m.p. 235°. Then 50 mg. (8.5%) of cyclic carbonate (XIV), m.p. 149–150°, and 120 mg. (12%) of unchanged XI were isolated, all three characterized by mixture melting points and comparative infrared spectra with authentic samples. The final residue (150 mg.) appeared to be mainly a mixture of the monobenzoate (VIII) and V, by its infrared spectrum.

The same results were obtained if a catalytic amount (6 mole %) of sodium hydride was employed.

**3,4-Di-O-benzoyl-1,2:5,6-di-O-isopropylidene-D-mannitol (XIII).**—Benzoylation of V or VIII with excess benzoyl chloride in pyridine overnight at room temperature gave an 85% yield of the dibenzoate as an oil which was free of hydroxyl absorption in the infrared. For analysis, the compound was absorbed from a benzene solution on a column of neutral alumina (Brockmann activity III), then eluted with 1:1 benzene–chloroform. The colorless oil had $\nu_{max}^{film}$ 1715 (C=O); 1260, 1100, 1080 (C—O—C); 715 cm.$^{-1}$ (benzoyl CH); $[\alpha]^{25}D$ +64.9 ± 0.7° (0.6%).

*Anal.* Calcd. for $C_{26}H_{30}O_8$: C, 66.4; H, 6.44. Found: C, 66.7; H, 6.24.

**Benzoate Equilibration of 3-O-Benzoyl-1,2:5,6-di-O-isopropylidene-D-mannitol (VIII) with Sodium Hydride.**—To a solution of 1.10 g. (3 mmoles) of dry VIII in 60 ml. of reagent toluene was added 130 mg. (3 mmoles) of 55% soduim hydride dispersion in mineral oil. After being refluxed for 90 min. protected from moisture, the mixture was spin evaporated to dryness *in vacuo*. The residue was suspended in 20 ml. of water containing 0.2 ml. of acetic acid; the mixture was extracted with chloroform (four 20-ml. portions). Dried with magnesium sulfate, combined extracts were evaporated to dryness *in vacuo*. Crystallization from ethyl acetate–petroleum ether gave 0.20 g. (25%) of debenzoylated product, V, identical with an authentic sample.

The filtrate was evaporated to dryness *in vacuo* leaving 0.7 g. of a semisolid. Further traces of V were removed by absorption on neutral alumina (Brockmann activity III) from a hexane solution, then elution with 8:1 benzene–methanol. The resultant 0.55 g. showed two spots on silica thin-layer chromatography with benzene–methanol (7:1) as the solvent system and iodine vapor as the detecting agent. The two spots had $R_f$ values of 0.77 and 0.96 and moved identically with authentic samples of VIII and 3,4-di-O-benzoyl-1,2:5,6-di-O-isopropylidene-D-mannitol (XIII), respectively.

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# Notes

## Nitration of Phenylcyclopropane. *ortho–para* Ratios for Nitration of Alkylbenzenes with Acetyl Nitrate[1]

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In connection with another study,[2] we had occasion to refer to the ultraviolet spectrum of *p*-nitrophenylcyclopropane obtained by Levina, Shabarov, and Patapov.[3] This spectrum, however, was inconsistent with data that we had accumulated[2] and was not typical of a *p*-nitroalkylbenzene. We, therefore, felt obliged to repeat their work in order to clarify the problem. Nitration at −40 to −20° with fuming nitric acid–acetic anhydride afforded a product whose ultraviolet spectrum was nearly identical with that previously published.[3] The proof of structure for the nitration product was based primarily on its oxidation with chromic acid to *p*-nitrobenzoic acid in 70% yield.[3] When our nitration product was subjected to gas chromatographic analysis, two major components in a ratio of 2:1 were observed. The smaller, slower-moving fraction crystallized on cooling (m.p. 32°) and gave an ultraviolet spectrum typical of a *p*-nitroalkylbenzene.[4] Furthermore, the infrared absorption pattern in the 5–6-μ region was typical of *p*-disubstituted benzenes.[5] The *larger*, faster-moving fraction could not be crystallized and showed a typical ultraviolet absorption spectrum for an *o*-nitroalkylbenzene.[4] In this case the infrared spectrum in the 5–6-μ region was typical of an *o*-disubstituted benzene.[5] Oxidation of the solid nitration product with chromic acid gave *p*-nitrobenzoic acid in 88% yield. The oil afforded 64% of *o*-nitrobenzoic acid under the same conditions. It is thus established that the cyclopropyl group, as expected, is an *ortho–para* director but that the major product is the *ortho* isomer.

Brown and Bonner have reported[6] *ortho–para* ratios for nitration of toluene, ethylbenzene, cumene, and *t*-butylbenzene with concentrated nitric acid–concentrated sulfuric acid at 40°. In order that our result with phenylcyclopropane could be compared directly, we have repeated the nitrations of these four alkylbenzenes with fuming nitric acid–acetic anhydride at −40°. This reagent gives results which are very similar to those from the "mixed acid" except that the yields are higher, the rate of decrease of the *ortho–para* ratio is greater, and smaller amounts of *meta* isomers were observed. When the nitrating mixture was prepared at room temperature and cooled to −40° for nitration, the *ortho–para* ratio for the branched alkylsubstituted benzene was much smaller, whereas with phenylcyclopropane the ratio was considerably higher. The nitration of phenylcyclopropane with this

(1) This work was supported, in part, by Cancer Research Funds of the University of California and by an American Cancer Society Institutional grant 1N 33D.

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(4) W. G. Brown and H. Reagan, *J. Am. Chem. Soc.*, **69**, 1032 (1947).

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 67–69.

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TABLE I

| Compound | $H_2SO_4$–$HNO_3$ ortho–para | $H_2SO_4$–$HNO_3$ % yield | $AcONO_2$[b] ortho–para | $AcONO_2$[b] % yield | $AcONO_2$[c] ortho–para |
|---|---|---|---|---|---|
| Toluene | 1.57[a] | 80[a] | 1.78 | 94 | 1.76 |
| Ethylbenzene | 0.93[a] | 80[a] | 0.86 | 93 | 0.90 |
| Cumene | .48[a] | 80[a] | .41 | 95 | .27 |
| *t*-Butylbenzene | .217[a] | 80[a] | .17 | 91 | .066 |
| Phenylcyclopropane | 2.10 | 70 | 1.99 | 93 | 4.0–4.7 |

[a] Ref. 6, the yields are given as approximately 80%. [b] Nitrating reagent prepared at −40°. [c] Nitrating reagent prepared at room temperature.

latter reagent was not reproducible. The range of *ortho–para* ratios is given in Table I.

The general agreement between the values obtained with acetyl nitrate and nitric acid–sulfuric acid mixtures indicates that the results are not due to the special *ortho* orientation property of acetyl nitrate which has been observed for nitration of anisole or acetanilide[7] with this reagent, but that phenylcyclopropane is inherently nitrated preferentially in the *ortho* position. This contention was confirmed by the fact that nitration of phenylcyclopropane with nitric acid–sulfuric acid afforded a product mixture with an *ortho–para* ratio not greatly different from that obtained with acetyl nitrate. The results of the nitration experiments are in Table I.

Bordwell and Garbisch recently have studied the reactions of acetyl nitrate with a series of styrenes and stilbenes.[8] They have found that, although the major products of these reactions result from addition to the ethylenic double bond, there is, in most cases, some nuclear substitution. These workers did not determine the *ortho–para* ratios, but they did indicate that the amount of *ortho*-substituted product was in excess of the *para* isomer.

The most common cases of high *ortho–para* ratios have been observed in nitrations of deactivated systems such as nitrobenzene, benzaldehyde, and ethyl benzoate.[9] All of these compounds have unsaturated systems, and interactions between the substituents and the attacking nitronium ion have been postulated. In the case of styrene similar interactions can also be thought of as existing between the incoming nitronium ion and the vinyl group, thereby directing substitution preferentially to the *ortho* position.

Stericly the cyclopropyl group should exert an effect similar to that of the isopropyl group. However, the contraction in size introduced by the strained three-membered ring should make the cyclopropyl group somewhat smaller so that its steric effect should be intermediate between those of an ethyl and an isopropyl group. This should have led to an *ortho–para* ratio of about 0.75.

The unsaturated nature of the cyclopropyl system has been observed in a number of situations.[10] These manifestations of unsaturation have been related to the double bond character of the three-membered ring caused by the highly strained carbon–carbon bonds which have approximately $sp^4$ hybrid orbitals.[11] The *ortho*-directing influence of the cyclopropyl system observed in this work appears to be still another example of the unsaturated character of this three-membered ring system.

Phenylcyclopropane was prepared from styrene according to the method[12] used by Doering and Hoffman to prepare norcarane from cyclohexene. The reaction between styrene and dibromomethylene, generated from bromoform by the action of potassium *t*-butoxide, afforded 1-phenyl-2,2-dibromocyclopropane. Reduction with sodium and wet methanol afforded phenylcyclopropane.

It should be pointed out that the earlier workers reduced their nitrophenylcyclopropane to the corresponding amine[3] and that studies on this reduction product cannot be completely valid since it too must have been a mixture.

## Experimental[13]

**1-Phenyl-2,2-dibromocyclopropane.**—To a stirred solution of 0.33 mole of potassium *t*-butoxide (prepared by adding 13 g. of potassium to the *t*-butyl alcohol at 70°) and 181 g. (200 ml., 1.74 moles) of styrene in 400 ml. of *t*-butyl alcohol at 15–20° was added dropwise 100 g. (0.4 mole) of bromoform. After stirring an additional 30 min., 300 ml. of water was added and the product extracted with pentane. The extract was dried over sodium sulfate and the solvent removed under reduced pressure. Vacuum distillation afforded 48.9 g. (53%) of 1-phenyl-2,2-dibromocyclopropane, b.p. 90–100° at 1 mm.

*Anal.* Calcd. for $C_9H_8Br_2$: C, 39.16; H, 2.97; Br, 57.92. Found: C, 39.24; H, 2.96; Br, 57.66.

**Phenylcyclopropane.**—To a stirred solution of 27.6 g. (0.1 mole) of 1-phenyl-2,2-dibromocyclopropane in 100 ml. of ether was added dropwise a solution of 270 ml. of methanol and 50 ml. of water and portionwise 46 g. (2 moles) of sodium over a 3-hr. period. An additional 23 g. (1 mole) of sodium and 180 ml. of methanol and 20 ml. of water was added and the reaction mixture stirred an additional 2 hr. A final 23 g. (1 mole) of sodium and 100 ml. of methanol was added and the reaction mixture stirred for 7 hr. The reaction mixture was diluted with water and extracted with ether. The ether extract was washed with dilute hydrochloric acid and dried over sodium sulfate. Removal of the ether *in vacuo* and vacuum distillation of the crude product afforded 9.90 g. (84%) of phenylcyclopropane, b.p. 93–97° at 45 mm.

***o*- and *p*-Nitrophenylcyclopropane.**—To a solution of 13.0 ml. of acetic anhydride and 4 ml. of fuming nitric acid at −40° was added dropwise 3.25 g. (0.027 mole) of phenylcyclopropane at a rate such that the temperature did not rise above −20°. The reaction mixture was poured into hot water and the product was extracted with ether. The ether extract was dried and the ether removed under vacuum. Crude distillation gave about 5 ml. of product, b.p. 77–120° at 1–3 mm. Gas chromatography (Aerograph Model A-90-C) on a 10-ft. silicone rubber, analytical column at 135° showed two main bands in addition to smaller amounts of other substances.

(7) For a discussion of the nature of this nitrating reagent see F. G. Bordwell and E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **82**, 3588 (1960).

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(12) W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(13) Melting points and boiling points are uncorrected. Microanalyses are by the Microanalytical Laboratory, Department of Chemistry, Berkeley, Calif.

Preparative scale gas chromatography on a 6-ft. Apiezon preparative column afforded sufficient quantities of the two main fractions for characterization.

The largest of the two main fractions had the smallest retention volume. Its infrared spectrum showed a typical *ortho*-disubstitution pattern between 5 and 6 $\mu$ and was, therefore, identified as *o*-nitrophenylcyclopropane. This substance is an oil ($n^{20}D$ 1.5606) which could not be made to crystallize; $\lambda_{max.}^{C_2H_5OH}$ 211, 249 m$\mu$; $\epsilon$ 1150; 4550. The smaller of the two main fractions, having the larger retention volume, showed an absorption pattern in the 5–6-$\mu$ region typical of *p*-disubstituted benzenes and was identified as *p*-nitrophenylcyclopropane. This isomer is a low melting solid, m.p. 32–33°; $\lambda_{max}^{C_2H_5OH}$ 218, 280 m$\mu$ ($\epsilon$ 8080, 11,000).

*Anal.* Calcd. for $C_9H_{10}NO_2$: C, 66.24; H, 5.56; N, 8.58. Found for *o*-nitrophenylcyclopropane: C, 65.98; H, 5.40; N, 8.54. Found for *p*-nitrophenylcyclopropane: C, 66.25; H, 5.54; N, 8.67.

**Oxidation of *o*-Nitrophenylcyclopropane.**—A sample of 0.50 g. (3.1 mmoles) of *o*-nitrophenylcyclopropane was heated under reflux for 2 hr. with a solution of 4.3 g. (43 mmoles) of chromic acid, 5.7 ml. of concentrated sulfuric acid, and 8.5 ml. of water. The reaction mixture was diluted with water and extracted with ether. The extract was dried and concentrated to give the crude product which on crystallization gave 0.33 g. (64%), m.p. 140–144° (lit.[14] m.p. 147–147.5°), of *o*-nitrobenzoic acid, identical with an authentic sample (mixture melting point and infrared spectrum).

**Oxidation of *p*-Nitrophenylcyclopropane.**—A sample of 100 mg. (0.61 mmole) of *p*-nitrophenylcyclopropane was heated under reflux for 2 hr. with a solution of 0.85 g. (8.5 mmoles) of chromic acid and 1.1 ml. of concentrated sulfuric acid in 2 ml. of water. The reaction mixture was diluted with water and the solid was collected to afford 90 mg. (88%) of *p*-nitrobenzoic acid, m.p. 240–242° (lit.[14] m.p. 239–240°), identical with an authentic sample (infrared spectra and mixture melting point).

**Nitrations of Alkylbenzenes and Analysis of the Product Mixtures.**—To a solution of 26.1 g. (24 ml., 0.26 mole) of acetic anhydride and 10.9 g. (7.3 ml., 0.16 mole) of fuming nitric acid (density 1.49–1.50) at −50° was added dropwise with stirring 0.05 mole of the alkylbenzene. The reaction mixture was allowed to come to room temperature (30 min.) and was poured into hot water. The product mixture was extracted with ether, the extract was dried, and concentrated to give the crude residue (always above 95% of the theoretical amount). This was dissolved in acetone in a 25-ml. volumetric flask and analyzed on a 10-ft. silicone rubber, analytical column (Aerograph A-90-C equipped with a disk integrator). The ratio of the areas under the two peaks was taken as the *ortho–para* ratio. Each analysis was carried out at least three times; the analyses were reproducible within ±1%. The total yields based on the gas chromatograms were always above 90%. These values are subject to errors of ±3%, owing to variations in the sample size. The gas chromatograms gave evidence for only very small amounts of unchanged starting materials, *meta* isomers, and polynitro compounds.

A second series of nitrations with acetic anhydride–fuming nitric acid prepared at room temperature was carried out in the same manner. Here also the yields were above 90%. In this case, nitration of phenylcyclopropane produced a rather wide range of *ortho–para* ratios.

**Nitration of Phenylcyclopropane with Nitric Acid–Sulfuric Acid.**—A sample of 2.3 g. of phenylcyclopropane was nitrated in 3.83 g. sulfuric acid and 1.42 g. of nitric acid according to the method of Brown and Bonner.[4] The crude yield was 2.30 g. (78%). The chromatographic analysis is given in Table I.

**Infrared and Ultraviolet Spectra.**—Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer. Ultraviolet spectra were recorded in 95% ethanol on a Carey Model 11 ultraviolet spectrophotometer.

**Acknowledgment.**—The authors wish to thank Dr. L. A. Strait for many helpful discussions and Mr. Michael Hrenoff for determining some of the infrared and ultraviolet spectra.

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## Competition Reactions of Cycloalkanes with Trichloromethanesulfonyl Chloride and Bromotrichloromethane

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The suggestion was made in an earlier publication that the hydrogen abstracting radical in the peroxide- and light-induced chlorinations of hydrocarbons with trichloromethanesulfonyl chloride (I) was not the trichloromethyl radical.[2] This conclusion was based on the difference in the relative reactivities of toluene and cyclohexane toward chlorination by I and toward bromination by bromotrichloromethane. Two different free radical chain sequences were suggested to account for the products obtained from the reaction of trichloromethanesulfonyl chloride with hydrocarbons (equation 1).

$$\underset{\text{I}}{Cl_3CSO_2Cl} + RH \longrightarrow RCl + SO_2 + HCCl_3 \quad (1)$$

CHAIN SEQUENCE A

$$R\cdot + Cl_3CSO_2Cl \longrightarrow RCl + Cl_3C\cdot + SO_2 \quad (2)$$

$$Cl_3C\cdot + RH \longrightarrow HCCl_3 + SO_2 \quad (3)$$

CHAIN SEQUENCE B

$$R\cdot + Cl_3CSO_2Cl \longrightarrow RCl + Cl_3CSO_2\cdot \quad (4)$$

$$Cl_3CSO_2\cdot + RH \longrightarrow Cl_3CSO_2H + R\cdot \quad (5)$$

$$Cl_3CSO_2H \longrightarrow HCCl_3 + SO_2 \quad (6)$$

In Chain Sequence A, the hydrogen abstraction from the hydrocarbon is performed by the trichloromethyl radical (equation 2) whereas in Chain Sequence B, the trichloro methanesulfinyl radical ($Cl_3CSO_2\cdot$) is postulated to be the hydrogen abstracting radical (equation 5). The trichloromethanesulfinic acid formed in this reaction is reported to be unstable, decomposing into chloroform and sulfur dioxide.[3] The peroxide- and light-induced brominations of hydrocarbons by bromotrichloromethane (equation 7) very likely involve the

$$BrCCl_3 + RH \longrightarrow RBr + HCCl_3 \quad (7)$$

free radical chain sequence (8 and 9), a sequence which almost certainly involves hydrogen abstraction

$$R\cdot + BrCCl_3 \longrightarrow RBr + Cl_3C\cdot \quad (8)$$

$$Cl_3C\cdot + RH \longrightarrow HCCl_3 + R\cdot \quad (9)$$

by a trichloromethyl radical.[4] A comparison of the relative reactivities of the medium-size cycloalkanes toward halogenation by trichloromethanesulfonyl chloride

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