Comparison of yields of a given compound by alternative syntheses (Table I) is revealing. Methoxyphenylation is a generally less efficient route than nitrophenylation and, in a particular instance, *o*-methoxyphenylation of 9-*p*-nitrophenylanthracene failed to yield the desired compound. Since homolytic *o*-methoxyphenylation of naphthalene has been observed,[2] failure here may be ascribed to one or more competing reactions, for example, abstraction from acetone and the Sandmeyer reaction.[1]

The ultraviolet absorption spectra of nineteen derivatives of 9,10-diphenylanthracene have been measured and the data for these compounds together with those for the parent hydrocarbon are recorded in Table II. Significantly, except for the disappearance of a shoulder in all compounds that posses a *p*-nitro group, the absorption maxima and extinction coefficients are essentially indistinguishable from those of 9,10-diphenylanthracene. In other words the red shifts in the longest wavelength absorption bands in anthracene, that result from substitution of phenyl groups at the 9,10-positions, are independent of the nature and position of substituents in the phenyl groups. Various interpretations of this type of bathochromic shift have been discussed.[3,4]

Experimental[5]

9-*o*-Methoxyphenylanthracene.—A solution of 17.5 g. (0.09 mole) of 9-anthrone in 200 ml. of warm benzene was added over a period of 15 min. to an ether solution of *o*-methoxyphenyllithium prepared from 21.5 g. (0.115 mole) of *o*-bromoanisole and 1.60 g. (0.225 g.-atom) of lithium. After the mixture had been stirred at 40–45° for 1 hr. it was poured into a mixture of ice and concentrated hydrochloric acid. The organic phase was separated, dried, and concentrated. The viscous residue was extracted with boiling ethanol to yield 10.5 g. (41%) of product. The analytical sample was recrystallized from benzene–hexane and melted at 176–177°: $\lambda_{max}^{ethanol}$ mμ (log ϵ), 255 (4.93), 346 (3.83), 364 (4.03), and 384 (4.00).

Anal. Calcd. for $C_{21}H_{16}O$: C, 88.70; H, 5.67; mol. wt., 284. Found: C, 88.91; H, 5.73; mol. wt., 292.

9-*m*-Methoxyphenylanthracene.—The required Grignard reagent was prepared under nitrogen in tetrahydrofuran from 2.8 g. (0.12 g.-atom) of magnesium and 22.0 g. (0.12 mole) of *m*-

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(1) Part III may be consulted for historical introduction and discussion of mechanism: S. C. Dickerman, A. M. Felix, and L. B. Levy, *J. Org. Chem.*, **29**, 26 (1964).

(2) P. S. Johnson and W. A. Waters, *J. Chem. Soc.*, 4652 (1962).

(3) H. H. Jaffe and M. Orchin, "Theory and Applications of Electronic Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 15.

(4) H. H. Jaffe and O. Chalvet, *J. Am. Chem. Soc.*, **85**, 1561 (1963).

(5) Melting points above 250° were taken on a Mel-Temp apparatus. Ultraviolet spectra were determined with a Cary Model 15 spectrophotometer. Infrared spectra were taken with a Baird Model 4-55 spectrophotometer using potassium bromide wafers. Analyses were performed by the Schwartzkopf Microanalytical Laboratory, Woodside 77, N. Y.