residue was distilled *in vacuo* to yield **13** (14.1 g, 71%), bp 76° (0.2 mm).

Anal. Calcd for $C_8H_{11}NO_2$: C, 62.72; H, 7.23; N, 9.14. Found: C, 62.98; H, 7.54; N, 8.97.

N-(**3-Bromopropyl**)**glutarimide** (**14**).—A solution of *N*-allylglutarimide (**13**) (50.0 g, 0.326 mol) stirred in 1600 ml of toluene was irradiated (G. E. Sunlamp-275W-100-125V) overnight. During the irradiation HBr was bubbled through the solution. The reaction was cooled, the toluene was removed *in vacuo*, and the residue was distilled to yield **14** (33.8 g, 44.5%), bp 132° (0.2 mm).

N-(**2-Bromopropyl**)**glutarimide** (**15**).—A stirred solution of *N*-allylglutarimide (**13**) (230 g, 1.50 mol) which still contained some HOAc in 4000 ml of toluene was irradiated (G. E. Sunlamp-275W-110-125V) overnight. During the irradiation HBr was bubbled through the solution. The toluene was removed *in vacuo* and the solid residue was dissolved in boiling EtOH and immediately cooled in an ice bath. Compound **15** (28.4 g, 8.5%), mp 58–60° (petroleum ether, bp 60–70°), was collected by filtration.

Anal. Calcd for $C_8H_{12}BrNO_2$: C, 41.09; H, 5.16. Found: C, 40.73; H, 5.36.

The EtOH was removed from the filtrate to yield an oil (70.0 g) which was identified as the ethyl ester of the ring-opened imide from its nmr spectrum.

2-Keto-8-methyl-7-oxa-Δ^5-1-azabicyclo[4.3.0]nonane (**16**).—A solution of *N*-(2-bromopropyl)glutarimide (**15**) (15.0 g, 0.06 mol) in 15 ml of ethylene glycol dimethyl ether was added to a stirred suspension of NaH (2.64 g of 57% in mineral oil, 0.063 mol) and refluxed for 3 days. The solid was removed by filtration and the filtrate was concentrated *in vacuo* to leave an oil which was distilled to yield **16** (7.10 g, 73.5%): bp 57° (0.2 mm); ir ($CHCl_3$) 1660 (C=O), 1710 cm^{-1} (C=C); nmr ($CDCl_3$) δ 1.40 (d, 3 H, CH_3), 2.35 (m, 4 H, CH_2CH_2), 3.3 (d, 1 H, HCH–), 3.9 (d, 1 H, HCH), 4.15 (m, 1 H, C=CH), 4.5 (m, 1 H, OCH).

Anal. Calcd for $C_8H_{11}NO_2$: C, 62.72; H, 7.23; N, 9.14. Found: C, 62.42; H, 7.28; N, 8.75.

N-**Allyl-α-phenylglutarimide** (**20**).—Allylamine (6.0 g, 0.10 mol) was added dropwise to a stirred solution of α-phenylglutaric anhydride (20 g, 0.10 mol) in 40 ml of C_5H_5N. The exothermic reaction was allowed to cool to 25° and then 200 ml of Ac_2O was added and the solution was refluxed for 3 hr. The solution was concentrated by distillation and the residue was distilled *in vacuo* to yield **20** (19.7 g, 82%), bp 148–152° (0.2 mm).

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59. Found: C, 73.06; H, 6.56.

Registry No.—**4**, 33821-94-2; **5**, 33821-95-3; **7**, 33821-96-4; **10**, 33821-97-5; **13**, 3880-20-4; **14**, 33821-99-7; **15**, 33822-00-3; **16**, 33822-01-4; **20**, 33822-02-5.

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Characteristics of Various Reactions of Bromine with Arylcyclopropanes[1]

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The reaction of bromine with *cis*- and *trans*-diphenylcyclopropane gives 1,3-addition products only while phenylcyclopropane gives 1,3-addition products and/or aromatic substitution. The rate of reaction and product composition for all arylcyclopropanes is highly sensitive to light, temperature, and change in solvent but insensitive to the presence of nitrobenzene and trinitrobenzene.

There is ample evidence for the ionic addition of halogen to an array of cyclopropanes taking place under diverse conditions. Cyclopropanes undergo C–C fission with halogen in the presence of Lewis acids to give mixtures of rearranged and unrearranged dihalides.[2] More highly strained cyclopropanes, such as those incorporated into polycyclic systems,[3] and cyclopropanols[4] undergo ionic C–C fission without catalysts.

Contrasting with the generality of ionic additions, free-radical addition to cyclopropanes is less frequent and when it does occur is often competing with free-radical substitution. The free-radical addition of chlorine to bicyclo[2.1.0]pentane has been reported[5] as has the peroxide-catalyzed addition of bromine to 1-alkyl-2-phenylcyclopropanes.[6] Spiropentane gives a mixture of nearly equal amounts of ring-opened and ring-substituted products on photochemical chlorination.[7] Thermal, photochemical, or peroxide-catalyzed chlorination of cyclopropane gives minor amounts of addition product,[8] and arylcyclopropanes are inert to *N*-bromosuccinimide addition of bromine in the presence of free-radical initiators.[9] Consistent with the last mentioned lack of reactivity are the reports that some cyclopropanes also are inert, or are nearly so, to free-radical chain polymerization[10] and halomethane and mercaptan additions.[11]

Our interest in the various modes by which halogens add to cyclopropanes and the conditions which promote one mode of addition as opposed to the other arose during an initial stage of study of bromine addition to *cis*- and *trans*-1,2-diphenylcyclopropane. We observed that the reaction of bromine with these two cyclopropanes in carbon tetrachloride solution was strongly influenced by light and consequently we suspected at first the involvement of a free-radical

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TABLE I

BROMINATION OF *cis*- AND *trans*-1,2-DIPHENYLCYCLOPROPANE

Expt	Diphenylcyclopropane	Conditions[a]	Time, hr	Product compn, % Cycloprop[b]	Product compn, % 1,3-DiBr-1,3-diphenyl[c]
1	Trans	Dark, O_2[d]	44	67	33, *dl*/*meso* = 52/48 ± 2
2	Trans	Light[e]	44[f]		100, *dl*/*meso* = 48/52 ± 2
3	Cis	Dark, O_2[d]	18	63	37, *dl*/*meso* = 17/83 ± 3
4	Cis	Light[e]	18[f]		100, *dl*/*meso* = 43/57 ± 2

[a] All solutions were in CCl_4 and were 0.25 *M* in diphenylcyclopropane and 0.25 *M* in bromine. Reactions were carried out in Pyrex at −20°. [b] Unconverted 1,2-diphenylcyclopropane. [c] Deviations are the maximum based on three nmr integrations of the product mixture from each experiment. [d] Reactions carried out under a slight positive pressure of oxygen. [e] Room light. [f] Minimum time for complete visual disappearance of the bromine color.

TABLE II

BROMINATIONS OF PHENYLCYCLOPROPANE IN THE DARK AND LIGHT

Expt	Conditions[a,b]	Solvent	*T*, °C	Time,[c] hr	Product compn, % Cycloprop	Product compn, % 1,3-DiBr	Product compn, % *p*-Br
1–6	Dark	CCl_4	−20	52	18 ± 2		82 ± 2
7–9	Dark	CCl_4	25	7		100	
10	Dark	$CHCl_3$[e]	−20	53	13	30	30[i]
11	Dark, O_2[d]	$CHCl_3$[e]	−20	53		18	82
12	Dark	EtAc	25	2	11	50	39
13	Dark	*n*-Hex	−20	53	10		90
14–15	Light[f]	CCl_4	−20	1.5–2.5		100	
16–19	Light[g]	CCl_4	−20	3.5		100	
20–22	Light, O_2[d,f]	CCl_4	−20	2.5–4.5	20 ± 6	30 ± 6	50 ± 6
23–26	Light	CCl_4	25	~5 min		100	
27	Light	CCl_4, MeOH[h]	25	1	20	80	Trace
28	Light	$CHCl_3$[e]	−20	~15		100	
29	Light	EtAc	25	2	16	60	24
30	Light	*n*-Hex	−20	5 min		100	

[a] All solutions were 0.25 *M* in cyclopropane and 0.25 *M* in bromine. Reactions were carried out in Pyrex unless indicated otherwise. [b] Room light unless indicated otherwise. [c] Except in those cases where unconverted phenylcyclopropane is listed as a component of the product mixture, the reaction time is the minimum time for complete visual disappearance of the bromine color. [d] Reactions carried out under a positive pressure of oxygen. [e] Alcohol-free chloroform. [f] Experiments were carried out on different days. [g] Irradiated with a 40-W incandescent bulb. [h] MeOH–phenylcyclopropane, 1:1 molar. [i] 23% unidentified product.

process. The initial observation of light dependency led us to turn our attention to the simpler phenylcyclopropane and explore the effect of light, temperature, solvent, and the presence of inhibitors on its reactivity. The results of these studies are presented in this paper.

Results

The first bromination of *cis*-1,2-diphenylcyclopropane was carried out in room light at 25° in carbon tetrachloride solution in a Pyrex container. A 2:1 molar ratio of bromine to diphenylcyclopropane was used. The reaction was exothermic. The product consisted of 8.5% *meso*- and 6.5% *dl*-1,2,3-tribromo-1,3-diphenylpropane and 85% 1,3-dibromo-1,3-diphenylpropane made up of a 1:1 ratio of *dl* and *meso* isomers. Evidence for the structure assignment of products and product composition is given in other sections of this paper. The second experiment involved *cis*-diphenylcyclopropane treated with bromine (1:1 molar ratio) in the dark at −20° for 14 hr. Some bromine color persisted. The product, obtained in 95% yield, consisted of a 15:85 mixture of *dl*- and *meso*-1,3-dibromo-1,3-diphenylpropane. The chief differences induced by lowering the temperature, reducing the concentration of bromine, and excluding light were the steric outcome and the diminished rate of bromination. On the basis of these first two experiments, we suspected that the bromine addition in the light was a free-radical chain process. Consequently in the series of reactions carried out thereafter, dark brominations of diphenylcyclopropanes were also run under a slight positive pressure of oxygen in order to help suppress any radical chain process. Results of treating *cis*- and *trans*-diphenylcyclopropanes with bromine in the light and dark at −20° in carbon tetrachloride solution are given in Table I. The results can be summarized as follows. *cis*-Diphenylcyclopropane reacts with bromine more rapidly than the trans isomer in both the light and the dark. Light has an accelerating effect on both cis and trans isomer reactivity. Only the cis isomer reacting with bromine in the dark shows any significant stereoselectivity and this is predominantly cis addition. In ancillary experiments carried out to check for kinetic or thermodynamic control of the dibromide product mixtures, we observed no change in the *dl*:*meso* ratios on treating mixtures of two different compositions (*dl*:*meso* 2.3 and 1.2) with bromine in carbon tetrachloride at −20 or 25° for 60 hr.

The influence of reaction conditions was studied more extensively in the case of phenylcyclopropane. Results are given in Table II.

Light and Temperature Effect.—A comparison of results for dark (Table II, expt 1–6) and light brominations (expt 14–15) carried out at −20° in carbon tetrachloride reveals two significant differences. The light reaction is more than 20 times faster than the dark reaction. Also, the light reaction gives only 1,3-addition product whereas the dark reaction affords only aromatic substitution, presumably electrophilic aromatic substitution. This latter result is consistent with

work of Levina[9a,12] who observed aromatic substitution of phenylcyclopropane taking place at −75°. Unfortunately, Levina did not report whether the reaction was carried out in the light or dark. Our experiments (16–19) show that artificial light also accelerates the reaction with bromine. At 25° the light reaction (expt 23–26) is again faster, by about 85 times, than the dark reaction. Changing the reaction vessel from Pyrex to quartz has no apparent effect on the light reaction in carbon tetrachloride at −20°. However, a light reaction carried out in chloroform at −20° is four times faster in quartz than in Pyrex, all other conditions being precisely the same. Light has very little effect on the reaction carried out in ethyl acetate (expt 12 and 29).

A comparison of results for the reaction carried out at −20° (Table II, expt 1–6) with those carried out at 25° (expt 7–9) shows that a 45° rise in temperature increases the rate and changes the mode of bromine reaction with phenylcyclopropane. Therefore light is a sufficient but not a necessary ingredient for 1,3-bromine addition. In contrast, the diphenylcyclopropanes give only addition products, the diasteromeric ratios of which are the same when formed from the *trans* isomer but differ when formed from the cis isomer in dark and light reactions.

Solvent Effect.—As can be seen from the data of Table II, solvent change has a pronounced effect on the rate and a smaller effect on the product composition of the light reaction. A reaction carried out in *n*-hexane (expt 30) is the most rapid. Use of chloroform as solvent (expt 28) diminishes the rate as does ethyl acetate (expt 29). Moreover, the light reaction in ethyl acetate also affords *p*-bromophenylcyclopropane. In contrast, the consumption of bromine in the dark reaction in ethyl acetate (expt 12) is faster than in carbon tetrachloride (expt 7–9). Similarly, the consumption of bromine in alcohol-free, degassed chloroform is 23 times faster in the dark at 25° than in carbon tetrachloride under the same conditions. These last-mentioned results were obtained by conducting dark reactions in cuvettes and following the decrease of the 415-nm bromine absorption maximum.

The addition of a small amount of methanol (2.2 mmol in 8 ml) to carbon tetrachloride has a large retarding effect on the light reaction (expt 27). The presence of ethanol in chloroform also strongly retards the light bromination and for this reason when chloroform is used as the solvent, the ethanol is first removed.

The presence of oxygen (expt 20–22) diminishes slightly the rate of bromine consumption in carbon tetrachloride in the light but more noticeable is the significant electrophilic aromatic bromination which results. Thus, in the aspect of product composition, the presence of oxygen tends to convert a light bromination at −20° to a dark bromination. The use of ethyl acetate as solvent (expt 29) tends toward the same result which is also suggested in the trace amount of *p*-bromophenylcyclopropane produced when methanol is added to carbon tetrachloride (expt 27).

Inhibitors and Attempted Radical Additions.—When a light bromination in carbon tetrachloride solution was carried out at 25 or −20° in the presence of nitrobenzene, the rate of bromine consumption was only two to three times slower than when no inhibitor was used. A light bromination carried out at 25° in carbon tetrachloride saturated with trinitrobenzene was not visibly retarded. At the same time, such a trinitrobenzene solution retarded the free-radical bromination of hexane by at least a factor of 6.

The absence of the usual inhibitory effect of the nitrobenzenes led us to search for other possible free-radical chain additions of phenylcyclopropane in order to ascertain whether or not phenylcyclopropane would show any reactivity whatsoever in the free-radical mode. Under conditions which promote free-radical chain addition of thiolacetic acid to 1-methylcyclohexene and 2-methylstyrene, phenylcyclopropane was unreactive. Bromotrichloromethane reacted when irradiated 48 hr in the presence of benzoyl peroxide but the product was 1,3-dibromo-1-phenylpropane, the product resulting from the addition of bromine afforded by the disproportionation of bromotrichloromethane. None of the product resulting from the simple addition of bromotrichloromethane could be detected. Levina[9b] reported that both 1,2-diphenylcyclopropane and phenylcyclopropane were stable to free-radical bromination. The conditions included NBS in carbon tetrachloride at 80° with ultraviolet irradiation and addition of benzoyl peroxide or azobisisobutyronitrile. We repeated Levina's experiments and obtained the same result.

Bromine–Phenylcyclopropane Complexes.—The changes produced by the presence of alcohols prompted us to seek evidence for their mode of interaction. We report in this section the results of some exploratory experiments.

Bromine and phenylcyclopropane are found to give rise to new absorption bands at 296 nm in carbon tetrachloride and 299 nm in *n*-hexane. These bands disappear in time as the bromine color is discharged. By comparison, the well-known bromine–benzene charge-transfer complex[13] shows a band at 292 nm in benzene solution. In carbon tetrachloride solution, we find the bromine–benzene band at 287 nm. The corresponding absorption maximum for bromine–phenylcyclopropane in chloroform could not be observed with certainty because of the fast dark reaction in this solvent. Reasonably the presence of the new bands which occur in *n*-hexane and carbon tetrachloride solution can be attributed to charge-transfer complexes similar to those which are well known for simple aromatic hydrocarbons and halogens.

When methanol is added to bromine in carbon tetrachloride, the 296-nm band disappears and only strong end absorption, reasonably from the methanol–bromine complex, is observed. This observation can be attributed to an expected greater stability and lower λ_{max} of the bromine–methanol complex compared to the bromine–phenylcyclopropane complex. Supporting this explanation is the known greater stability and lower λ_{max} of iodine–alcohol complexes relative to iodine–aromatic hydrocarbon complexes.[14] Also supporting the explanation is the observation that the

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bromine–phenylcyclopropane complex in hexane is observed at 299 nm while the bromine–methanol complex in the same solvent occurs at 269 nm. The exact position of the bromine–methanol complex in carbon tetrachloride could not be measured because of the interference of the solvent.

Structure Determination.—The relative position of bromine atoms in the dibromide product was shown by conversion of a *dl,meso* dibromide mixture (1:1) with zinc dust in methanol to a hydrocarbon mixture consisting of 33% *cis*-, 64% *trans*-1,2-diphenylcyclopropane, and 3% 1,3-diphenylpropane. Also the diastereomeric dibromides were hydrolyzed with aqueous silver nitrate to a mixture of *dl*- and *meso*-1,3-diphenyl-1,3-propanediol which was separated into the pure diastereomeric diols through borate ester formation.[15]

The nmr of the 1,3-dibromide (*dl*:*meso* = 1) included two low field triplets and a high field triplet imposed on a more complex multiplet. Full spectral data is given in the Experimental Section. The combination of the high field triplet with one of the two low field triplets was recognized as an A_2X_2 resonance pattern stemming from the four methylene and methine protons of *dl*-1,3-dibromo-1,3-diphenylpropane. The high field complex multiplet in conjunction with the remaining low field triplet constituted the ABX_2 pattern which originated from four methylene and methine protons of *meso*-1,3-dibromo-1,3-diphenylpropane. The distinction as to which of the two low field triplets represented X_2 of A_2X_2 and which represented X_2 of ABX_2 was made by examining the nmr of a second sample of the 1,3-dibromide. This sample was prepared by aluminum isopropoxide reduction of benzalacetophenone followed by treating the resulting 1,3-diphenyl-2-propen-1-ol with hydrogen bromide, first at 0° to obtain the allylic bromide, and than at 60° to obtain the dibromide. In the nmr of this dibromide sample, the highest field triplet matched the intensity of the lowest field triplet. Therefore lowest and highest field triplets were assigned to the *dl* diastereomer. The lowest and intermediate field triplets were observed in a ratio of 2.3:1 meaning that the ratio of *dl*:*meso* diastereomers was also 2.3. The ratio of the two low field triplet intensities was used routinely to ascertain the *dl* to *meso* ratio.

The two minor solid tribromides (8.5 and 6.5%) isolated when the light bromination of *cis*-1,2-diphenylcyclopropane was carried out at a high bromine concentration were studied by nmr also. The 6.5% diastereomer was assigned the *dl* configuration on the basis of nmr properties consistent with an AMX proton system representing the diastereomeric protons at C_1 (A or M) and C_3 (M or A) and the remaining proton at C_2 (X). Close inspection of the eight-line multiplet displayed by the 8.5% diastereomer revealed a striking similarity to known A_2B[16] proton systems. The 8.5% diastereomer was believed to possess one of two possible *meso* configurations since protons at C_1 and C_3 (A_2) have an enantiomeric relationship.

The two tribromides were prepared by adding bromine to 3-bromo-1,3-diphenyl-2-propene, an intermediate utilized in the synthesis of *dl*- and *meso*-1,3-dibromo-1,3-diphenylpropanes. The pure tribromides were identical in every respect with those obtained in the bromination of *cis*-1,2-diphenylcyclopropane. Reasonably the two tribromides obtained in the exothermic addition of bromine to *cis*-1,2-diphenylcyclopropanes were formed by hydrogen bromide elimination from 1,3-dibromo-1,3-diphenylpropane and then bromine addition to the resulting olefin.

Discussion

The results disclosed in the previous section reveal that the reactivity of bromine with the arylcyclopropanes studied is complex, responding in rate and product composition to changes, some quite small, in light, temperature, and solvent. In the following discussion we give our preferred explanations, when there is some basis for doing so, and point out the unsolved problems raised by our work.

The formation of *p*-bromophenylcyclopropane in the dark in carbon tetrachloride would appear to be an electrophilic substitution reaction. In the more polar chloroform at −20°, 1,3-addition begins to appear. Reasonably this dark addition could be the usual electrophilic addition type since it becomes more competitive as the polarity of the solvent increases.

Should 1,3-electrophilic addition be accepted as one pathway then there must be a second route to 1,3-addition products since the light effect is clearly evident and simple electrophilic addition reactions are not known to be promoted by light. Yet the observed insensitivity toward inhibitors and the large response to change in solvent are characteristics inconsistent with a radical chain mechanism for the light promoted 1,3-addition. Also, the observed lack of reactivity of phenylcyclopropane with reagents which readily react with olefins in the radical chain mode tends to support the evidence obtained from solvent change and inhibition experiments. Whatever the path for the fast light-promoted addition also might be the path for the dark addition which occurs at 25° in carbon tetrachloride. Alternatively this 25° dark reaction might be a temperature-enhanced 1,3-electrophilic addition. At present we prefer the two path explanation for formation of 1,3-addition products. One of these pathways is a slow 1,3-electrophilic addition occurring in the dark at −20° and the other a light-induced process of unspecified nature which is favored in nonpolar solvents.

The above explanation also is consistent with the diphenylcyclopropane results. That the cis isomer reacts more rapidly in both dark and light reactions than the trans isomer may be attributed to the extra ground state destabilization of the cis as opposed to the trans isomer. Based on heat of combustion data, the cis isomer is destabilized by 13 kcal/mol relative to the trans isomer.[17] Release of strain also may explain why addition of bromine to both isomers predominates completely over aromatic ring substitution. Only in the dark reaction of the more highly strained cis isomer is the addition stereoselective. This reactivity characteristic observed only for the dark re-

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action, along with light catalysis of the bromine addition to both isomers, again would implicate more than one route to 1,3-addition products but the reason for stereoselectivity in the case of the cis isomer and not the trans is not clear.

Another point worthy of attention is the circumstantial evidence which associates bromine–arylcyclopropane complex formation with the rate of the 1,3-light addition. This association follows from the observation that methanol addition simultaneously reduces both the rate of addition and the concentration of the bromine–phenylcyclopropane complex in carbon tetrachloride solution. One can only speculate at present on the particular role of this complex in the light reaction and its importance in general to bromine–arylcyclopropane reactivity.

The studies reported here help establish the reaction condition limits for a given type of bromine arylcyclopropane reaction. Consequently, the results are proving to be a useful guide in isolating various reaction types for further detailed study.

Experimental Section

Spectra were obtained as follows: nmr in CCl_4 solution (unless otherwise indicated) 1% TMS (τ 10.00), Varian A-60A, symbols s, d, t, q, and m refer to singlet, doublet, triplet, quartet, and multiplet, respectively; ir in CCl_4 solution (unless otherwise indicated) Perkin-Elmer 137, 0.05-mm sample and reference cells, symbols s, m, b, w, sh, and br refer to strong, medium, weak, sharp, and broad, respectively; mass spectrum at 70 eV and 160–165° with an all glass heated inlet, Hitachi Perkin-Elmer RMU 6E; uv in solution as indicated, Cary 15.

Melting points were determined on a Köfler micro hot stage and are uncorrected. Glc was performed on a Varian-Aerograph Model 200 using conditions as indicated. The elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Evaporation of solvent or concentration of solution was done at the rotary evaporator at reduced pressure.

Arylcyclopropanes.—1,2-Diphenylcyclopropane was prepared from benzylideneacetophenone in 84% yield by a reported method.[18] Isomers were separated on a spinning band distillation column to obtain cis [bp 116° (0.2 mm)] and trans [125° (0.2 mm)]. Phenylcyclopropane was prepared by a known method.[19]

Uv of Bromine–Arene Complexes.—The spectra of the bromine–phenylcyclopropane complex in CCl_4 and $CHCl_3$ solution was determined in 1-cm cells by a method similar to that employed by Benesi and Hildebrand.[20] A 4-ml, 9.0×10^{-4} M solution of bromine was added in the dark to a solution of 0.05 ml of phenylcyclopropane in 5 ml of the appropriate solvent. Solvent was added to bring the volume to 10 ml and the spectrum of this solution immediately was determined between 280 and 350 nm. The reference beam was balanced with the same phenylcyclopropane solvent pair. The procedure for determining the bromine–benzene complex was the same except benzene replaced phenylcyclopropane.

The effect of added methanol on the bromine–benzene complex was determined in the following manner. The spectrum of a 4.5×10^{-5} M solution of bromine in benzene was determined with benzene as the reference. The λ_{max} at 292 nm diminished 2% in 10 min. Addition of 0.1 ml of methanol to both reference and sample cells resulted in a reduction in the optical density (A) from 1.66 to 1.32 and a shift in λ_{max} from 292 to 283 nm. Only 5 min elapsed between determining the first and the second spectrum.

Bromination Procedures.—In performing brominations in the dark at 25°, substrate and bromine solutions were placed in separated blackened flasks. These were attached to a blackened U tube. This apparatus was inverted to start the reaction. In performing brominations at −20° the apparatus was placed in the constant temperature bath before and after inversion. The reaction was stopped by the addition of aqueous $Na_2S_2O_3$. The CCl_4 layer was separated, washed with water, and dried ($CaCl_2$). Evaporation of the solvent gave a residue which was analyzed for percentage composition as follows. The relative amounts of unconverted phenylcyclopropane and bromine containing products were determined through comparison of integration values for cyclopropyl protons in the region τ 7.8–9.7 and noncyclopropyl, nonaromatic protons in the region τ 4.6–7.7. The relative amounts of unconverted phenylcyclopropane and *p*-bromophenylcyclopropane were then determined by glc which utilized an 0.25 in. × 5 ft 10% Q F-1 on Chromosorb W column at 130°. Nmr and glc properties of 1,3-dibromo-1-phenylpropane[18] and *p*-bromophenylcyclopropane[12] were used as comparison standards.

For reactions carried out under oxygen, the apparatus consisted of a three-neck flask equipped with an efficient overhead stirrer and a gas inlet tube for the introduction of oxygen. The entire apparatus was blackened for dark reactions. The work-up and analysis procedures were the same as those described above for dark reactions carried out in the U-tube apparatus.

Reactions were also carried out in the dark at 25° using degassed CCl_4 and $CHCl_3$. A solution 0.25 M in phenylcyclopropane and bromine was introduced into a 1-mm cuvette containing a 0.9-mm spacer. The cuvette was placed in the spectrometer and the rate of disappearance of bromine was determined by following the optical density (A) at 415 nm. Values of (1/A) and the corresponding time (hr) for reactions no. 1 and 2 in CCl_4 solution were: 1.05, 1.0 (0); 1.15, 1.10 (1); 1.25 (3); 1.35, 1.30 (4); 1.45, 1.35 (5); 1.55, 1.45 (6); 1.60, 1.50 (7). For the reaction run in $CHCl_3$ the values were: 1.30 (0), 4.70 (1), 5.30 (1.25), 5.90 (1.5), 6.60 (1.95), 7.40 (2.25), 8.70 (3.0 hr).

Reactions carried out in the presence of nitrobenzene (20 wt % of phenylcyclopropane) or trinitrobenzene (TNB) (saturated) were performed in Pyrex flasks at 25 and −20° in room light in CCl_4. These reactions were compared with those carried out at the same time but containing no inhibitor. Reaction solutions contained 0.620 g of phenylcyclopropane to which 10 ml of a 0.09 g/ml solution of bromine in CCl_4 was added.

The bromine addition in *n*-hexane was carried out in the following manner. To a solution of 0.126 g of phenylcyclopropane in 2 ml of *n*-hexane at −20° in a Pyrex test tube was added 2 ml of a freshly prepared bromine in *n*-hexane solution (0.09 g/ml) also at −20°. The color discharged in 5 min at −20° in room light. The solvent was evaporated to obtain a yellow oil (0.276 g) which when analyzed by nmr showed the presence of 90% 1,3-dibromo-1-phenylcyclopropane and 10% phenylcyclopropane. In the dark reaction, an aqueous $Na_2S_2O_3$ solution was added to remove any unconsumed bromine.

The inhibitory effect of a solution of CCl_4 saturated with TNB was determined in the following manner. To a solution containing 1 ml of *n*-hexane, 3 ml of CCl_4, and 225 mg of azobisisobutyronitrile at 60° was added 2 ml of a 0.09 g/ml solution of bromine in CCl_4. The bromine color was discharged in 10 min. A second solution containing precisely the same quantities of reactants and solvent, except that the solvent was saturated with TNB, decolorized after 1 hr at 60°.

Bromine Addition to 1,2-Diphenylcyclopropane.—In a typical light-induced addition, 0.194 g of *cis*-1,2-diphenylcyclopropane (1.0 mmol) was dissolved in 2 ml of CCl_4 in a Pyrex flask. A 2-ml solution of bromine in CCl_4 (0.090 g/ml) then was added in one portion and the resulting solution was kept at 25° in room light until the color disappeared (<5 min). The solvent was evaporated to give 1,3-dibromo-1,3-diphenylpropane (*meso*/*dl* = 1): brown oil; nmr τ 2.75 (s, 10 H, Ar H), 4.88 (t, J = 7 Hz, 1/2 H, *dl*-ArCHBr), 5.20 (t, J = 7 Hz, 1/2 H, *meso*-ArCHBr), 7.19 (t, J = 7 Hz, *dl*-CH_2), 6.6–7.5 (m, *meso*-CH_2); ir 1500 (m, sh), 1460 (m, sh), 1225 (m), 690 cm^{-1} (s, br); mass spectrum *m/e* 356, 354, 352 ($M^+ + 4$, $M^+ + 2$, M^+), 375 and 373 ($C_{15}H_{14}Br^+$), 194 ($C_{15}H_{14}^+$). Parent ions at *m/e* 312, 310, 308, corresponding to $C_{15}H_{14}BrCl$, or fragment ions at *m/e* 231, 229, corresponding to $C_{15}H_{14}Cl^+$, were not detected.

Anal. Calcd for $C_{15}H_{14}Br_2$: C, 50.88; H, 3.98; Br, 45.14. Found: C, 51.00; H, 3.96; Br, 45.27.

1,3-Dibromides isolated in the above-described manner were of sufficient purity to give satisfactory analyses for $C_{15}H_{14}Br_2$. Synthetic mixtures of *dl*- and *meso*-dibromides and unconverted phenylcyclopropane in CCl_4 did not change composition on evaporation of solvent.

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Zinc Debromination of 1,3-Dibromo-1,3-diphenylpropane.—A 4.50-g sample of the dibromide (*dl*/*meso* = 1) in 50 ml of anhydrous methanol was stirred 4 hr at 25° with 2.0 g of zinc dust. The mixture was filtered and the filtrate was concentrated. The residue was dissolved in ether and the solution was washed with water and dried ($MgSO_4$). Evaporation of the solvent produced 2.3 g of residue containing *cis*- (33%), *trans*-1,2-diphenylcyclopropane (64%), and 1,3-diphenylpropane (3%) as determined by glc (0.25 in. × 5 ft, 20% SE-30 on Chromosorb W, 225°). Identification was made by chromatographic comparison. The sample of 1,3-diphenylpropane used for comparison was prepared by hydrogenation of *trans*-1,2-diphenylcyclopropane.[21]

Hydrolysis of 1,3-Dibromo-1,3-diphenylpropane.—A solution of 6.28 g of the dibromide in 370 ml of acetone was treated with a solution of 6.2 g of $AgNO_3$ in 370 ml of water. The silver bromide (calcd 6.65 g; obsd 6.45 g) was removed by filtration and the filtrate was concentrated. The largely aqueous residue was extracted with ether. The ether extract was washed with 5% aqueous $NaHCO_3$ and then water and dried ($MgSO_4$). Evaporation of solvent gave 2.60 g (64%) of a mixture of diastereomeric 1,3-diphenyl-1,3-propanediols, mp 116–118° (benzene).

A 3.0-g sample of diastereomeric diols was separated through a known method[15] utilizing borate ester formation. In this manner was obtained 1.2 g of *dl*-diol, mp 128–129° (benzene). Reduction ($NaBH_4$) of 1,3-diphenyl-1,3-propanedione followed by borate ester formation gave a comparison sample of the *dl*-diol: mp 128–129°; nmr τ 2.70 (s, 10 H, Ar H), 5.09 (t, J = 6 Hz, 2 H, >CH), 6.85 (s, 2 H, OH), 7.90 (t, J = 6 Hz, 2 H, CH_2); ir 3400, 3350 (d, s), 1400 (m, sh), 1030 (d, br, s), 930 cm^{-1} (m).

Also obtained from the 3.0-g mixture of diastereomeric diols was 0.98 g of *meso*-diol:[15] mp 106–107° (benzene); nmr ($CDCl_3$) τ 2.71 (s, 10 H, Ar H), 4.9–5.3 (m, 2 H, >CH), 6.08 (s, 1 H, OH), 6.10 (s, 1 H, OH), 7.6–8.4 (m, 2 H, CH_2); ir 3400 (s, br), 1065 (m, sh), 780 cm^{-1} (m, br).

1,3-Dibromo-1,3-diphenylpropane.—According to the method of Lutz and Weiss,[22] a 20.8-g sample of benzylideneacetophenone (0.1 mol) was reduced to the unsaturated alcohol (mp 54–56°) in 76% yield using aluminum isopropoxide. A 9.5-g portion of the alcohol in 200 ml of anhydrous ether at 0° was treated with 3.0 g of dry HBr. The resulting solution was kept at 25° for 1 hr. Removal of excess HBr and solvent by evaporation produced 11.4 g (93%) of crude *trans*-1,3-diphenyl-3-bromo-1-propene, mp 45–48°. The crude allylic bromide was heated at 60° and treated with dry HBr for 15 hr. Thereafter the mixture was dissolved in petroleum ether and the resulting solution was washed successively with water, 5% aqueous $NaHCO_3$, and water and then dried ($CaCl_2$). Evaporation of the solvent gave a quantitative yield of 1,3-dibromo-1,3-diphenylpropane (*dl*/*meso* = 2.3).

Light Addition with Excess Bromine.—Addition in room light of 17 g of bromine (107 mmol) in one portion to 10.33 g of *cis*-1,2-diphenylcyclopropane (53 mmol) in 10 ml of CCl_4 produced a reaction which was exothermic to the extent that the CCl_4 was heated momentarily to reflux. The resulting solution was kept at 25° for 4 days. Evaporation of solvent and excess bromine gave 20.4 g of a yellow semisolid of which 14.3 g was treated with 100 ml of *n*-hexane. The 1.56 g of insoluble material (fraction 1) was filtered off and the filtrate was cooled overnight whereupon an additional 0.65 g of solid (fraction 2) was obtained. The mother liquors were evaporated giving 9.63 g of 1,3-dibromo-1,3-diphenylpropane (*dl*/*meso* = 1.0) which was identified by spectral data.

Fraction 1 was stirred in hot *n*-hexane. The insoluble material, 731 mg (8.5%), was filtered off and recrystallized from benzene giving *meso*-1,2,3-tribromo-1,3-diphenylpropane: mp 178–180°; nmr (CS_2) τ 2.4–2.9 (m, 10 H, Ar H), 4.6–5.2 (8-line m, 3 H, CHBr).

Anal. Calcd for $C_{15}H_{13}Br_3$: C, 41.61; H, 3.03; Br, 55.58. Found: C, 41.51; H, 3.08; Br, 55.37.

Fraction 2 was dissolved in the *n*-hexane mother liquor from which the *meso* tribromide was obtained and the resulting solution was cooled overnight. The resulting solid, 971 mg (6.5%), was collected by filtration and recrystallized from ethanol giving *dl*-1,2,3-tribromo-1,3-diphenylpropane: mp 130–132°; nmr (CCl_4) τ 2.72 (s, 10 H, Ar H), 3.89 (d, J = 2 Hz, 1 H, ArCHBr), 4.70 (d, J = 12 Hz, 1 H, ArCHBr), 5.55 (q, J = 12 and 2 Hz, 1 H, CHBr).

Anal. Calcd for $C_{15}H_{13}Br_3$: C, 41.61; H, 3.03. Found: C, 41.32; H, 3.33.

1,2,3-Tribromo-1,3-diphenylpropane.—To 5.2 g of 1-bromo-1,3-diphenylpropene in 100 ml of CCl_4 was added dropwise 3.2 g of bromine in 20 ml of CCl_4 and the resulting solution was stirred at 30° for 27 hr. Evaporation of solvent left 6.1 g (74%) of solid tribromides which was separated by fractional crystallization giving 2.2 g of *meso*, mp 179–181° (benzene), and 3.6 g of *dl*, mp 132–134°.

Attempted Additions to Phenylcyclopropane. Thiolacetic Acid.—Employing conditions previously described for the free-radical addition of thiolacetic acid[23] to olefins, 760 mg (10 mmol) of freshly distilled thiolacetic acid was added slowly at 25° to 1.18 g (10 mmol) of phenylcyclopropane in 8 ml of CCl_4 under irradiation with a 100-W bulb. No increase in the temperature of the reaction was noted. Benzoyl peroxide (~20 mg) was added and the solution was heated to reflux for 24 hr. An nmr of the crude reaction mixture displayed only signals corresponding to thiolacetic acid and unconverted phenylcyclopropane.

Bromotrichloromethane.—A mixture of 1.18 g of phenylcyclopropane (10 mmol), 2.0 g of bromotrichloromethane (10 mmol), and 10 mg of benzoyl peroxide was degassed and sealed in a Vycor tube which was irradiated at 25° with a low-pressure mercury vapor lamp for 48 hr. A small amount of insoluble, high melting (>300°) material was filtered off. The nmr of the filtrate indicated the presence of 77% phenylcyclopropane and 23% 1,3-dibromo-1-phenylpropane. This material, with additional benzoyl peroxide, was irradiated for 4 days; the nmr indicated the presence of 58% phenylcyclopropane and 42% 1,3-dibromo-1-phenylpropane. The phenylcyclopropane was removed by steam distillation and the residue was taken up in acetone. Aqueous $AgNO_3$ was added and the resulting solution was kept at 25° for 6 days. The solid was filtered off, the filtrate was concentrated, and the resulting largely aqueous residue was extracted with ether. The ether extract was washed with aqueous $NaHCO_3$ and water and then dried ($MgSO_4$). Evaporation of the ether gave 0.644 g of 1-phenyl-1,3-propanediol: nmr ($CDCl_3$) τ 2.7 (d, Ar H), 5.7 (q, J = 6 and 7 Hz), 6.3–7.0 (m), 7.40 (s, OH), 7.5–8.1 (m); glc (15% XF-1, 200°) 5.9 min. These properties were identical with those of a solvolysis product obtained from a sample of 1,3-dibromo-1-phenylpropane.

Registry No.—*cis*-Diphenylcyclopropane, 1138-48-3; *trans*-diphenylcyclopropane, 1138-47-2; phenylcyclopropane, 873-49-4; *meso*-1,3-dibromo-1,3-diphenylpropane, 33686-80-5; *dl*-1,3-dibromo-1,3-diphenylpropane, 33735-98-7; *dl*-1,3-diphenyl-1,3-propanediol, 5355-61-3; *meso*-1,3-diphenyl-1,3-propanediol, 5381-86-2; *trans*-1,3-diphenyl-3-bromo-1-propene, 33686-82-7; *meso*-1,2,3-tribromo-1,3-diphenylpropane, 33686-83-8; *dl*-1,2,3-tribromo-1,3-diphenylpropane, 33686-84-9; 1-phenyl-1,3-propanediol, 4850-49-1.

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