through one of the carbon atoms) and the corresponding symmetry-adapted substituent orbital.
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(11) S. W. Tobey, K. S. Wittemore, and M. Z. Laurandos, Abstracts, 136th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept 1968, No. ORGN-168.
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(14) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2367 (1961).
(15) R. Breslow and P. Gal, *J. Am. Chem. Soc.*, **81**, 4747 (1959).

Substituent Effects in the Homolytic Brominolysis of Substituted Phenylcyclopropanes

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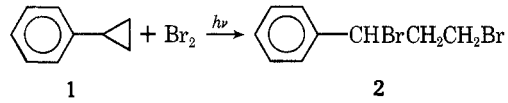
Competitive photochemical brominolyses of substituted phenylcyclopropanes in carbon disulfide at 20 °C gave linear Hammett plots with σ^+ ($\rho = -1.84$, correlation coefficient −0.996) or with σ ($\rho = -2.16$, correlation coefficient −0.982). The substituent effect is similar to that found in homolytic bromination of toluenes, and is similarly interpreted in terms of a polar transition state for the displacement reaction.

Bimolecular homolytic substitutions at carbon (SH2 reactions) are seldom encountered. The best known examples are cleavages of cyclopropane rings by halogen atoms.[1] Although this process has been investigated with respect to its kinetic order,[2] stereochemistry,[1,3,4] and regiospecificity,[3,5] it has not been studied with respect to the electron demands at the involved carbon atoms in the transition state, except for one preliminary study[2b] which gave some gross (not site-specific) substituent effects. The present study provides this information for the leaving carbon radical by a Hammett study of brominolysis of substituted phenylcyclopropanes.

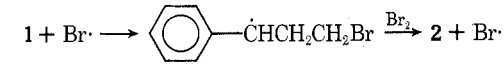
The bromination of phenylcyclopropane (**1**) under a variety of conditions has been studied by LaLonde, Ferrara, and Debboli,[6] who found a light-induced bromination in carbon tetrachloride at 25 °C to give exclusively 1,3-dibromo-1-phenylpropane (**2**). Although the simplest and most obvious



1 **2**

mechanism for this process is a conventional free-radical chain (Scheme I), those authors were unwilling to endorse that

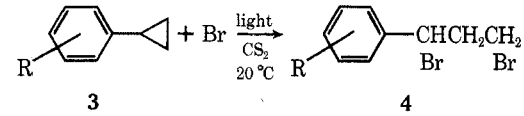
Scheme I



mechanism, partly because they could not demonstrate inhibition with nitrobenzene or trinitrobenzene and partly because of the general unreactivity of cyclopropanes toward free-radical ring opening. Our preference was to accept Scheme I as the mechanism in view of the abundant evidence cited above for homolytic halogenolysis of cyclopropanes, and we have in fact found that although the reaction of **1** with bromine is not retarded by nitrobenzene (in agreement with LaLonde), it is strongly inhibited by isoamyl nitrite. Without isoamyl nitrite, a solution of **1** and bromine decolorized fully in 7 min of illumination. With added isoamyl nitrite, an identical mixture showed no visible decoloration after 1 h of illumination.

A series of substituted phenylcyclopropanes were prepared by conventional methods, some by way of electrophilic substitutions on **1** and some from substituted acetophenones through a Mannich condensation and subsequent pyrazoline formation and thermolysis.[7] Details are in the Experimental Section. Substituents were chosen to avoid reactions of the substituent with bromine, to avoid activation of the aromatic ring toward electrophilic substitution, and to avoid charged groups which might reduce solubility in nonpolar solvents.

All of the phenylcyclopropanes (**3**) reported here underwent light-induced addition of bromine in carbon disulfide at 20



3 **4**

a, R = *p*-phenyl
b, R = *p*-Cl
c, R = *p*-Br
d, R = *m*-Br
e, R = *p*-I
f, R = *p*-CN
g, R = *p*-NO_2

°C to give the 1,3-dibromo-1-arylpropanes (**4**). The NMR spectra of the 1,3-dibromides were very similar, all showing the benzylic doublet of doublets at δ 4.93–5.10, the central methylene multiplet at δ 2.1–3.0, and the terminal methylene multiplet at δ 3.0–3.6. Control reactions in the absence of light showed no significant reaction for any of the compounds **3** in 30 min or longer, except that **3a** gave a 22.5% yield of **4a** in 1 h in the dark. All but **3f** and **3g** gave 100% yields of **4** in 18 min or less when illuminated with a sunlamp. The reaction of **3a** in the light was complete in 2 min. **3f** and **3g** gave reactions only 70% (1 h) and 19% (2 h) complete, respectively, under illumination, but no products other than **4f** and **4g** were detected. It is important that no exchange of aryl halogen for bromine was observed in recovered **3b** and **3e** (dark reactions) or **4b** and **4e** (from photoreactions).

To obtain relative rate constants for the brominolyses of compounds **3**, it was found necessary for practical reasons to measure each in competition with *p*-chlorotoluene (which gives α-bromination) rather than in competition with one another. The mixtures obtained from more than one of the phenylcyclopropanes were not easily analyzed by NMR or gas chromatography, whereas the NMR signals from *p*-chlorobenzyl bromide (δ 4.27) and *p*-chlorobenzal bromide (δ 6.52) were cleanly resolved with respect to the spectra of compounds **3** and **4**, and permitted accurate quantitative analysis. It was shown that the hydrogen bromide formed in bromination of the *p*-chlorotoluene does not react with either **1** or **3f** under the conditions used in the competitive reactions.

Table I lists the results of competitive brominations of the phenylcyclopropanes against *p*-chlorotoluene, with k_2 being the rate constant for brominolysis of the cyclopropane and k_1

Table I. Competitive Rates of Bromination Relative to *p*-Chlorotoluene in Carbon Disulfide at 20 °C under Illumination

Substrate	Log (k_2/k_1)	Substrate	Log (k_2/k_1)
3a	+0.95 ± 0.07	**3c**	+0.20 ± 0.04
1	+0.62 ± 0.04	**3d**	−0.13 ± 0.02
3e	+0.32 ± 0.05	**3f**	−0.66 ± 0.02
3b	+0.28 ± 0.04	**3g**	−0.87 ± 0.03

Table II. Competitive Rates of Bromination Relative to *p*-Cyanophenylcyclopropane in Carbon Disulfide at 20 °C under Illumination

Substituted toluene	Log (k_1/k_2)
p-Cl	+0.66 ± 0.02
p-Br	+0.60 ± 0.03
m-Br	+0.072 ± 0.03
m-NO_2	−0.86 ± 0.06

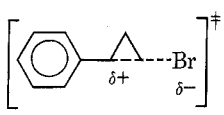
being the rate constant for bromination of the toluene. The errors shown are combined statistical errors from the average deviations of successive NMR integrations in each run and from average deviations of three separate determinations of log k_2/k_1 for each compound.

The data from Table I are plotted against σ^+ values[8] in Figure 1. The least-squares slope (ρ^+) is −1.85 and the correlation coefficient is −0.996. A similar plot (not shown) using ordinary Hammett σ values gives a slope of −2.16 and a correlation coefficient of −0.982. This plot is less satisfactory than the σ^+ plot, but not sufficiently inferior to conclude with certainty that the rates correlate with σ^+.

The data for the ring-opening brominolyses are strikingly similar to those for abstraction of benzylic hydrogens from substituted toluenes by bromine atoms. Thus at 19 °C in benzene the benzylic bromination follows σ^+ with a ρ of −1.76.[9] In view of the expected sensitivity of this process to solvent changes,[10] it was decided to investigate the substituent effect briefly in CS_2 solvent to make certain that the apparent similarity to the cyclopropane cleavages was not the result of a cancellation of opposite effects. Data for relative rates of four toluenes (k_1) vs. *p*-cyanophenylcyclopropane (k_2) in CS_2 at 20 °C are shown in Table II.

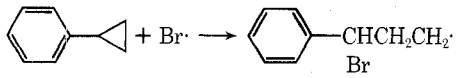
The data in Table II correlate with σ^+ to give ρ −2.67 and correlation coefficient −0.988. The correlation with σ gives ρ −3.26 and correlation coefficient −0.996. The slight superiority of the σ correlation with these few data must be considered insignificant in view of the established superiority of σ^+ correlations in more extensive studies.[9,11]

The most acceptable interpretation of the present data is that the transition state for cyclopropane brominolysis has some charge separation like that (but perhaps smaller in magnitude) postulated to account for the negative ρ and correlation with σ^+ in the hydrogen abstractions:



Cognizance must be taken of recent criticisms by Zavitsas of this kind of interpretation,[12] but satisfying counterarguments are also now on hand.[13]

It must be noted that the site of attack on the cyclopropane ring could be at the benzylic carbon:



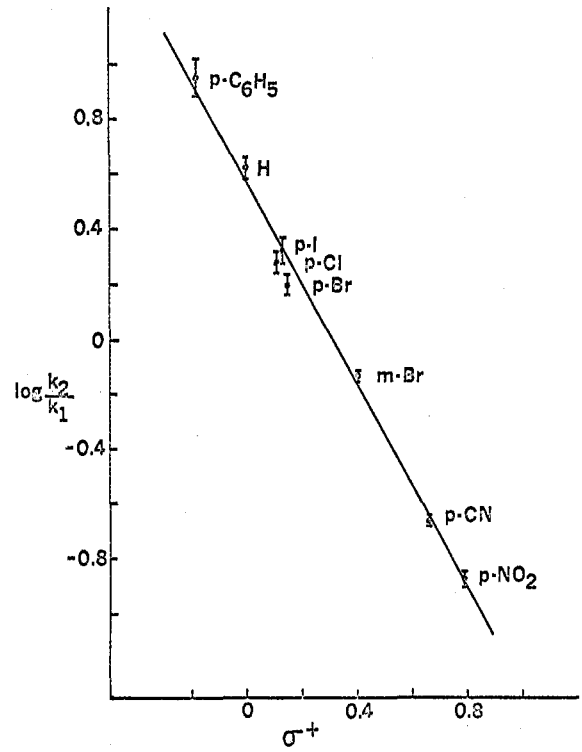


Figure 1.

Such benzylic attack has been proposed by Shea and Skell[3] to account for the regiospecificity in additions of bromine to 1-alkyl-2-phenylcyclopropanes, where the leaving-group radical would be secondary. The substituent effects observed in the present work seem most easily accommodated with the β-attack as proposed, but further experiments are needed to exclude benzylic attack rigorously.

The significance of the present results with respect to the fundamental nature of the SH2 reaction at carbon is not yet clear. It is interesting that the only cases of such reactions are those in which polarized transition states are possible and, as shown here, occur. The generality of the finding will be evident after the completion of the future experiments which it suggests.

Experimental Section[14]

Phenylcyclopropane (1) was prepared in 50% yield by the method of Peterson and Skell.[15] It had bp 57.5 °C (9 mm) [lit.[15] bp 60 °C (13 mm)] and had infrared[16] and NMR[17] spectra identical with those reported.

ω-Dimethylamino-*p*-chloropropiophenone Hydrochloride. Following a similar procedure by Maxwell,[18] dimethylamine hydrochloride (126 g, 1.54 mol), paraformaldehyde (51.0 g, 0.57 mol) and *p*-chloroacetophenone (208 g, 1.35 mol) were mixed and then dissolved in 500 ml of 95% ethanol. Concentrated HCl (5 ml) was added to ensure that all dimethylamine was in its hydrochloride form. The mixture was refluxed on a steam bath for 30 h. The hot solution was then poured into a large Erlenmeyer flask with 200 ml of 95% ethanol. Crystals formed as the solution cooled. These crystals along with a second crop from the mother liquor were recrystallized from a mixture of absolute ethanol and acetone. The material was then dried under vacuum for 20 h to give 208.9 g (62%) of white crystals, mp 174 °C (lit.[7] mp 174 °C).

Anal. Calcd for $C_{11}H_{15}Cl_2NO$: C, 53.24; H, 6.09; Cl, 28.58; N, 5.65. Found: C, 53.48; H, 6.18; Cl, 28.91; N, 5.75.

***p*-Chlorophenylcyclopropane (3b).** ω-Dimethylamino-*p*-chloropropiophenone hydrochloride (169.8 g, 0.686 mol) was dissolved in 500 ml of hot methanol and added slowly to a solution of 82.3 g (1.4 mol) of 85% hydrazine hydrate and 28.0 g (0.70 mol) of sodium hydroxide in 600 ml of absolute methanol. The mixture was stirred and refluxed. After 4.5 h the flask was fitted with a distillation head and the methanol was removed by distillation. The residue was partitioned between ether and water. The ether layer was dried over anhydrous

magnesium sulfate. The ether was removed by means of a Rotavap. The remaining material was distilled slowly from a 300-ml Pyrex flask using a Woods Metal bath. Most of the product was collected with a pot temperature of 230–260 °C and a head temperature of 180–200 °C. The distillate was diluted with diethyl ether and extracted successively with 3% aqueous hydrochloric acid and saturated aqueous sodium bicarbonate. The ether layer was dried over anhydrous sodium sulfate. The solvent was removed by means of a Rotavap leaving 37.6 g of a clear liquid (36% yield of crude product). Further purification of the material was accomplished by distillation at reduced pressure through a 20-cm column of glass helices. The clear liquid product (bp 59 °C, 0.1 mm) [lit.[7] bp 110–115 °C (15 mm)] was found to be homogeneous on VPC with a 10 ft × 0.25 in. o.d. column of 25% SE-30 on Firebrick at 200 °C with a flow rate of 60 ml/min. The infrared spectrum corresponded peak for peak with that of *p*-chlorophenylcyclopropane as reported by Levina and co-workers.[16] The NMR spectrum (CCl_4) showed absorptions at δ 7.10 (d, 2 H, J = 9 Hz), 6.83 (d, 2 H, J = 9 Hz), 1.98–1.50 (m, 1 H), and 1.10–0.37 (m, 4 H).

ω-Dimethylamino-*p*-phenylpropiophenone Hydrochloride. Dimethylamine hydrochloride (49.2 g, 0.60 mol), paraformaldehyde (19.8 g, 0.22 mol), and *p*-phenylacetophenone (84.0 g, 0.50 mol) were mixed in their solid forms and dissolved in 700 ml of hot 95% ethanol. Concentrated hydrochloric acid (5 ml) was added to ensure that all dimethylamine was in its hydrochloride form. The solution was refluxed for 48 h over a steam bath and was then poured into an Erlenmeyer flask. White crystals formed as the solution slowly cooled. Two crops of crystals were collected. After recrystallization from absolute ethanol, the crystals were dried under vacuum to yield 85.3 g (59%) of product (mp 185–186 °C). An analytical sample was recrystallized three times from absolute ethanol and dried under vacuum.

Anal. Calcd for $C_{17}H_{20}ClNO$: C, 70, 47; H, 6.91; Cl, 12.26; N, 4.84; O, 5.52. Found: C, 70.62; H, 6.66; Cl, 12.37; N, 4.58.

***p*-Phenylphenylcyclopropane (3a).** ω-Dimethylamino-*p*-phenylpropiophenone hydrochloride (85.3 g, 0.294 mol) was dissolved in 500 ml of absolute methanol and the solution was added dropwise to a second solution of 0.30 mol of sodium hydroxide and 0.60 mol of 85% hydrazine hydrate in 1000 ml of refluxing methanol. Refluxing was continued for 24 h. Methanol solvent was removed by distillation, and the remaining white residue was partitioned between diethyl ether and water. The ether layer was separated, dried over anhydrous magnesium sulfate, and filtered. The ether was removed on a Rotavap to leave a residue which was then heated to 240–300 °C at 43 mm pressure while a white-yellow solid distillate (45.3 g, 79%) was collected, bp 210–215 °C (43 mm). The solid was purified by eluting it through an 18-in. column of silica gel with chloroform as the solvent. The first elutions were placed on a Rotavap to remove the solvent. The white solid material thus obtained had mp 69–71 °C. After the material was zone refined, mp 71–72 °C was obtained. The infrared spectrum showed bands at 3100–3300 (m), a series of weak bands 1950–1560, 1445 (m), 1410 (m), 1120 (m), 1080 (m), 1050 (m), 1020 (m), 908 (m), 893 (m), 830 (s), 813 (s), 762 (s), 721 (s), and 690 cm^{-1} (s). The NMR spectrum (CCl_4) showed absorptions at δ 7.55–7.07 (m, 7 H), 6.93 (d, 2 H, J = 8 Hz), 2.07–1.57 (m, 1 H), 1.10–0.50 (m, 4 H).

Anal. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.28; H, 7.30.

ω-Dimethylamino-*m*-bromopropiophenone hydrochloride was prepared by a procedure closely similar to that shown above for the *p*-chloro compound, but with the reflux period extended to 3 days. The yield of white crystals from methanol was 118.1 g (73%), mp 202.5–203.5 °C (lit.[7] mp 205 °C).

***m*-Bromophenylcyclopropane (3d).** ω-Dimethylamino-*m*-bromopropiophenone hydrochloride (118.1 g, 0.405 mol) was allowed to react with 18.0 g (0.45 mol) of sodium hydroxide in 700 ml of 95% ethanol. The precipitated sodium chloride was removed by filtration, and the filtrate was added dropwise during 1 h to a refluxing solution of 47.0 g (0.8 mol) of 85% hydrazine hydrate in 300 ml of 95% ethanol. Refluxing was continued for another 0.5 h, after which time ethanol was removed slowly by distillation. After most of the ethanol had been removed, the remaining mixture was filtered to remove undissolved salts. The filtrate was heated to temperatures of 200–300 °C with a Woods Metal bath while a distillation head and condenser were used to collect the product. The collection of product was begun at the approximate boiling point of hydrazine (120 °C). The material which was collected was partitioned between ether and water. The ether layer was dried over anhydrous sodium sulfate, subsequently filtered and concentrated by means of a Rotavap. A total of 50.6 g of crude product was obtained. The crude product was distilled at reduced pressure with collection of the product (35.6 g, 32.5%) at 87–88 °C (3 mm) [lit.[7] bp 98–100 °C (14 mm)]. The material appeared homogeneous by GC analysis on a 10 ft column of 20% SE-30 on Chromosorb P at 225 °C. The infrared spectrum showed bands at 3070 (m), 3000 (m), 1600 (s), 1570 (s), 1475 (s), 1455 (m), 1420 (m), 1225 (w), 1170 (w), 1095 (w), 1078 (m), 1053 (m), 1023 (m), 998 (m), 910 (s), 865 (w), 810 (m), 778 (s), and 687 cm^{-1} (s). The NMR spectrum (CCl_4) showed absorptions at δ 7.25–6.70 (m, 4 H), 2.05–1.58 (m, 1 H), 1.13–0.43 (m, 4 H).

Anal. Calcd for C_9H_9Br: C, 54.85; H, 4.60; Br, 40.55. Found: C, 54.65; H, 4.48; Br, 40.39.

***p*-Bromophenylcyclopropane (3c)** was prepared by the method of Levina.[19] To a stirred solution of 12.0 g (0.104 mol) of phenylcyclopropane in 200 ml of chloroform at −75 °C was added over 5 min 19.2 g (0.12 mol) of bromine. After 4 h, the mixture was washed with 200 ml of 10% aqueous sodium sulfite. The organic layer was added slowly (caution!) to a cooled solution of 0.2 mol of sodium ethoxide in absolute ethanol. The resulting solution was refluxed for 1.5 h, and the solvent was removed by a Rotavap. The residue was partitioned between ether and water. The ether layer was dried over anhydrous magnesium sulfate and distilled at reduced pressure to yield 17.1 g (83%) of a colorless liquid (bp 102–106 °C, 9 mm; mp 14 °C) [lit.[19] bp 116 °C (15 mm); mp 15 °C)]. The product was subjected to VPC on a 15 ft × 0.25 in. o.d. column of 5% SE-30 on Chromosorb P at 200 °C with a flow rate of 50 ml/min. Under these conditions only one peak was observed. The infrared spectrum showed bands at 3070 (w), 3000 (w), 1485 (s), 1454 (w), 1403 (w), 1225 (w), 1173 (w), 1100 (m), 1073 (s), 1045 (m), 1008 (s), 900 (m), 815 (s), 744 (m), and 707 cm^{-1} (w). The NMR spectrum (no solvent, only Me_4Si added) showed absorptions at δ 7.18 (d, 2 H, J = 8.3 Hz), 6.67 (d, 2 H, J = 8.3 Hz), 1.88–1.39 (m, 1 H), 1.03–0.31 (m, 4 H).

***p*-Iodophenylcyclopropane (3e).** A solution of 40.0 g (0.202 mol) of *p*-bromophenylcyclopropane in 100 ml of dry tetrahydrofuran was added dropwise to a refluxing, stirred suspension of 9.8 g (0.4 g-atom) of magnesium turnings in 200 ml of dry tetrahydrofuran under a nitrogen atmosphere. The mixture was allowed to cool and stirred for 2.5 h, after which a solution of 51 g (0.2 mol) of iodine in 100 ml of tetrahydrofuran was added slowly. The addition was terminated when an iodine color persisted. The mixture was filtered to remove precipitated salts and unreacted magnesium. The filtrate was then extracted with 10% aqueous sodium thiosulfate to remove unreacted iodine. The organic layer was dried over anhydrous magnesium sulfate and filtered. Most of the solvent was removed on a Rotavap. GC analysis of the remaining material was done using a 6 ft × 0.25 in. o.d. column of 25% SE-30 on 60/80 Firebrick at 200 °C and a flow rate of 60 ml/min. A ratio of *p*-bromophenylcyclopropane to some higher boiling component was found to be 14:154. Thus, 92% conversion of *p*-bromophenylcyclopropane was obtained. The product was purified by distillation at reduced pressure, followed by zone refining. A white, crystalline solid (bp 99 °C, 2.4 mm; mp 46–47 °C) was obtained. The infrared spectrum showed bands at 3030 (w), 2970 (m), 1895 (w), 1640 (w), 1480 (m), 1445 (m), 1418 (m), 1395 (s), 1360 (m), 1340 (m), 1220 (w), 1170 (w), 1115 (m), 1098 (s), 1045 (s), 1018 (s), 1003 (m), 900 (s), 812 (s), 738 (w), and 705 cm^{-1} (m). The NMR spectrum (CCl_4) showed absorptions at δ 7.40 (d, 2 H, J = 8.3 Hz), 6.66 (d, 2 H, J = 8.3 Hz), 2.00–1.48 (m, 1 H), 1.10–0.37 (m, 4 H).

Anal. Calcd for C_9H_9I: C, 44.28; H, 3.72; I, 51.99. Found: C, 44.16; H, 3.70; I, 51.57.

***p*-Cyanophenylcyclopropane (3f).** To a stirred suspension of 10.6 g (0.118 mol) of cuprous cyanide in 35 ml of pyridine at 165 °C was added dropwise 16.0 g (0.0812 mol) of *p*-bromophenylcyclopropane. After 48 h at 165 °C the reaction mixture was distilled directly from the flask at reduced pressure. The crude product mixture was analyzed by VPC on a 3 ft × 0.25 in. o.d. column of 25% SE-30 on 60/80 Firebrick at 230 °C with a flow of 50 ml/min. Three components were observed to be present. The two peaks with lowest retention times had retention times the same as those of pyridine and *p*-bromophenylcyclopropane. A careful distillation of the mixture yielded 6.6 g (56%) of a clear liquid (bp 118 °C, 5 mm) [lit.[7] bp 150 °C (14 mm)] [lit.[20] bp 84 °C (1–2 mm)]. This material was found to be homogeneous by VPC analysis under the conditions mentioned above. The infrared spectrum (NaCl plates) showed bands at 3070 (w), 3000 (m), 2225 (s), 1610 (s), 1510 (m), 1460 (m), 1415 (m), 1225 (m), 1185 (m), 1175 (m), 1115 (m), 1048 (s), 1022 (m), 900 (s), and 828 cm^{-1} (s). The NMR spectrum (CCl_4) showed absorptions at δ 7.42 (d, 2 H, J = 8.3 Hz), 7.07 (d, 2 H, J = 8.3 Hz), 2.15–1.67 (m, 1 H), 1.25–0.53 (m, 4 H).

Anal. Calcd for $C_{10}H_9N$: C, 83.88; H, 6.33; N, 9.78. Found: C, 83.65; H, 6.34; N, 9.67.

***p*-Nitrophenylcyclopropane (3g).** *p*-Nitrophenylcyclopropane was obtained from the nitration of phenylcyclopropane.[20,21] Phenylcyclopropane (35 g, 0.23 mol) was dissolved in 150 ml of acetic anhydride. The temperature was lowered to −40 °C, and 40 ml of nitric

acid was added in a dropwise manner. The mixture was stirred for 0.5 h at −40 °C and poured into hot water (Caution—do not allow the temperature of the reaction mixture to rise above −20 °C until it is added to water!). The resulting mixture was extracted with ether, and the organic layer was dried over anhydrous magnesium sulfate. The solvent was removed by means of a Rotavap. VPC analysis on a 3 ft × 0.25 in. o.d. column of 25% SE-30 on 60/80 Firebrick at 200 °C with a flow rate of 85 ml/min showed two major components with retention times of 2.45 and 3.65 min. The peak integrations were 4.1 and 1.0, respectively. Phenylcyclopropane had a retention time of 0.65 min. The two components were separated by preparative VPC under conditions similar to those listed above. The component with a retention time of 2.45 min was identified as *o*-nitrophenylcyclopropane. The compound with a retention time of 3.65 min was identified as the para isomer. The ortho–para isomer mixture was distilled carefully at reduced pressure through a 20-in. column of glass helices. A total of 19 separate fractions were taken. The separation of the two isomers was not entirely clean. *o*-Nitrophenylcyclopropane (with less than 3% of the para isomer as an impurity) had a boiling point of 105 °C, 1.7 mm [lit.[20] bp 99–100 °C (3 mm)]. The infrared spectrum of *o*-nitrophenylcyclopropane (NaCl plates) showed bands at 3070 (m), 2990 (m), 1680 (m), 1610 (m), 1520 (s), 1345 (s), 1280 (m), 1030 (m), 903 (m), 852 (s), 784 (s), 744 (s), and 704 cm^{-1} (m). The NMR spectrum of *o*-nitrophenylcyclopropane (CCl_4) showed absorptions at δ 7.81–7.05 (m, 4 H), 2.60–2.08 (m, 1 H), 1.20–0.50 (m, 4 H).

p-Nitrophenylcyclopropane (with less than 3% of the ortho isomer as an impurity) had a boiling point of 123 °C 1.5 mm [lit.[20] bp 100–115 °C (3 mm)]. The *p*-nitrophenylcyclopropane thus obtained was zone refined continuously for 1 week. A melting point of 31 °C (lit.[20] mp 30–31 °C) was obtained. The infrared spectrum (NaCl plates) showed bands at 3060 (m), 2990 (m), 1600 (s), 1510 (s), 1435 (m), 1340 (s), 1267 (m), 1230 (m), 1185 (m), 1104 (s), 1050 (s), 897 (s), 857 (s), 823 (m), 783 (m), 745 (s), and 694 cm^{-1} (m). The NMR spectrum (CCl_4) showed absorptions at δ 7.97 (d, 2 H, J = 9 Hz), 7.08 (d, 2 H, J = 9 Hz), 2.21–1.72 (m, 1 H), 1.33–0.60 (m, 4 H).

Anal. Calcd for $C_9H_9NO_2$: C, 66.24; H, 5.56; N, 8.58. Found: C, 65.97; H, 5.64; N, 8.43.

Bromination of Substituted Phenylcyclopropanes at 20 °C in the Dark. To a solution of 2.5 mmol of a substituted phenylcyclopropane in 40 ml of carbon disulfide at 20 °C in the dark was added 2.5 mmol of bromine in 10 ml of carbon disulfide. After the desired reaction time, 7.5×10^{-3} mol of sodium thiosulfate dissolved in 20 ml of water was added. The reaction mixture was maintained in the dark until all bromine color had disappeared. Carbon tetrachloride (30–40 ml) was added to the mixture, and the organic layer was removed and dried over anhydrous $MgSO_4$. The solution was then filtered and solvent removed on a Rotavap. NMR spectra of the residues were taken using CCl_4 as a solvent and Me_4Si as a reference. The phenylcyclopropanes used and the lengths of the bromination reactions were **1** (60 min), **3a** (60 min), **3b** (120 min), **3c** (120 min), **3d** (30 min), **3e** (120 min), **3f** (180 min), and **3g** (180 min). Only **3a** and **3b** produced detectable amounts of **4**, in 22.5 and 3.3% yields, respectively. The ^1H NMR spectrum of **4a** showed signals at δ 5.10 (doublet of doublets, 1 H), 3.5–3.15 (m, 2 H), and 2.75–2.25 (m, 2 H). The spectrum of **4b** showed similar multiplets at δ 5.05, 3.45–3.1, and 2.7–2.25.

NMR Spectra of the Photochemical Bromine Adducts of Phenylcyclopropanes. A substituted phenylcyclopropane was dissolved in carbon disulfide. The solution was stirred and was maintained at 20 ± 2 °C by means of a cold water bath. The solution was irradiated by means of a 275-W GE sunlamp through a glass wall of the water bath. A solution of bromine in carbon disulfide was added, and the reaction was allowed to proceed until the solution decolorized or until the desired time interval had elapsed. The solvent was then removed by means of a Rotavap. In those cases where the solution was not fully decolorized, the remaining bromine was removed with the solvent on the Rotavap. The rate of solvent removal on the Rotavap was regulated so that the flask remained cold. NMR spectra were taken of the residues.

NMR spectrum of the alkyl protons in 1-(4-biphenyl)-1,3-dibromopropane (**4a**) (CS_2): δ 4.98 (doublet of doublets, 1 H), 3.45–3.00 (m, 2 H), 2.7–2.1 (m, 2 H). 1,3-Dibromo-1-phenylpropane (**2**) (CS_2): δ 7.17 (s, 5 H), 5.05 (doublet of doublets, 1 H), 3.65–3.00 (m, 2 H), 3.00–1.80 (m, 2 H). 1-(*p*-Chlorophenyl)-1,3-dibromopropane (**4b**) (CS_2): δ 7.17 (s, 4 H), 5.05 (doublet of doublets, 1 H), 3.65–3.10 (m, 2 H), 3.00–1.80 (m, 2 H). 1-(*p*-Bromophenyl)-1,3-dibromopropane (**4c**) (CS_2): δ 7.30 (d, 2 H, J = 8.5 Hz), 7.15 (d, 2 H, J = 8.5 Hz), 5.03 (doublet of doublets, 1 H), 3.75–3.00 (m, 2 H), 3.00–1.80 (m, 2 H). 1,3-Dibromo-1-(*p*-iodophenyl)propane (**4e**) (CCl_4): δ 7.70 (d, 2 H, J = 8.5 Hz), 7.17 (d, 2 H, J = 8.5 Hz), 5.15 (doublet of doublets, 1 H), 3.85–3.25 (m, 2 H), 2.90–2.20 (m, 2 H). Alkyl protons in 1-(*m*-bromophenyl)-1,3-dibromopropane (**4d**) (CS_2): δ 4.96 (doublet of doublets, 1 H), 3.65–3.00 (m, 2 H), 2.95–2.10 (m, 2 H). 1-(*p*-Cyanophenyl)-1,3-dibromopropane (**4f**) (CS_2): δ 7.58 (s, 4 H), 5.23 (doublet of doublets, 1 H), 3.70–3.30 (m, 2 H), 2.85–2.35 (m, 2 H). Alkyl protons on 1,3-dibromo-1-(*p*-nitrophenyl)propane (**4g**) (CCl_4): δ 5.28 (doublet of doublets, 1 H), 3.75–3.40 (m, 2 H), 2.95–2.45 (m, 2 H).

Inhibition of the Photobromination of Phenylcyclopropane. Three simultaneous photobrominations were carried out. Flask A contained a carbon disulfide solution which was 0.05 M in phenylcyclopropane. Flask B contained a carbon disulfide solution which was 0.05 M in phenylcyclopropane and 0.025 M in nitrobenzene. Flask C contained a carbon disulfide solution which was 0.05 M in phenylcyclopropane and 0.025 M in isoamyl nitrite. All three flasks were the same size and contained the same volume of solution. The flasks were immersed in a bath at 20 ± 2 °C. The bath contained water and had Pyrex glass walls. Bromine (0.54 equiv for each equivalent of phenylcyclopropane) was quickly added to each flask in the dark. A 275-W GE sunlamp was positioned such that the distance to each flask was the same. Both flask A and flask B decolorized in less than 7 min of irradiation. Flask C did not decolorize after 1 h of irradiation with the sunlamp.

Bromination of *p*-Chlorotoluene in the Dark at 20 °C in Carbon Disulfide. A carbon disulfide solution of *p*-chlorotoluene was treated with bromine in the dark for 1 h. The reaction procedure was the same as that for the bromination of substituted phenylcyclopropanes in the dark (above). A 60-MHz NMR spectrum of the product was identical with that of starting material.

Photobromination of *p*-Chlorotoluene in Carbon Disulfide at 20 °C. A carbon disulfide solution which was 0.05 M in *p*-chlorotoluene and 0.04 M in bromine was stirred and maintained at 20 ± 2 °C. The solution was illuminated with a sunlamp through the Pyrex flask. After 30 min of illumination the bromine color had disappeared. The carbon disulfide solvent was removed by means of a Rotavap, and a 60-MHz NMR spectrum of the product mixture was taken (CS_2 solvent). The methyl group of the unreacted *p*-chlorotoluene appeared at δ 2.27, the methylene group of *p*-chlorobenzyl bromide appeared at δ 4.32, and the methine proton of *p*-chlorobenzal bromide appeared at δ 6.45.

Control Study of Possible HBr–Bromine Reaction of Phenylcyclopropane at 20 °C in the Dark. To a solution of 81 ml of 0.157 M hydrogen bromide in carbon disulfide (12.7 mmol HBr in solution) at 20 °C was added 5.0 mmol of bromine in 14 ml of carbon disulfide. The mixture was stirred and 0.59 g (5.0 mmol) of phenylcyclopropane was added in the dark. After 1 h, 15 mmol of sodium thiosulfate dissolved in 40 ml of water was added. The reaction mixture was maintained in the dark until the bromine color was discharged. Carbon tetrachloride (70 ml) was added and the organic phase was removed and dried over anhydrous magnesium sulfate. The solution was filtered and the solvent removed on a Rotavap. The NMR of the crude product in carbon disulfide showed resonances for phenylcyclopropane only. None of the ring-opened product was observed. Some sulfur was formed in the dark reaction.

Control Study of Possible Reactions of Phenylcyclopropanes with Hydrogen Bromide. Phenylcyclopropane (0.295 g, 2.5×10^{-3} mol) was dissolved in 49 ml of 0.128 N hydrogen bromide in carbon disulfide (a total of 6.3×10^{-3} mol of HBr in solution). The solution was irradiated for 10 min at 20 °C with a 275-W GE sunlamp. The carbon disulfide solvent was removed by means of a Rotavap, and an NMR spectrum was taken of the residue. The NMR spectrum was identical with that of phenylcyclopropane, and no other peaks were observed.

p-Cyanophenylcyclopropane (1.25×10^{-3} mol) was dissolved in 24.0 ml of 0.057 M HBr in CS_2. The solution was maintained at 20 °C and illuminated with a sunlamp for 20 min. After removal of the solvent on a Rotavap, an NMR spectrum showed the residue to be *p*-cyanophenylcyclopropane.

Competitive Brominations of Substituted Phenylcyclopropanes. Approximately 2.5×10^{-3} mol of *p*-chlorotoluene and 2.5×10^{-3} mol of the desired substituted phenylcyclopropane were weighed into a 100-ml Pyrex round-bottom flask. In the bromination of *p*-nitrophenylcyclopropane, 5.0×10^{-3} mol of *p*-nitrophenylcyclopropane and 2.5×10^{-3} mol of *p*-chlorotoluene were used. In the bromination of *p*-phenylphenylcyclopropane, 1.25×10^{-3} mol of *p*-phenylphenylcyclopropane and 2.5×10^{-3} mol of *p*-chlorotoluene were used. A Teflon coated stirring bar was placed in the flask along with 47 ml of carbon disulfide. The flask was immersed in a water bath at 20 ± 2 °C, and the solution was stirred by means of a magnetic stirrer. The flask was illuminated through the water bath with a 275-W GE sunlamp. A 1.0 M solution of bromine in carbon disulfide (2.0 ml) was added. For the bromination of *p*-phenylphenylcyclopropane, only

1.0 ml of the bromine solution was added. Illumination and stirring were continued until the bromine color disappeared. The lengths of time required to decolorize bromine in the competitive brominations p-C_6H_5, H, p-Cl, p-Br, p-I, m-Br, p-CN, and p-NO_2 were approximately 3, 4, 5, 9, 7, 10, 20, and 30 min, respectively.

The Teflon stirring bar was removed, and the flask was placed on a Rotavap to remove excess carbon disulfide solvent. The rate of solvent removal was regulated such that the flask remained cold to the touch throughout the removal of solvent. Solvent removal was terminated when 2–5 ml of the solvent remained in the flask. A sample of the reaction mixture was added to an NMR tube along with 2 drops of 50% tetramethylsilane. A 60-MHz NMR spectrum of the product mixture was taken. All peaks except those in the aromatic region were integrated three times. The integral amplitude was adjusted so that the largest peak grouping integrated nearly full scale on the chart paper.

Each NMR spectrum consisted of the following groupings of peaks: aromatic absorptions δ 8.2–6.8 (A_1); the benzylic proton of the ring-opened dibromide, doublet of doublets, δ 4.9–5.2 (A_2); the methylene protons of p-chlorobenzyl bromide, singlet, δ 4.3–4.4 (A_3); the terminal methylene group of the ring-opened dibromide, δ 3.0–3.7 (A_4); the central methylene protons of the ring-opened dibromide plus a methyl absorption for unreacted p-chlorotoluene plus the benzylic proton of unreacted substituted phenylcyclopropane, δ 3.1–1.4 (A_5); the methylene protons of unreacted substituted phenylcyclopropane, δ 1.3–0.4 (A_6). In the competitive brominations of p-nitrophenylcyclopropane vs. p-chlorotoluene, small amounts of p-chlorobenzal bromide were produced with singlet absorption at δ 6.5–6.6 (A_7).

Values of log (k_2/k_1) were calculated from the relationship

$$\log k_2/k_1 = \log \left[\log \frac{(y - B)}{y} \Big/ \log \frac{(x - A)}{x} \right]$$

where k_2 is the rate constant for bromination of the phenylcyclopropane (y) and k_1 is the rate constant for bromination of p-chlorotoluene (x). B and A are the respective amounts of y and x consumed in the reaction. The relative values of the quantities in the equation are related to the NMR integrals by the relations $y - B = A_6/4$; $y = A_6/4 + A_2$:

$$x - A = (A_5 - A_4 - A_6/4)/3$$
$$x = (A_5 - A_4 - A_6/4)/3 + A_7 + A_3/2$$

Five artificial reaction mixtures were prepared using known quantities and subjected to the analysis. In each case, the calculated log k_2/k_1 was well within the statistical error of the theoretical value.

Competitive Brominations of Substituted Toluenes. The same procedure as used for the competitive brominations of phenylcyclopropanes was employed, with p-cyanophenylcyclopropane as the constant competitor.

Registry No.—**1,** 873-49-4; **2,** 17714-42-0; **3a,** 35076-77-8; **3b,** 1798-84-1; **3c,** 1124-14-7; **3d,** 1798-85-2; **3e,** 57807-27-9; **3f,** 1126-27-8; **3g,** 6921-44-4; **4a,** 58873-50-0; **4b,** 19714-76-2; **4c,** 58873-51-1; **4d,** 58873-52-2; **4e,** 58873-53-3; **4f,** 58873-54-4; **4g,** 58678-85-6; ω-dimethylamino-p-chloropropiophenone hydrochloride, 1798-83-0; ω-dimethylamino-p-phenylpropiophenone hydrochloride, 5409-63-2; dimethylamine hydrochloride, 506-59-2; p-phenylacetophenone, 92-91-1; ω-dimethylamino-m-bromopropiophenone hydrochloride, 2192-15-6; m-bromoacetophenone, 2142-63-4; o-nitrophenylcyclopropane, 10292-65-6; p-chlorotoluene, 106-43-4.

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X-Ray Crystal Structure Analysis of Triquinacene at 90 K

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The crystal structure of the $C_{10}H_{10}$ hydrocarbon triquinacene, whose three multiply fused cyclopentene rings adopt an unusual cup-shaped geometry having pπ orbitals projected toward the center of the concave face, has been determined at 90 K from three-dimensional x-ray counter data. A crystal grown in a stream of cold nitrogen gas was found to have space group $R\bar{3}$ and a (hexagonal) unit cell of a = 7.272 (5) Å and c = 23.557 (13) Å, with six molecules per cell. The structure was refined using 484 unique reflections with $I > 3\sigma_I$ to a final conventional R factor of 0.052. The molecule has nearly ideal C_{3v} symmetry but, because of packing considerations, only a threefold axis is utilized in the crystalline state.

Homoaromatic character is thought to be present in several cationic and anionic species having one or two homoconjugate linkages.[2,3] Comparable properties have not been uncovered in neutral molecules, presumably because the driving force underlying charge dissipation is no longer present to encourage electronic delocalization, at least to the same extent. As concerns possible neutral six-electron homoaromatic analogues of benzene, the four hydrocarbons **1–4** have commanded recent attention. Two of these, *cis,cis,cis*-1,4,7-cyclononatriene (**2**)[4] and triquinacene (**3**),[5] have three