2-Amino-3-benzylquinoxaline (22).—2-Benzyl-3-chloroquinoxaline (10 g) was added to ethanol (400 ml) that had been saturated with ammonia gas at 0° and the solution was heated at 170° for 8 hr. The reaction mixture was concentrated, filtered to remove ammonium chloride, and evaporated to dryness. Recrystallization from ethanol gave the aminoquinoxaline (4 g), mp 155–157°.

Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.1; H, 5.6; N, 17.9. Found: C, 76.1; H, 5.3; N, 17.8.

Interaction of 2-Amino-3-benzylquinoxaline with Diethyl Carbonate.—The amino compound (5 g) was dissolved in toluene (250 ml) containing sodium hydride (2.1 g of 53% mineral oil dispersion). The apparatus was arranged such that any ethanol formed could be removed after condensation. Diethyl carbonate (25 ml) was added dropwise over 30 min to the boiling reaction mixture and refluxing was continued for 4.5 hr. The solution was then evaporated to dryness and acidified with dilute acetic acid. The solid was filtered off, dissolved in chloroform, and extracted with 2 *N* potassium hydroxide. The dried chloroform solution was passed through an alumina column and the major fraction was recrystallized from ethanol to give the urethane **24** (2 g): mp 132°; nmr δ 4.43 ($C_6H_5CH_2$), 4.22 (q), 1.26 (t, C_2H_5O).

Anal. Calcd for $C_{18}H_{17}N_3O_2$: C, 70.3; H, 5.6; N, 13.7. Found: C, 70.2; H, 5.5; N, 13.7.

The alkaline extract was acidified with hydrochloric acid and the yellow solid was filtered off and dried. After three recrystallizations from isopropyl alcohol, the yellow pyrroloquinoxalone **23** (0.6 g), mp 296–300°, was obtained: mass spectrum *m/e* 261; ir 3360, 3200, 1660 cm^{-1}.

Anal. Calcd for $C_{16}H_{11}N_3O$: C, 73.6; H, 4.2; N, 16.1. Found: C, 73.3; H, 4.0; N, 16.0.

The mother liquors were evaporated and the residue was recrystallized successively from acetic acid and isopropyl alcohol (Norit) to give colorless crystals (1.2 g) of **25**: mp 297–298°; ir 3350 and 1745 cm^{-1}; mass spectrum *m/e* 277.

Anal. Calcd for $C_{16}H_{11}N_3O_2$: C, 69.3; H, 4.0; N, 15.2. Found: C, 69.0; H, 4.4; N, 15.1.

The mother liquors were again evaporated and the residue was extracted with chloroform. The extract gave a solid (120 mg) which, when recrystallized from ethanol, yielded 2,3-dihydro-3-ethyl-3-phenyl-1*H*-pyrrolo[2,3-*b*]quinoxalin-2-one (**26**): mp 217–218°; ir 1740 cm^{-1}; mass spectrum *m/e* 289.

Anal. Calcd for $C_{18}H_{15}N_3O$: C, 74.7; H, 5.2; N, 14.5. Found: C, 74.4; H, 5.3; N, 14.4.

Reaction of 22 with Diethyl Carbonate and Sodium Hydride.—The pyrroloquinoxalone **22** (320 mg), diethyl carbonate (7 ml), and sodium hydride (0.15 g, 53% oil dispersion) were refluxed in toluene (100 ml) for 36 hr. The solution was evaporated to dryness and acidified with dilute acetic acid. The product was dissolved in chloroform and the solution was extracted with 1 *N* potassium hydroxide. Acidification of the alkaline extract gave **26** (180 mg) having an infrared spectrum identical with that obtained previously.

Hydrolysis of 2,3-Dihydro-3-hydroxy-3-phenyl-1*H*-pyrrolo[2,3-*b*]quinoxalin-2-one.—Compound **25** (0.6 g) was dissolved in 2 *N* potassium hydroxide solution (15 ml) and heated on the steam bath overnight. The precipitated material was collected, dissolved in chloroform, chromatographed on silica gel, and recrystallized from ethanol to give 2-amino-3-benzoylquinoxaline (0.12 g), mp 168–169°, mass spectrum *m/e* 249.

Anal. Calcd for $C_{15}H_{11}N_3O$: C, 72.3; H, 4.5; N, 16.9. Found: C, 71.9; H, 4.2; N, 16.9.

Methylation of 2,4-Dihydro-3-phenyl-1*H*-pyrrolo[2,3-*b*]quinoxalin-2-one (22).—The pyrroloquinoxalone (0.33 g) was dissolved in acetone (75 ml) and, after the addition of methyl iodide (3 ml) and anhydrous potassium carbonate (1.5 g), the mixture was refluxed overnight. The product was worked up in the usual manner and chromatographed on neutral alumina in chloroform. 1,3-Dimethyl-2,3-dihydro-3-phenylpyrrolo[2,3-*b*]quinoxalin-2-one (**29**) (0.25 g) was eluted and recrystallized from aqueous ethanol to give colorless crystals: mp 129–130°; nmr δ 3.47 (NCH_3) and 1.95 (CCH_3); ir 1740 cm^{-1}.

Anal. Calcd for $C_{18}H_{15}N_3O$: C, 74.7; H, 5.2; N, 14.5. Found: C, 74.4; H, 5.2; N, 14.8.

Registry No.—**2**, 34731-45-8; **3**, 34712-59-9; **4**, 34712-60-2; **5**, 34731-46-9; **7**, 34731-47-0; **9**, 34731-48-1; **12**, 34731-49-2; **13**, 34712-61-3; **16** (R = CH_3), 34731-50-5; **16** (R = *n*-octyl), 32444-98-7; **17**, 34731-52-7; **18** (R = CH_2Ph), 34731-53-8; **19**, 30747-72-9; **20**, 32444-97-6; **22**, 34731-56-1; **23**, 34731-57-2; **24**, 34712-62-4; **25**, 34731-58-3; **26**, 34731-59-4; **28**, 33904-61-9; **29**, 34731-61-8; 2-amino-3-benzylquinoxaline, 34731-62-9.

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Notes

Reactions of Arylcyclopropanes with *N*-Bromosuccinimide in Hydroxylic Solvents[1]

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Earlier we observed that the reactivity of bromine with arylcyclopropanes in hydrocarbon and halogenated hydrocarbon solvents is very sensitive to light, temperature, and solvent. These reactions resulted in the formation of aryldibromopropanes and products of aromatic ring substitution.[2] It was also of interest to explore the action of electropositive bromine on arylcyclopropanes in more polar, hydroxylic solvents. Therefore phenylcyclopropane (**1a**), *p*-bromophenylcyclopropane (**2a**), and *cis*- (**3a**) and *trans*-1,2-diphenylcyclopropane (**4a**) were treated with *N*-bromosuccinimide (NBS) in methanol solution. In addition, the diphenylcyclopropanes were treated with NBS in 1,2-dimethoxyethane–water. The distributions of product components were determined in most cases by glc analyses and are summarized in Table I. The principal products were isolated and the structures were determined by spectral and elemental analyses

(1) (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for their support of this work. (b) Paper X in a series dealing with carbon–carbon bond fission in cyclopropanes. For paper IX, see ref 2.

(2) R. T. LaLonde, P. B. Ferrara, and A. D. Debboli, Jr., *J. Org. Chem.*, **37**, 1094 (1972).

TABLE I

REACTANTS AND PRODUCTS. THE REACTION OF ARYLCYCLOPROPANES (ACP) WITH *N*-BROMOSUCCINIMIDE (NBS)[a]

ACP	NBS/ACP[b]	Product mixture, % composition[c]		
		ACP	Aromatic substitution Product	
1a, A = H; B = H	1.05	**1a**, 11	**2a**, 9	**1c**, A = B = H; Y = OCH_3; Z = Br, 80
2a, A = Br; B = H	1.1	**2a**, 12		**2c**, A = Br; B = H; Y = OCH_3; Z = Br, 83
3a, A = H; B = *cis*-C_6H_5	1.11	**3a**, 5		**3c**, A = H; B = C_6H_5; Y = Z = OCH_3, 86
3a	1.0[d]	**3a**, 20[e]		**3d**, A = H; B = C_6H_5; Y = Z = OH, 40
				3e, A = H; B = C_6H_5; Y = Br; Z = OH, 34
4a, A = H; B = *trans*-C_6H_5	1.0	**4a**, 55	**5a**, 32	**3c**, 9
4a	2.0		**5a**, 72	**3c**, 19
4a	2.0[f]		**5a**, 100	
5a, A = Br; B = *trans*-BrC_6H_4				

[a] Reaction conditions were NBS and ACP in methanol for 7 days at room temperature in the dark unless indicated otherwise. [b] Mole ratio of NBS to ACP. [c] The distribution of unconsumed reactant and products was determined by glc analysis unless indicated otherwise. [d] The reaction was carried out in water–dimethoxyethane for 3 days at room temperature in the dark. [e] The product distribution was determined by weight. Minor products are given elsewhere. [f] The reaction was carried out in water–dimethoxyethane for 5 days at room temperature in the dark.

and in some cases were correlated with known compounds.

As the results of Table I show, phenyl-, *p*-bromophenyl-, and*ci s*-diphenylcyclopropanes give mainly the products resulting from addition across the cyclopropane ring. The action of NBS on *cis*-diphenylcyclopropane in dimethoxyethane–water gives a complex mixture which consists not only of **3d** and **3e** but also 4% 3-hydroxy-1,3-diphenyl-1-propanone and 2% benzalacetophenone, products likely resulting from subsequent NBS oxidation and oxidation and elimination, respectively.

In contrast to phenylcyclopropanes **1a**, **2a**, and **3a**, *trans*-diphenylcyclopropane (**4a**) undergoes largely aromatic ring substitution giving *trans*-1,2-di-*p*-bromophenylcyclopropane (**5a**). In methanol some small amount of addition product is formed, and, like the cis isomer, addition occurs across the σ bond joining the two substituted carbons. In dimethoxyethane–water **5a** is the only detectable product.

The formation of para-substituted **5a** and **2a** is consistent with many previous examples of the directional influence of a cyclopropyl group and also with uv studies showing that cyclopropyl groups attached to aromatic rings are electron donors.[3] Seemingly the dissimilarity in the principal mode of *cis*- and *trans*-diphenylcyclopropane reactivity can be traced back to differences in the ground state levels. The cis isomer is known to be less stable.[4] According to molecular models, the difference in stability would seem to result from the crowding of the two phenyl groups in the cis isomer coupled with the more favorable conformation of the trans isomer wherein both phenyl groups bisect the plane of the cyclopropane ring and thereby allow maximum overlap of p-rich σ bonds of the cyclopropane ring with the π bonds of the phenyl groups.[5] Consequently an element of strain, not present in the trans isomer, is relieved in the addition to the cis isomer. As for the trans isomer, the second phenyl group can better donate electrons to the phenyl group undergoing attack in the electron-demanding process of electrophilic aromatic substitution. Therefore the energy of the transition state is lowered relative to that for aromatic substitution of the cis isomer.

Interestingly, the dimethoxydiphenylpropane addition products from *cis*- and *trans*-diphenylcyclopropane differ in diastereomeric composition. The cis isomer largely undergoes overall trans addition, resulting in a mixture of dimethoxypropanes rich in the *dl* diastereomer (*dl*/meso = 2). The trans cyclopropane gives equal amounts of *dl* and meso dimethoxypropanes. Selective isomer stereospecificity was previously observed in the dark, bromine addition to the diphenylcyclopropanes in carbon tetrachloride solution. There, the cis isomer gave predominantly the meso dibromide, indicating cis addition to the σ bond,[2] whereas the trans isomer again gave meso and *dl* dibromides in equal amounts. Presently we have insufficient evidence to offer an explanation for predominant cis addition in carbon tetrachloride and overall trans addition in methanol. The nature of the addition products first formed and the stereochemistry of subsequent solvolysis, including the ramifications of possible 1,3 neighboring group participation,[6] are imponderables at this time.

Experimental Section

Spectra were obtained as follows: nmr in $CDCl_3$ solution (unless otherwise indicated), 1% TMS (10.00 τ), Varian A-60A, symbols s, d, t, q, and m used in connection with nmr refer to singlet, doublet, triplet, quartet, and multiplet, respectively; ir in CCl_4 solution, 0.05-mm sample and reference cells (unless otherwise indicated), Perkin-Elmer 137, symbols s, m, w, sh, br, and sp used in connection with ir refer to strong, medium, weak, shoulder, broad and sharp, respectively.

Melting points were determined on a Köfler micro hot stage and are uncorrected. Glc was performed on a Varian Aerograph Model 200 using columns 5 ft × 0.25 in. containing the liquid

(3) (a) R. M. Kellogg and J. Buter, *ibid.*, **36**, 2236 (1971); (b) R. C. Hahn, P. H. Howard, S.-M. Kong, G. A. Lorenzo, and N. L. Miller, *J. Amer. Chem. Soc.*, **91**, 3558 (1969); (c) L. A. Strait, R. Ketcham, D. Jambotkar, and V. P. Shah, *ibid.*, **86**, 4628 (1964).

(4) (a) L. B. Rodewald and C. H. DePuy, *Tetrahedron Lett.*, 2699 (1970); (b) R. J. Crawford and T. R. Lynch, *Can. J. Chem.*, **46**, 1457 (1968).

(5) (a) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); (b) G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, **86**, 4042 (1964); (c) G. L. Closs and H. B. Klinger, *ibid.*, **87**, 3265 (1965).

(6) For recent references to 1,3-halonium ions see P. E. Peterson and W. F. Boron, *ibid.*, **93**, 4076 (1971).

phase on Chromosorb W. The elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

All reactions carried out in methanol solution were run for 7 days at room temperature in the dark and are referred to as standard reaction conditions. The standard procedure for processing the reaction mixture consisted of pouring the methanol solution into 50–100 ml of water and extracting the resulting mixture with ether (2–3 × 25 ml). The combined ether extracts were washed with water (2 × 25 ml) and dried (anhydrous $MgSO_4$). Evaporation of the ether at the rotary evaporator gave the crude product mixture.

Phenylcyclopropane.—Phenylcyclopropane was prepared by a known method.[7] A 473-mg sample (4.0 mmol) in 8 ml of absolute MeOH was treated with 750 mg (4.2 mmol) of NBS in 8 ml of MeOH under the standard reaction conditions. Processing by the standard procedure gave 776 mg of a clear, colorless liquid. Quantitative glc analysis using a 15% XF-1 at 130° established the presence of three components in 9, 11, and 80%. Comparative glc on 10% QF-1 (150°), 15% XF-1 (130°) and 20% Se-30 (180°) established the identity of the two minor components as phenylcyclopropane (11%) and *p*-bromophenylcyclopropane (9%). The major component was isolated and purified by preparative glc and was identified as 1-methoxy-3-bromo-1-phenylpropane: nmr τ 2.60 (s, 5 H, ArH), 5.60 (q, J = 5.5, 7.5 Hz, 1 H, ArC**H**OCH$_3$), 6.1–6.7 (m, 2 H, CH_2Br), 6.73 (s, 3 H, OCH_3), 7.3–8.2 (m, 2 H, CH_2); ir 2900 (m, sp), 1620 (w, sp), 1100 (s, br) 700 cm^{-1} (s, br).

Anal. Calcd for $C_{10}H_{13}BrO$: C, 52.42; H, 5.72; Br, 34.88. Found: C, 52.62; H, 5.76; Br, 35.04.

***p*-Bromophenylcyclopropane.**—*p*-Bromophenylcyclopropane was prepared by a known method.[8] A 394-mg sample (2.0 mmol) in 4 ml of absolute MeOH was treated with 390 mg (2.2 mmol) of NBS in 4 ml of absolute MeOH under the standard reaction conditions. Processing by the standard procedure afforded 513 mg containing 12% unconverted *p*-bromophenylcyclopropane and 83% of the major component according to glc. A third unidentified component was detected by nmr (m, τ 8.18–8.40, and m, τ 8.6–8.7). Purification of the major component by preparative glc using a 10% QF-1 column (175°) gave 1-methoxy-3-bromo-1-*p*-bromophenylpropane: nmr τ 2.82 (A_2 of A_2B_2 m, 2 H, ArH), 2.75 (B_2 of A_2B_2 m, 2 H, ArH), 5.62 (q, J = 8, 5.5 Hz, 1 H, ArC**H**OCH$_3$), 6.3–6.7 (m, 2 H, CH_2Br), 6.75 (s, 3 H, CH_3O), 7.6–8.1 (m, 2 H, CH_2).

Anal. Calcd for $C_{10}H_{12}Br_2O$: C, 38.98; H, 3.98; Br, 51.89. Found: C, 38.89; H, 3.99; Br, 51.89.

***cis*-1,2-Diphenylcyclopropane. A. Methanol.**—A mixture of *cis*- and *trans*-1,2-diphenylcyclopropane was prepared by a known method.[9] Isomers were separated on a spinning band column to obtain pure cis, bp 116° (0.2 mm), and trans isomers, bp 125° (0.2 mm). A 970-mg sample (5.0 mmol) of the cis isomer in 10 ml of absolute MeOH was treated with 1.0 g (5.6 mmol) of NBS in 10 ml of the same solvent under standard reaction conditions. Processing by the standard procedure afforded 933 mg of product mixture consisting of 5% unconverted cyclopropane, 9% of an unidentified component, and 86% of the major component according to glc. Isolation of the major component from a sample by preparative glc using a 20% Se-30 column at 215° gave the known 1,3-dimethoxy-1,3-diphenylpropane:[10] mp 57–58°; nmr τ 2.69 (s, 10 H, ArH), 5.46 (q, J = 6, 7 Hz, *dl*-ArC**H**OCH$_3$),[11] 5.86 (J = 7 Hz, *meso*-ArC**H**OCH$_3$), 6.78 (s, OCH_3), 6.90 (s, OCH_3), 7.98 (q, J = 6, 7 Hz, *dl* CH_2), 7.5–8.3 (m, *meso*-CH_2), ratio of integrated intensities, τ 5.46/5.83 and 6.78/6.90 = *dl*/meso = 2; ir 2900 (s, sp), 1350 (s, sp), 1100 (s, br), and 700 cm^{-1} (s, br). Recrystallization of a sample of the crude product mixture from pentane gave 1,3-dimethoxy-1,3-diphenylpropane, mp 57–58°; nmr *dl*/meso = 2.

A solution of 1,3-dibromo-1,3-diphenylpropane (*dl*/meso = 1.0)[2] (2.08 g, 5.3 mmol), 1.08 g (6.0 mmol) of NBS, and 600 mg of succinimide in 24 ml of absolute MeOH was kept at room temperature for 7 days in the dark. Processing in the standard manner gave 1.19 g of crude 1,3-dimethoxy-1,3-diphenylpropane: nmr as above, 5.46/5.83 and 6.78/6.90 = *dl*/meso = 1.

B. Dimethoxyethane–Water.—To 3.492 g (18 mmol) of *cis*-1,2-diphenylcyclopropane in 300 ml of 1,2-dimethoxyethane and 110 ml of water was added in one portion 3.45 g (18 mmol) of NBS. This solution was then stirred at room temperature for 3 days in the dark. Thereafter the mixture was poured into 500 ml of water and the resulting mixture was extracted repeatedly with ether. The ether extract was washed with water and dried (anhydrous $MgSO_4$). Removal of the ether at the rotary evaporator gave 4.51 g of crude product mixture which was separated by glc using silica gel GF-254 and 97% $CHCl_3$–3% EtOAc. Thereby was obtained 925 mg of *dl*- and *meso*-1,3-dihydroxy-1,3-diphenylpropane [R_f 0.18; nmr (CD_3COCD_3) τ 2.5–2.9 (10 H, ArH), 4,9–5.3 (m, 2 H, ArC**H**OH), 6.57 (2 H, OH), 7.7–8.3 (m, 2 H, CH_2); ir 3300 (s, br), 1400 (m, sp), 1150 (br, d), 935 cm^{-1} (m, sp) and consistent with spectra of *dl* and meso diols obtained by another method],[2] 74 mg of 3-hydroxy-1,3-diphenylpropan-1-one [R_f 0.37; mp 49–51° from petroleum ether (bp 30–60°); semicarbazone mp 179–180°;[12] nmr τ 2.0–2.9 (m, 10 H, ArH), 4.70 (q, J = 6 Hz, 2 H, CH_2); ir 3600 (m, br), 1625 (s, br), 1455 (s, sp), 1210 cm^{-1} (s, br)], 760 mg of 1-bromo-3-hydroxy-1,3-diphenylpropane [R_f 0.57; nmr (CCl_4) 2.6–2.9 (m, 10 H, ArH), 5.13 (m, 1 H, ArC**H**OH), 5.60 (q, J = 5.8 Hz, ArC**H**Br), 7.25 (s, 1 H, OH), 7.0–8.0 (m, 2 H, CH_2); ir 3600 (m, br), 1300 (s, br)], 50 mg of benzalacetophenone (R_f 0.70), and 460 mg of *cis*-1,2-diphenylcyclopropane (R_f 0.95). Samples of 1-bromo-3-hydroxy-1,3-diphenylpropane darkened rapidly even when extreme precautions were taken to prevent it. Attempts to obtain a satisfactory analysis were unsuccessful.

Hydrolysis of 1-Bromo-3-hydroxy-1,3-diphenylpropane.—To 58 mg (0.2 mmol) of 1-bromo-3-hydroxy-1,3-diphenylpropane obtained as indicated above, in 3.7 ml of acetone was added in one portion 450 mg (0.2 mmol) of silver nitrate in 3.7 ml of water and the resulting slurry was stirred overnight at room temperature. The silver bromide (calcd: 38 mg; found: 34 mg) was filtered off and the acetone was removed from the filtrate at the rotary evaporator. The aqueous residue was extracted with ether and the extract was washed with water, 5% aqueous $NaHCO_3$, and water and then dried (anhydrous $MgSO_4$). Vacuum evaporation of the ether gave 45 mg of 1,3-diphenyl-1,3-propanediol whose spectra were consistent with those from a sample of meso and *dl* diol obtained earlier.[2]

***trans*-1,2-Diphenylcyclopropane. A. Methanol.**—*trans*-1,2-Diphenylcyclopropane was obtained as described above. A solution of 970 mg (5.0 mmol) of the cyclopropane in 10 ml of absolute MeOH was treated with 2.0 g (11 mmol) of NBS in 8 ml of absolute MeOH under standard reaction conditions. Processing by the standard procedure afforded 1.526 g of a moist, white solid. Glc analysis (20% Se-30, 225°) established the presence of 72% *trans*-1,2-*p*-bromophenylcyclopropane, 19% 1,3-dimethoxy-1,3-diphenylpropane, and 9% of at least six unidentified substances. Isolation of the 1,3-dimethoxy-1,3-diphenylpropane by glc and subsequent nmr analyses of the purified sample showed *dl*/meso = 1.

The remaining portion of crude product mixture was triturated several times with cold ether to obtain *trans*-1,2-*p*-bromophenylcyclopropane: mp 114–115°; nmr (CCl_4) τ 2.66 (A_2 of A_2B_2 m, 4 H, ArH), 3.10 (B_2 of A_2B_2 m, 4 H, ArH), 7.98 (A_2 of A_2B_2 m, 2 H, ArCH), 8.69 (B_2 of A_2B_2 m, 2 H, CH_2); ir 1490 (s, sp), 1010 cm^{-1} (s, sp).

Anal. Calcd for $C_{15}H_{12}Br_2$: C, 51.17; H, 3.44; Br, 45.39. Found: C, 51.31; H, 3.57; Br, 45.40.

In a similar manner 970 mg (5.0 mmol) of *trans*-1,2-diphenylcyclopropane was treated with 1.0 g (5.6 mmol) of NBS in a total of 20 ml of absolute MeOH in the standard manner and the reaction mixture was processed according to the standard procedure. Thereby was obtained 946 mg of a product mixture which consisted of 55% unconverted *trans*-1,2-diphenylcyclopropane, 32% *trans*-1,2-*p*-bromophenylcyclopropane, and 9%

(7) T. F. Corbin, R. C. Hahn, and H. Shechter, *Org. Syn.*, **44**, 30 (1964).

(8) R. Yu. Levina, P. A. Gembitskii, V. N. Kostin, S. M. Shostakovskii, and E. G. Treschchova, *Zh. Obshch. Khim.*, **33**, 365 (1963).

(9) S. G. Beech, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 4686 (1952).

(10) J. W. Copenhaver, U. S. Patent 2,768,212 (1956); *Chem. Abstr.*, **52**, 433c (1958).

(11) The combination of the low-field quartet (τ 5.46) with the high-field quartet (τ 7.98) was taken as an A_2X_2 resonance pattern stemming from the four methylene and methine protons of *dl*-1,3-dimethoxy-1,3-diphenylpropane. The low-field triplet (τ 5.86) in conjunction with the high-field complex multiplet (τ 7.5–8.3) constituted the ABX_2 pattern which originated from the four methylene and methine protons of *meso*-1,3-dimethoxy-1,3-diphenylpropane.

(12) D. S. Noyce, W. A. Pryor, and A. H. Bottini, *J. Amer. Chem. Soc.*, **77**, 1402 (1955).

1,3-dimethoxy-1,3-diphenylcyclopropane according to glc analysis (20% Se-30, 225°).

B. Dimethoxyethane–Water.—To 2.036 g (11 mmol) of *trans*-1,2-diphenylcyclopropane in 132 ml of 1,2-dimethoxyethane and 48 ml of water was added in one portion 4.1 g (23 mmol) of NBS. The resulting solution was kept at room temperature for 5 days in the dark. Thereafter the solution was poured into 1 l. of water and the mixture was extracted with ether (3 × 250 ml). The ether extract was washed with water and dried (anhydrous $MgSO_4$). Vacuum evaporation of the ether left a white solid whose glc analysis (Se-30, 225°) showed a single peak in addition to solvent. Two recrystallizations from ethanol–water gave 2.4 g of *trans*-1,2-*p*-bromophenylcyclopropane whose spectral properties were identical with those given above.

Registry No.—**1a**, 873-49-4; **1c**, 34733-61-4; **2a**, 1124-14-7; **2c**, 34733-62-5; **3a**, 1138-48-3; (±)-**3c**, 34733-63-6; *meso*-**3c**, 34733-64-7; **3e**, 34712-58-8; **4a**, 1138-47-2; **5a**, 34733-66-9; NBS, 128-08-5.

Rearrangement and Cleavage Processes in Crowded Cyclohexadienyl Carbonium Ions

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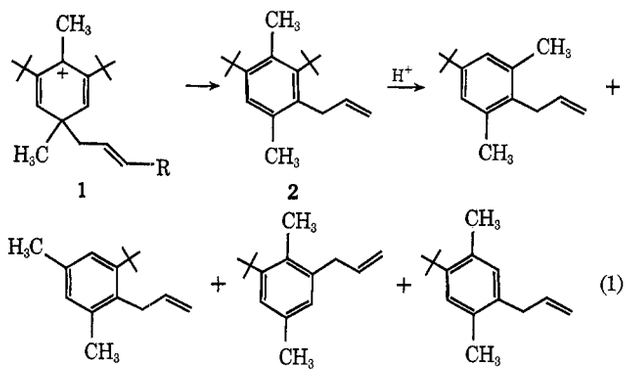
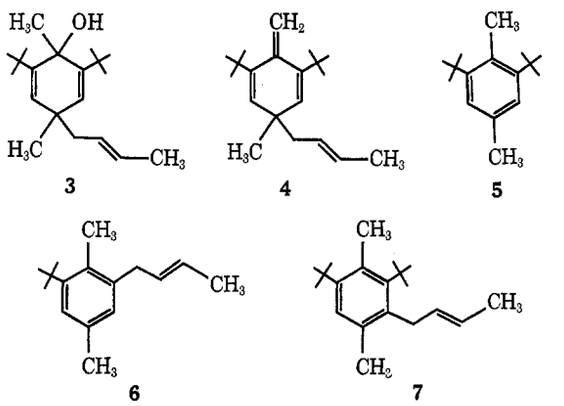
In an earlier paper[1a] we reported that carbonium ion **1** (R = H) rearranges to give the normal [1,2] migration product **2**. Rearrangement of **2**, in turn,



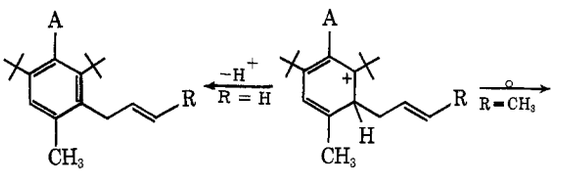
(1)

proceeds in surprisingly mild acid conditions to give the products shown in eq 1. The ease of rearrangement of **2** and the unusual nature of its rearrangement products were attributed to steric effects favoring protonation at the most hindered position on the ring.[1] We have now prepared several additional highly crowded cyclohexadienyl carbonium ions, in order to compare their reactions with those of **1**.

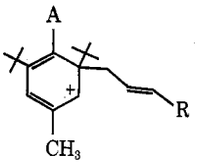
We first substituted a crotyl group (a better migrating group[2]) for the allyl group in **1**. Reaction of cyclohexadienol **3**[3] with 10% sulfuric acid in acetic acid gave two products in the ratio 6:1. These products were isolated by preparative vpc. The major product was identified as 2,6-di-*tert*-butyl-*p*-xylene (**5**),[3] while the minor product was assigned the structure 2-(*trans*-2-butenyl)-6-*tert*-butyl-*p*-xylene (**6**). (Evidence for structural assignments is discussed below.) When either **3** or the semibenzene **4**[3] was refluxed in benzene solution in the presence of Florisil (magnesium fluorosilicate), a mildly acidic heterogeneous catalyst,[4] **5** was again the major product, constituting from 60 to 75% of the total product, while **6** was obtained in 8–10% yield. A third component, constituting 20–30% of the product, was obtained under these conditions, however, and was assigned structure **7**. Compound **7** was found to be unchanged on prolonged refluxing in the presence of Florisil. Furthermore, on prolonged standing in sulfuric acid in acetic acid, **7** reacted to give a complex mixture of products. These were not isolated due to the small amount of **7** available. Vpc analysis, however, showed that **6** was only a minor component of the mixture. Thus, formation of **6** in the Florisil catalyzed reaction occurs predominantly during the initial rearrangement of carbonium ion **1** (R = CH_3) rather than as a result of further rearrangement of **7**.



The products obtained from carbonium ion **1** closely resemble those obtained from reactions of 2,6-di-*tert*-butylcyclohexadienones in acid.[2] With either the dienone or **1**, no cleavage of an allyl group from the ring takes place,[1,2] while crotyl groups undergo appreciable cleavage.[2] That a higher yield of cleavage product is obtained from **1** than from the cyclohexadienone may be attributed to the fact that the energy gained by formation of an aromatic ring from **1** is greater than that resulting from formation of a phenol from a protonated cyclohexadienone. With either the dienone or cyclohexadienyl carbonium ion, initial [1,2] migration of a crotyl group to form **8** is immediately



8, A = CH_3, OH



followed, in sulfuric acid–acetic acid solution, by a second [1,2] migration of the crotyl group to the carbon

(1) (a) K.-H. Lai and B. Miller, *Tetrahedron Lett.*, 3575 (1971); (b) K.-H. Lai and B. Miller, *Tetrahedron*, **28**, 2221 (1972).

(2) B. Miller and H. Margulies, *J. Amer. Chem. Soc.*, **87**, 5106 (1965); B. Miller, *ibid.*, **87**, 5115 (1965).

(3) B. Miller and K.-H. Lai, *ibid.*, **94**, 3471 (1972).

(4) M. J. Gentles, J. B. Moss, H. L. Herzog, and E. B. Hershberg, *ibid.*, **80**, 3702 (1958).