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Cyclopropane Ring Opening by Photolytically Generated Bromine Atoms

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Bromine atoms, generated by irradiation by a mercury lamp bearing a filter to assure that only wavelengths >310 nm passed, were permitted to react with a series of 1,2-diarylcyclopropanes in carbon tetrachloride solution. The major product in all cases (>80%) was the 1,3-dibromo-1,3-diarylpropane. Kinetic data at approximately 10^{-3} M gave a rate expression $dBr_2/dt = -k(\text{cyclopropane})(\text{bromine})^{1/2}$. A Hammett treatment of the data gave $\rho = -0.5$ for both the cis series and the trans series. Synthesis of several possible minor products and their comparison with the reaction mixture by TLC is reported. Possible reactions such as induced isomerization are thus eliminated from consideration.

The addition of halogens to cyclopropanes to give ring opening products is generally accepted as one of the unusual properties of the three-membered ring. In studies of the 1,2-diphenylcyclopropanes and phenylcyclopropane with bromine, LaLonde[2] delineated three reaction modes: type A, photocatalyzed, nonpolar solvents, free-radical-like ring opening; type B, electrophilic ring opening; and type C, aromatic substitution. This paper addresses itself to type A reactions in the 1,2-diarylcyclopropane series.

Results

It is important to assure that the reactions which we have studied were the same as those that LaLonde observed. Our work was aimed at determining something about the reaction's sensitivity to electron density of the cyclopropane ring and, hence, used a number of compounds not used in LaLonde's work. We shall return to examine those that do overlap after considering the general character of our study.

We synthesized a series of 1,2-diarylcyclopropanes by standard methods[3,4] and characterized them by elemental analysis, molecular weights, and spectral examinations (cf. Table I).

Carbon tetrachloride solutions of these compounds were subject to irradiation from a medium-pressure mercury arc (GE-AH-4) equipped with a Corning no. 5031 filter. This filter was effective below 310 nm as seen by the failure of this assembly to expose any malachite green leucocyanide after 1 hr of irradiation.

Irradiation of the carbon tetrachloride solutions of the cyclopropanes in the absence of bromine gave no rearrangement or ring opening products after several hours with this system. Mixtures of the cyclopropane solutions with equimolar bromine under dark conditions showed no detectable reaction after 48 hr. For reference, the photochemical studies were 90% complete on the order of 120 min.

The reaction was shown to utilize 1 mol of bromine per mole of cyclopropane and to produce no HBr, except in the cases of the *p*-methyl and *p*-dimethylamino compounds which were not included in the kinetic study as a result.

Major products were isolated by chromatography and characterized by spectral means. In two cases, *p*-chloro and unsubstituted, the 1,3-diaryl-1,3-dibromopropanes were synthesized and the compounds compared with the isolated material and with the TLC and GLC of the reaction mixtures. Several minor product candidates, 1,2-diphenyl-1,3-dibromopropane, 1,3-diphenyl-1,2-dibromopropane, and 1,3-diphenylpropene, were synthesized and found to be absent from the appropriate crude product mixture. The minor products remain unknown as their molecular weight and elemental analyses were quite variable and their mobility and volatility in chromatography were very low. Polymers or polyhalogenated by-products are likely.

Is the reaction we have studied the same as that of LaLonde?

We believe that it is for several reasons. The 1,2-diphenylcyclopropane cases studied by us at room temperature have nearly identical yields of 1,3 products [90% (isolated) vs. 100% "crude"] and the meso/*dl* ratios measured in the NMR are similar (trans, 52:48 vs. 62:38; cis, 57:43 vs. 41:59) but our reaction times were much shorter and activated species of higher concentration. All of the conditions of reaction and the rest of the data collected are essentially the same within experimental error.

Our comparative kinetic studies were made on a total of 42 runs (plus some used to establish the best instrumental parameters, etc.). Concentration dependence studies were run on the 1,2-diphenylcyclopropanes using GLC to check the spectrophotometric results in a few cases in order to

Table I
Physical Properties of the Substituted Cyclopropanes

Compd	Bp, °C (Torr)	$n^{25}D$	Uv λ_{max} nm	Uv ϵ_{max}	NMR, ppm	Ref	Registry no.
trans-1,2-Diphenylcyclopropane	115–118 (1)	1.5987			2.10 (m), 1.28 (m), 7.05 (m)	10, 3a, 6	1138-47-2
cis-1,2-Diphenylcyclopropane	73 (0.25)	1.5925	220	1.6×10^4	2.38 (m), 1.34 (m), 6.96 (m)	3a, 6, 9	1138-48-3
trans-1-*p*-Methylphenyl-2-phenylcyclopropane	142–146 (0.6)[b]	1.5895	(EtOH) 234	2.19×10^4	1.28 (m), 2.05 (m), 7.00 (m), 2.28 (s)	*a*	56363-35-0
cis-1-*p*-Methylphenyl-2-phenylcyclopropane	94–95 (0.1)	1.5808	223	1.78×10^4	1.22 (m), 2.22 (m), 6.82 (m), 2.05 (s) (2:2:9:3)	*a*	56363-36-1
trans-1-*p*-Chlorophenyl-2-phenylcyclopropane		1.6066	(EtOH) 236	2.58×10^4	1.30 (m), 2.11 (m) 7.09 (m) (2:2:9)	*a*	56363-37-2
cis-1-*p*-Chlorophenyl-2-phenylcyclopropane		1.5951	225	1.55×10^4	1.30 (m), 2.32 (m), 6.95 (m) (2:2:9)	*a*	2001-61-8
trans-1-*m*-Chlorophenyl-2-phenylcyclopropane		1.6062	233	2.28×10^4	1.28 (m), 2.00 (m), 7.08 (m) (2:2:9)	*a*	56363-38-3
cis-1-*m*-Chlorophenyl-2-phenylcyclopropane	96–98 (0.5)	1.5925	(EtOH) 216	1.94×10^4	1.37 (m), 2.40 (m), 6.92 (m) (2:2:9)	*a*	56363-39-4
trans-1-*p*-Fluorophenyl-2-phenylcyclopropane	130 (1.3)	1.5779	(EtOH) 230	1.73×10^4	1.30 (m), 2.00 (m) 7.00 (m) (2:2:9) 118.4 (m) ($CFCl_3$)	8	1611-89-8
cis-1-*p*-Fluorophenyl-2-phenylcyclopropane	125 (1.3)	1.5655	(EtOH) 220	1.46×10^4	1.30 (m), 2.31 (m), 6.90 (m) (2:2:9) 117.9 (m) ($CFCl_3$)	*a*	1611-88-7
trans-1-*p*-Methoxyphenyl-2-phenylcyclopropane	mp 78.5–79.5		(EtOH) 232	1.98×10^4	1.32 (m), 2.10 (m), 7.0 (m), 3.75 (s) (2:2:9:3)	*a*, *c*	34221-26-6
cis-1-*p*-Methoxyphenyl-2-phenylcyclopropane	141 (0.45)	1.5885	229	1.14×10^4	1.28 (m), 2.31 (m), 6.78 (m), 3.45 (s) (2:2:9:3)	*a*	53400-00-3
trans- + *cis*-1-(*p*-dimethylaminophenyl)-2-phenylcyclopropane	145–147° (0.2)	1.6140			1.28 (m), 2.03 (m), 7.10 (m), 2.76 (s) and 1.30 (m), 2.30 (m), 6.55 (m), 2.69 (m)	*a* *b*	56363-40-7 56363-41-8

[a] Elemental analysis agreed within less than 0.08 in carbon, 0.09 in hydrogen, and (as appropriate) 0.19 in chlorine and 0.19 in fluorine. [b] Cis about 15% of the mixture. [c] Mol wt 223.

guarantee that the cyclopropane was being used up at the same rate as the bromine. Each of the runs was found to fit the appropriate three-halves order expression. Further support for this comes from plotting the appropriate functions for the integrals of the three-halves order. Invariably the plot was linear and gave excellent integral fit regardless of the relative concentration relationship. The correlation coefficient from a linear regression analysis (R) obtained for each run ranged from 0.999993 to 0.992670 with an average of 0.9981 for plots of the appropriate arctangent and ln terms when the concentrations were not equimolar.

Our studies of relative rates for use in the Hammett treatment varied enough from run to run to make the slope of the resultant curves at best approximate ($\rho = -0.5 \pm 0.1$ for both cis and trans).

Approximate data on the effect of the intensity of the light was obtained by assuming normal radial dependence and changing the path length to the reaction cells. The rate was found to be proportional to the light intensity to a fractional power (0.4–0.7), a range that seems to agree fairly well with the theoretically half-order value for two bromine atom chain carriers.

Quantum yields using a cinnamic acid–bromine actinometer were obtained. Unfortunately, the value for the actinometer seems to be in dispute[5] but, as an order of magnitude, the value for the cyclopropane reaction appears to be about 100.

Experimental Section

Preparation of 1,2-Phenyl-Substituted Cyclopropanes. All of the cyclopropanes used in this study were prepared by the pyrolysis of the corresponding 1- or 2-pyrazoline. Only the *p*-chlorophenyl compound offered any difficulty with respect to the stability of the intermediate heterocycle but all of these compounds were used as soon as possible after isolation as they formed intractable tars on standing. In the *p*-chlorophenyl case the 1-pyrazoline failed to give the desired cyclopropane but the 2-pyrazoline did so if the pyrolysis reaction was not delayed after isolation of the nitrogen compound.

The preparation of the 1-pyrazoline was carried out by the treatment of styrene with the appropriately substituted phenyldiazomethane.[3] Pyrolysis gave trans cyclopropanes.

The 2-pyrazolines were prepared from the corresponding chalcones (1,3-diphenylpropenones) and hydrazine.[4] Pyrolysis gave mixtures of cis and trans cyclopropanes (Table I). Isomers were separated by distillation through a 20-plate spinning band column.

Preparation of the 1,3-Diphenylpropenes. 1,3-Diphenyl-2-propanol was prepared by the $LiAlH_4$ reduction of dibenzyl ketone. After work-up, the crude alcohol was distilled (2 Torr) through an 18-in. alumina column maintained at 330°C by a furnace. The resulting distillate was fractionated to give a 78% yield of olefin. Fractions were identified as cis or trans by GLC on Carbowax 20M at 250°C where the mixed olefin was found resolvable.

Products were characterized by boiling point, refractive index, uv, ir, and NMR spectra, and elemental analysis.

Preparation of 1,2-Dibromo-1,3-diphenylpropane. To a solution of 1.0 g (0.005 mol) of *trans*-1,3-diphenylpropene in 10 ml of CCl_4 was added 0.05 mol of Br_2 until the color persisted for 30 min. No HBr was noted.

Separation of the product and recrystallization from benzene gave mp 105–107°C (lit.[11] 111–112°C); ir 2915, 2838, 590, 560, 510 cm^{-1}; NMR multiplets centered at 3.18, 3.83, 4.59, 5.00 ppm and an unsymmetric doublet centered at 7.23 ppm.

Preparation of 1,3-Dibromo-1,3-diphenylpropane. 1,3-Diphenyl-1,3-propanediol was prepared as reported by Zimmerman.[12]

The product recrystallized from benzene melted at 129–130°C (lit.[12] 128–130°C) and showed broad OH absorption at 3350 cm^{-1}.

To 2.7 g (0.012 mol) of 1,3-diphenyl-1,3-propanediol in 25 ml of heptane was added 12 g of PBr_3. The system was warmed gently until a single phase was formed. After standing for 1 hr a syrupy phase appeared from which the heptane layer was decanted. After about half of the heptane had been evaporated, the solution was streaked on two 20 × 20 cm, 1 mm thick silica gel H plates and developed with a 2:1 benzene–heptane solvent. The edges of the plate were developed with formaldehyde and sulfuric acid. The untreated portion between the colored spots that appeared was shaved off and washed with ethyl ether, and the ether was evaporated. A nearly colorless viscous oil remained which had the following physical constants: ir 2910, 2840, 1260, 695 (doublet), 600 cm^{-1}; NMR multiplets at 2.90, 4.80, 5.12 ppm and a singlet at 7.26 ppm.

Anal. Calcd for $C_{15}H_{14}Br_2$: C, 50.88; H, 3.98; Br, 45.14. Found: C, 50.97; H, 3.78; Br, 45.09.

Preparation of 1-*p*-(Chlorophenyl)-3-phenyl-1,3-dibromopropane. By the analogous route to that used for the unsubstituted compound, the title compound was prepared and isolated.

Its physical properties were: oil, ir 2920, 2860, 725, 695, and 645 cm^{-1}. The compound was quite unstable and both the NMR and elemental analysis indicated that some decomposition had occurred during shipping.

Anal. Calcd for $C_{15}H_{13}ClBr_2$: C, 46.37; H, 3.37; Br, 41.13. Found: C, 51.53; H, 3.82; Br, 35.73.

Preparation of 1,2-Diphenyl-1,3-propanediol. The basic carbon structure was established by a Reformatsky reaction between ethyl 2-bromo-2-phenylethanoate and benzaldehyde.[13] The alcohol was prepared by the lithium aluminum hydride reduction of the keto ester. This compound was a thick, viscous gum which could not be induced to crystallize: lit.[13] mp 112°C (erythro), 115–118°C (threo). Other properties were ir 3350, 3080, 3060, 3030, 2940, 2870, 1620, 1510, 1475, 1200, 1030, 1010, 910, 850, 730, 690 cm^{-1}.

Comparison of Dibromides with the Photolysis Product. Treatment of 1,2-diphenylpropane-1,3-diol with PBr_3 in ether solution gave a dibromide which was resolvable from 1,3-diphenyl-1,3-dibromopropane when compared on 0.25-mm silica gel H thin layer chromatograms with 25% $HCCl_3$ in CCl_4 as the eluting solvent mixture.

When the photolysis products and the two dibromides were compared under these conditions with 2% formaldehyde–sulfuric acid as the developing reagent, no indication of the 1,2-diphenyl compound was found in the photolysis mixture. The two synthetic halides developed to different colors, had slightly different R_f values when separate (0.60 for the 1,3 vs. 0.55 for the 1,2), and could be seen in the presence of each other at 5% of the 1,2 in the presence of the 1,3.

Isolation of the Major Product from the Bromination Reaction. For both the cis and the trans of the cyclopropanes indicated, the following sequence was used.

The reaction was permitted to go to completion in the presence of excess bromine under room illumination. In all cases the bromine used up was found to correspond with the number of moles of cyclopropane present.

The solutions resulting from such treatment and those resulting from kinetic runs were subjected to TLC analysis.

Development of silica gel H plates with 2:1 to 3:1 benzene–heptane mixtures followed by development with 2% formaldehyde and sulfuric acid showed the disappearance of the spot characteristic of the cyclopropane and the appearance of three spots in each case. If the plates were heated slightly to aid the initial application of the solutions, other spots appeared in addition.

The major product was isolated either by column chromatography or by streaking a TLC plate (as above).

***cis*- and *trans*-1,2-Diphenylcyclopropane.** The major band amounted to 84.2% of the recovered product and was identical with 1,3-dibromo-1,3-diphenylpropane as described above in ir, NMR, and elemental analysis.

***cis*- and *trans*-1-(*p*-Chlorophenyl)-2-phenylcyclopropane.** The product from this reaction contained 89% of the 1,3-dibromo product which was identical with that prepared above in ir.

Anal. Calcd for $C_{15}H_{13}ClBr_2$: C, 46.37; H, 3.37. C, 47.91; H, 3.63.

***cis*- and *trans*-1-(*p*-Fluorophenyl)-2-phenylcyclopropane.** The products were the same and separation of the major products showed 95% of the 1,3-dibromo compound as seen by ir 2950, 2910, 2850, 590, 570 cm^{-1}; NMR multiplets at 2.90, 4.96, and 7.20 ppm.

Anal. Calcd for $C_{15}H_{13}Br_2F$: C, 48.51; H, 3.52; Br, 42.95. Found: C, 48.10; H, 3.44; Br, 43.19.

***cis*- and *trans*-1-(*p*-Methoxyphenyl)-2-phenylcyclopropane.** The products from this set of reactions contained 88% of a major product which had essentially identical ir spectra with the earlier 1,3 products with the addition of bands at 1628 and 590–570 (doublet) cm^{-1}; mol wt (by vapor pressure osmometer) 379 vs. 384 calculated; NMR showed mixture present. Attempts to countersynthesize the expected product gave a nearly identical mixture which could not be separated.

***cis*- and *trans*-1-(*m*-Chlorophenyl)-2-phenylcyclopropane.** The major product was 81% of the recovered material. Its properties were: mol wt (vapor pressure osmometer) 390, 380 calculated; ir 2970–2950 (doublet), 2900, 2850, 593, and 550 cm^{-1}; NMR multiplets centered at 2.90, 4.90, and 7.25 ppm.

Anal. Calcd for $C_{15}H_{13}Br_2Cl$: C, 46.37; H, 3.37; Br, 41.14. Found: C, 46.01; H, 3.38; Br, 41.17.

Kinetic Studies. The kinetic studies were of two types: studies carried out to measure the general form of the rate equation and studies to obtain relative rate data.

In the first type the rate data were obtained by use of a flow system in which the mixed solution was circulated before a Corning no. 5031 filter-equipped GE-AH-4 Hg lamp and through a DK-1A set at 5800 Å to permit the measurement of the rate of disappearance of Br_2. Except at these two points the system was in total darkness during irradiation because of a black felt blanket placed over the assembly.

The system was filled with the starting solution and circulated without irradiation. In no case was any indication of a change in the bromine concentration noted over a period of 30 min, the time characteristic of the reaction of the irradiated solutions. A series of runs with various of the substituted cyclopropanes was made in the concentration ranges of 0.5 to 0.003 *M* cyclopropane and 0.1 to 0.003 *M* in bromine. In all cases the flow system had a path length of 0.5 mm for the irradiating light.

The second type involved a comparative method in which 1-cm cuvettes were placed close together on the arc of a circle of radius 30.5 cm with the mercury lamp at the center. Periodically during irradiation, the mercury lamp was shuttered and the bromine concentration measured with a DU spectrometer set at 500 nm. The six cuvettes which were used contained initially the same bromine concentration and as nearly as possible the same concentrations of the various substituted cyclopropanes. During each run the cuvettes were rotated through the various sites to eliminate any bias from that source.

On duplicate runs, the variously substituted cyclopropanes were rotated through the various cuvettes to assure strictly comparable irradiation. Larger circles (radii of 35.5, 50.8, and 161 cm) were prepared in the same way and used to obtain qualitative data on the intensity dependence. All manipulations for these studies were carried out in total darkness aided by only a pen light except during actual irradiation.

The results obtained from these studies are summarized in Tables II and III.

Qualitative data about the quantum yield was obtained by the following experiments.

Five cuvettes containing the solution of interest were set into a slot cut in a short section of 2 × 4. The entire assembly was placed

Table II
Relative Rate Constants[a]

Substituent	Cis	Trans
H	1.00	1.00
p-Cl	0.81 ± 0.03	0.80 ± 0.04
m-Cl	0.75 ± 0.09	0.64 ± 0.03
p-F	0.93 ± 0.03	0.90 ± 0.04
p-OCH_3	1.5 ± 0.2	1.4 ± 0.2

[a] $k \cong 2.9 \times 10^{-4}$ $l.^{1/2}$ $mol^{-1/2}$ sec^{-1} for the unsubstituted case under the described experimental conditions (cf. Experimental Section).

under a small light-tight box equipped with an entrance opening of 1 × 6 cm which was lined up with the lamp and the cuvettes to provide a straight line as seen through a small hole at the back of the box. All interior surfaces were painted black.

In the first experiment all of the cuvettes were filled with an actinometer solution that was 0.05 *M* in bromine. The solution was the cinnamic acid–bromine system.[5]

Periodically the lamp was shuttered and the Br_2 concentration of each of the cuvettes measured with the DU spectrometer. All five cuvettes showed reaction occurring from the very beginning with the effect of the reduced intensity obvious.

In a like manner the first cuvette was filled with the substituted cyclopropane system at 0.05 *M* in both bromine and cyclopropane and the remaining cuvettes were filled with the cinnamic acid actinometer. The quantum yield calculated from comparison of the first and second cuvettes in each case indicated that the two reactions had similar quantum yields of about 10^2. Since the quantum yield of the actinometer seems, at best, to be approximately defined, an order of magnitude is all that one may hope to obtain. The use of uranyl oxalate in the wavelength region that is used for this reaction required such long irradiation times relative to those of the reaction under study that it is doubtful that such things as lamp variations would permit meaningful measurements to be made.

Charge Transfer Spectra. After LaLonde's report[2] of the charge transfer complex between Br_2 and phenylcyclopropane, which we confirmed, we examined some of the diarylcyclopropanes for similar complexes.

Scans were run from 310 to 420 nm for two conditions of relative concentration: 1:1 at ca. 5×10^{-4} *M* in both the cyclopropane and Br_2, and at 5×10^{-4} *M* in bromine and ca. 10^{-2} *M* in the cyclopropane. The value of the absorbance at 420 nm was used to generate the appropriate absorbance for bromine at other wavelengths. When the synthetic spectrum thus generated was subtracted from the measured spectrum the residue was taken as produced by the interaction of the cyclopropane and the bromine. Spectra run with the cyclopropane omitted and with the bromine omitted showed that the new absorption was not due to impurities, etc., in solvent or reactants. The region studied was limited by consideration of the effective range of the filter used in the kinetic studies.

The *cis*-diphenylcyclopropane initially showed a broad new absorption between 310 and 340 nm. Over 4–5 min in the dark this absorption increased and then died away. No reaction of the bromine was observed as measured by changes in its absorbance during this period. LaLonde's observations with the phenylcyclopropane case showed direct relation to bromine decline. Neither *trans*-diphenyl nor *trans*-*p*-methoxydiphenyl showed any absorbance in the scanned region.

Discussion

From our kinetic studies, it is clear that for these aryl cyclopropanes the rate expression in the concentration range of 3×10^{-3} to 5×10^{-2} *M* is first order in cyclopropane and half order in bromine.

Our data seem to fit a classical radical chain reaction best where product is 1,3-dibromo-1,3-diarylpropane.

$$Br_2 \xrightarrow[k_1]{h\nu} 2Br \quad (1)$$

$$Br + \text{cyclopropane} \xrightarrow{k_2} \text{radical} \quad (2)$$

$$\text{radical} + Br_2 \xrightarrow{k_3} \text{product} + Br \quad (3)$$

$$2Br \xrightarrow{k_4} Br_2 \quad (4)$$

$$\text{radical} + Br \xrightarrow{k_5} \text{product} \quad (5)$$

$$2 \text{ radical} \xrightarrow{k_6} \text{dimer} \quad (6)$$

If one assumes a nearly photosteady state with step 4 as the only significant termination step for the 10^{-3} *M* range, the rate expression fits the experimentally determined one.

Such a classical radical mechanism leads to prediction of certain properties for the reaction which a reading of the literature finds wanting or unusual.

The first question is the lack of significant competition from hydrogen abstraction rather than ring opening. The available literature on chlorine reactions under similar conditions shows that the abstraction process does compete when the energetically more favorable HCl is formed rather than HBr.[14,15]

Table III
Runs Representative of the Extremes in the Kinetic Runs (from a Total of 42 Runs)[a]

Substituent	Cyclopropane, mol/l. × 10^3	Bromine, mol/l. × 10^3	Slope y × 10^3	Correlation coefficient	Grouping
cis-*m*-Cl	3.32	3.17	6.12	0.9926(7)	Poorest correlation
trans-*p*-CH_3O	3.04	3.13	5.86	0.9931(7)	
trans-*p*-H	4.06	4.18	5.23	0.9938(9)	
cis-*p*-Cl	3.26	3.15	6.43	0.9999(9)	Best correlation
cis-*m*-Cl	3.42	3.17	5.14	0.9999(7)	
trans-*p*-F	3.02	2.84	4.77	0.9999(3)	
cis-*p*-CH_3O	2.68	3.18	1.56	0.9997(2)	Cases where one reactant
trans-*p*-F	3.34	3.03	6.95	0.9997(2)	is over 10% more con-
trans-*m*-Cl	3.19	2.84	3.35	0.9984(2)	centrated than the other
trans-*p*-Cl	3.19	2.84	4.04	0.9996(4)	
trans-*p*-H	3.59	3.17	7.92	0.0995(5)	
cis-*p*-CH_3O	3.73	3.17	10.89	0.9986(4)	
cis-*p*-CH_3O	3.73	3.17	10.29	0.9993(0)	
trans-*p*-H	3.59	3.17	7.61	0.9995(6)	

[a] Runs with the cyclopropane at 10 times the bromine concentration were made. Because the analysis required work-up before GC analysis of intermediate reaction samples and only the peaks of the starting materials were cleanly resolvable, the values obtained are, at best, rough. They did, nevertheless, give 0.995 for a correlation coefficient for the ½ order equation. These were not included in the 42 runs of this table.

One of these studies is on unsubstituted cyclopropane.[15] The photolysis was carried out in CCl_4 at 0 and at 68°C. As seen with the bromine (cf. below), the lower temperature favored the ring opening but substitution was a major process. Use of *tert*-butyl hypochlorite gave only substitution on cyclopropane itself. Rather than ring substitution, however, these workers found that methylcyclopropane gave little ring opening and a good deal of methyl substitution.

The second case is bicyclopentane,[14] where one must tread with care. Nevertheless, the two processes competed about equally at moderate temperature under irradiation. Ring opening was favored by lower temperature and both processes favored by peroxide addition.

The competition between substitution and ring opening when bromine is the halogen and the substituents are alkyl groups may not be only radical competition as the use of more polar solvents leaves doubts.[16,17] Nevertheless, when the temperature was held at −78°C and photolysis performed, rapid ring opening was the nearly exclusive result for an entire series of alkyl-substituted cyclopropanes.[16] The reaction of 1,2,3-trimethylcyclopropane gave some substitution of the product but no substitution that could be shown to be solely a reaction of the starting material.[17]

Only competition between aromatic substitution and ring opening occurs at low temperature in the dark for phenylcyclopropane with Br_2. Cyclopropane ring substitution products are not seen.[2,18]

In itself, it does not seem surprising that there should be a balance between these competing reactions for the radical processes and, as such, merely tells us that the E_a for ring opening is less than that for C–H bond breaking.

The effects of inhibitors and initiators in the aromatic systems is more of a problem for the proposed mechanism. For the 1,2-diaryl cases the literature records the following.

Levina[18] tried to brominate the diphenyl case using *N*-bromosuccinimide at 80° in carbon tetrachloride. Use of irradiation in conjunction with or separate from benzoyl peroxide or AIBN had no effect on the reaction. No product was formed. He also reported this to be true for phenylcyclopropane. LaLonde[2] has confirmed his results.

When studying the ionic reaction of the 1,2-diphenyl compound LaLonde[2] added isoamyl nitrite to the reaction carried out in chloroform. The rate of the trans isomer dropped by about a third but that of the cis isomer increased by about the same factor.

Studies with phenylcyclopropane as the substrate offers further signs of unusual lack of dependence on general radical conditions. The presence of trinitrobenzene had no effect on the photolytic halogenation.

Attempts to get other radical reactions to occur were equally unsuccessful as conditions that led to rapid addition of thiolacetic acid to olefins gave no reaction with the phenylcyclopropane substrate. Attempts to add bromotrichloromethane to the ring under irradiation and with benzoyl peroxide gave only the 1,3-dibromo-1,3-diphenylpropane in low yield after 48 hr. The tetrahalide had decomposed to give bromine.

On the other hand, addition of hydrolyic solvents and amines to these 1,2-diarylcyclopropanes under photolytic conditions has been reported.[19] The author suggests that the process involves a reaction of the cyclopropane excited state.

In the face of such conflicting data the radical nature of the process is in doubt, although the conditions otherwise are certainly strongly suggestive of such a mechanism. The LaLonde[2] proposal that a charge transfer absorption for a complex of the halogen molecule and the cyclopropane is implicated, coupled with his observation of such absorptions, seemed to circumvent this problem. Our rate equation and the failure to find significant charge transfer bands in the region open to our filter system seems to place this solution to the inhibitor–initiator insensitivity in doubt also.

Our mechanism is not far from that proposed by Shea and Skell[16] except that they propose a "solvated" bromine atom associated with the aromatic ring as a step between 1 and 2. Their proposal then explains the ring opening as controlled by transfer of the bromine atom to the benzyl carbon.

In analogy with other ring opening studies, reduction for example, one might note that the association is with the most highly conjugated bond of the cyclopropane ring as noted by Norin and Dauben.[20] Perhaps the association can be visualized as an edge complex such as proposed by Ketley[21] and Irwin.[22]

There is not sufficient definition in the data on stereochemical relationships to permit comment on these proposals. Although our *dl* vs. meso ratios for the dibromides from the cis and trans symmetrical cyclopropanes are different from 50:50 and from LaLonde's, it is not clear that the separation technique has not modified them. We found that the separated 1,3-dibromides from the *p*-F, *m*-Cl, and *p*-methoxy series were also resolvable into *dl* and meso in the NMR and were essentially 50:50 in all cases.

Our Hammett treatment, at best rather qualitative, could certainly be accommodated by either approach of the bromine atom in search of electron density.

It can be said that it does not appear that the reaction of cyclopropane with bromine atoms in nonpolar solvents is fully understood.

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Registry No.—1,2-Dibromo-1,3-diphenylpropane, 56363-42-9; *trans*-1,3-diphenylpropene, 3412-44-0; 1,3-dibromo-1,3-diphenylpropane, 17714-40-8; 1,3-diphenyl-1,3-propanediol, 5471-97-6; 1-*p*-(chlorophenyl)-3-phenyl-1,3-dibromopropane, 56363-43-0; 1-(*p*-chlorophenyl)-2-phenyl-1,3-dibromopropane, 56363-44-1; 1-(*p*-fluorophenyl)-2-phenyl-1,3-dibromopropane, 56363-45-2; 1-(*m*-chlorophenyl)-2-phenyl-1,3-dibromopropane, 56363-46-3.

References and Notes

(1) Presented in 1966 to the Faculty of the Naval Postgraduate School in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
(2) (a) R. T. LaLonde, P. B. Ferrara, and A. D. Debboli, Jr., *J. Org. Chem.*, **37**, 1094 (1972); (b) R. T. LaLonde and A. D. Debboli, Jr., *ibid.*, **38**, 4228 (1973).
(3) For the 1-pyrazoline route: (a) C. G. Overberger and J.-P. Anselme, *J. Am. Chem. Soc.*, **86**, 658 (1964); (b) C. G. Overberger, N. Weinshenker, and J.-P. Anselme, *ibid.*, **87**, 4119 (1965).
(4) For the 2-pyrazoline route: (a) N. Kishner, *J. Russ. Phys. Chem. Soc.*, **47**, 110 (1913); *Chem. Abstr.*, **9**, 3051 (1915); (b) H. E. Knipmeyer, "A Study of *cis*- and *trans*-1,2-Diphenylcyclopropane", University Microfilms, Ann Arbor, Mich., 1956.
(5) (a) A. Bethoud and J. Beraneck, *J. Chim. Phys. Phys.-Chim. Biol.*, **24**, 213 (1927); (b) W. H. Bauer and F. Daniels, *J. Am. Chem. Soc.*, **56**, 2014 (1934); (c) R. F. Brown and F. Daniels, *ibid.*, **62**, 2820 (1940).
(6) D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer, *J. Am. Chem. Soc.*, **83**, 4838 (1961).
(7) H. E. Knipmeyer, "A Study of *cis*- and *dl-trans*-1,2-Diphenylcyclopropane", University Microfilms, Ann Arbor, Mich., 1956.
(8) Yu. S. Shabarov et al., *Zh. Obshch. Khim.*, **35**, 243 (1965).
(9) T. V. Van Auken, *J. Am. Chem. Soc.*, **84**, 3736 (1962).
(10) D. E. Applequist and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 874 (1956).
(11) M. Bokadia, *J. Chem. Soc.*, 1658 (1962).
(12) H. E. Zimmerman and J. English, *J. Am. Chem. Soc.*, **76**, 2285 (1954).
(13) J. Conceill, J. Gabord, and J. Jacques, *Bull. Soc. Chim. Fr.*, 2653 (1966).
(14) D. E. Applequist, G. F. Fanta, and B. W. Henrickson, *J. Am. Chem. Soc.*, **82**, 2368 (1960).

(15) C. Walling and P. S. Fredericks, J. Am. Chem. Soc., 84, 3326 (1962).
(16) K. J. Shea and P. S. Skell, J. Am. Chem. Soc., 95, 6728 (1973).
(17) G. C. Maynes and D. E. Applequist, J. Am. Chem. Soc., 95, 856 (1973).
(18) Yu. S. Shabarov, S. N. Burenko, and R. Ya. Levina, Zh. Org. Khim., 4, 66 (1968).
(19) (a) S. S. Hixon, J. Am. Chem. Soc., 93, 5293 (1971); (b) J. Chem. Soc., Chem. Commun., 1170 (1972).
(20) (a) T. Norin, Acta Chem. Scand., 19, 1289 (1965); (b) W. G. Dauben and E. I. Deviny, J. Org. Chem., 31, 3974 (1966).
(21) A. D. Ketley and J. A. Braatz, Chem. Commun., 959 (1968).
(22) W. J. Irwin and F. J. McQuillin, Tetrahedron Lett., 1968 (1973).

Reactions of Diaryliodonium Salts with Sodium Alkoxides‡

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The reaction of a diaryliodonium salt with a metal alkoxide to give an alkyl aryl ether plus an aryl iodide is considered to be of synthetic utility. We have found, however, that an aromatic hydrocarbon, an aryl iodide, and an aldol resin (or a ketone if the alkoxide is derived from a secondary alcohol) are frequently the major products. We now present evidence that the latter products arise by a radical chain reaction, while the former products are the result of an aromatic nucleophilic displacement reaction. Furthermore, the yields of alkyl aryl ether plus aryl iodide can be increased markedly by the addition of a radical trap to the reaction mixture to inhibit the undesired, competing process. Some important solvent effects and differences with triarylsulfonium alkoxide reactions are also discussed.

Several widely used textbooks of organic chemistry depict the reaction of a diphenyliodonium cation with an alkoxide anion (or other base) to produce a phenyl alkyl ether plus iodobenzene as an example of an aromatic SN reaction and as a potentially useful synthetic procedure. One of the major purposes of this article is to point out that, under ordinary conditions of reaction, the alkyl aryl ether is frequently a minor product, the major products being benzene, iodobenzene, and an aldol resin (or a ketone, depending on the structure of the alkoxide ion). However, with the use of a suitable additive, such as 1,1-diphenylethylene, the alkyl aryl ether becomes the major product in all cases.

Diaryliodonium salts are known to be versatile arylating agents.[1-3] Whereas the early mechanistic studies provided indications that the reactions of diaryliodonium cations with bases were of the aromatic SN type,[4-6] later investigations provided convincing evidence that radical reactions could also take place.[7-11] That aromatic SN reactions of diaryliodonium cations with aromatic amines can take place with prior formation of a hypervalent iodine intermediate was demonstrated by Reutov and his coworkers,[12-15] who also showed that the corresponding reactions with aliphatic amines have an important radical component.[16-19]

We have recently demonstrated that radical chain reactions compete with aromatic SN reactions when diaryliodonium salts are treated with sodium alkoxides.[20] The same combination of mechanistic pathways has been shown to occur in the reactions of triarylsulfonium salts with sodium alkoxides,[21] and furthermore, it has been demonstrated that the balance between these routes is a delicate one, being influenced strongly by various factors, such as the presence of radical inhibitors, the polarity of the solvent, and the structure of both the triarylsulfonium cation and the alkoxide anion.[22] We now wish to report in detail on the factors which influence the ratio of the competing modes of reaction of diaryliodonium cations with alkoxide anions.

The most striking demonstration of the occurrence of competing aromatic SN and radical chain reactions in the reaction of a diaryliodonium salt with a sodium alkoxide is the effect of the addition of a radical inhibitor, such as 1,1-diphenylethylene. For example, the reaction of 5.0×10^{-4} mol of phenyl-*p*-tolyliodonium fluoroborate with 7.0×10^{-4} mol of sodium ethoxide in 2.0 ml of ethanol solution at 71° for 90 min was found to give phenetole (9.5% yield), *p*-methylphenetole (2.6%), benzene (34%), toluene (36%), iodobenzene (56%), *p*-iodotoluene (47%), and a mixture of biaryls (0.01%). When the same reaction was carried out in the presence of 5.0×10^{-4} mol of 1,1-diphenylethylene, however, there was obtained phenetole (55%), *p*-methylphenetole (22%), benzene (5.2%), toluene (4.8%), iodobenzene (31%), and *p*-iodotoluene (62%). These and additional data are shown in Tables I–IV. Clearly, 1,1-diphenylethylene is functioning as an inhibitor of a radical reaction which produces benzene and toluene; however, the presence of 1,1-diphenylethylene does not affect the rate of production of phenetole and *p*-methylphenetole, which arise by conventional aromatic SN reactions. It is evident from the data presented in Tables I–IV that the presence of a relatively small amount of diphenylpicrylhydrazyl in the reaction solution also results in the inhibition of the radical chain reactions.

As previously suggested,[20] and in analogy with the chain mechanism indicated for the decomposition of triarylsulfonium alkoxides,[21,22] a possible radical chain process for the conversion of diphenyliodonium isoproxide, for example, to a mixture of benzene, iodobenzene, and acetone is shown below.

1. Initiation

$$Ph_2I^+ + Me_2CHO^- \rightleftharpoons Ph_2I{-}O{-}CHMe_2 \rightleftharpoons (Ph_2I\cdot, \cdot O{-}CHMe_2)^{\alpha} \rightleftharpoons Ph_2I\cdot + \cdot O{-}CHMe_2 \rightleftharpoons Ph\cdot + PhI$$

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