[Contribution from the Department of Chemistry, University of Michigan]

Unsaturated Sulfonic Acids. VI. Photobromination of 2-Phenylethene-1-Sulfonyl Chloride[1,2]

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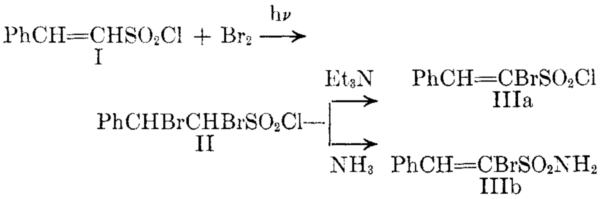
Received October 12, 1955

Photobromination of 2-phenylethene-1-sulfonyl chloride (I) in carbon tetrachloride gives a mixture of the dibromide (II) and the desulfonation products 1,2-dibromo-1-chloro-2-phenylethane (IV) and 1,1,2-tribromo-2-phenylethane (V). The formation of II requires the presence of small amounts of oxygen. When oxygen is removed, photobromination is very rapid, but II cannot be detected. Desulfonation is promoted by strong light and higher temperatures. With limited amounts of bromine, the rate of photobromination is given by $-d[Br_2]/dt = k[Br_2]^{3/2}$. Photobromination of I in acetic acid gives a mixture of II, IV, and V, but the proportions are not very sensitive to changing conditions. The rate in acetic acid is complex, but the *initial* rate is represented by $-d[I]/dt = k[I]I_a^{1/2}$ (where I_a is light intensity).

The photobromination of *trans*-2-phenylethene-1-sulfonyl chloride (I) in carbon tetrachloride solution was reported to form a dibromide (II) which was identified as the crystalline 1-bromo-2-phenylethene-1-sulfonyl chloride (IIIa) through treatment with triethylamine.[3] Since difficulty was subsequently encountered in obtaining consistent yields of IIIa, a more detailed study was undertaken. The effects of solvent, temperature, light intensity, and oxygen upon the products and rate of photobromination form the subject of this paper.

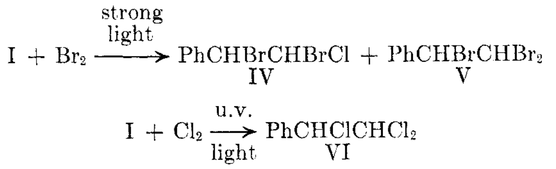
Photobromination in carbon tetrachloride. Products. It was verified that carbon tetrachloride solutions of I absorbed bromine in the dark at a very slow rate. Removal of oxygen did not noticeably alter bromine uptake in the dark.



$$\underset{\text{I}}{PhCH{=}CHSO_2Cl} + Br_2 \xrightarrow{h\nu} \underset{\text{II}}{PhCHBrCHBrSO_2Cl} \begin{cases} \xrightarrow{Et_3N} \underset{\text{IIIa}}{PhCH{=}CBrSO_2Cl} \\ \xrightarrow[NH_3]{} \underset{\text{IIIb}}{PhCH{=}CBrSO_2NH_2} \end{cases}$$

When a solution of I and bromine prepared in the ordinary way was illuminated with room fluorescent lights at ambient temperature, the bromine was slowly absorbed. The formation of II was demonstrated by conversion to IIIa or, more conveniently, IIIb. When a spotlight was placed close to the flask in an attempt to accelerate the reactions, the yield of II (as IIIa or IIIb) fell markedly, although the bromine disappeared much more rapidly. The major products in strong light were IV and V, arising from desulfonation. Raising the temperature during illumination also promoted the formation of IV and V.

Chlorine did not react with I in room light, but when an equimolar mixture of I and chlorine in carbon tetrachloride was irradiated with ultraviolet light (passed by Pyrex glass), VI was formed in 86% yield.



$$I + Br_2 \xrightarrow{\text{strong light}} \underset{\text{IV}}{PhCHBrCHBrCl} + \underset{\text{V}}{PhCHBrCHBr_2}$$

$$I + Cl_2 \xrightarrow[\text{light}]{\text{u.v.}} \underset{\text{VI}}{PhCHClCHCl_2}$$

Even at moderate light intensities, the yields of II (as IIIa) were erratic. This variation appears to result in part from trace quantities of oxygen. When nitrogen was bubbled through a solution of I in carbon tetrachloride before and after adding the bromine, decolorization was complete in 5–15 minutes (compared to 8 hours for a blank run without nitrogen treatment). Very little II (as IIIa) was formed and the major products were IV and V. The yield of IIIa from the blank using high-grade reagents was also low; in a similar blank experiment with commercial chemicals, the yield of IIIb was 38%. With reagent-grade chemicals, the yield of IIIa was raised to 38% by bubbling oxygen through the solution before adding the bromine. Therefore, a certain amount of oxygen must be present to permit formation of II.

With a positive pressure of oxygen (10–15 mm.) in room light, the yield of IIIa was only 20%, and a substantial amount of peroxidic material was formed, together with IV and V. Similarly, in strong light in an oxygen atmosphere, no IIIa was isolated, but 69% (calc'd as IV) of mixed IV and V was obtained, together with peroxidic material.

Photobromination in carbon tetrachloride. Rate study. The rate of bromine disappearance at low bromine concentrations was independent of the concentration of I from zero to 100% reaction, since plots of $[Br_2]$ *vs.* time with constant $[Br_2]_0$ and varying $[I]_0$ were congruent. The rate was proportional to $[Br_2]^{3/2}$ with our experimental conditions over the first two-thirds of the reaction, since plots (Figure 1) of the integrated form ($[Br_2]^{-1/2}$ *vs.* time) of Eqn. 1 were straight lines for 60–80% extent of reaction. The data could not be fitted to

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[1] Paper V, Rondestvedt and Chang, *J. Am. Chem. Soc.*, **77**, 6532 (1955).

[2] Presented at the New York meeting of the American Chemical Society, September, 1954. A portion of this work was abstracted from the Ph.D. Dissertation of R. L. Grimsley, 1954.

[3] Rondestvedt, *J. Am. Chem. Soc.*, **76**, 1926 (1954).

first- or second-order equations.

$$-d[Br_2]/dt = k[Br_2]^{3/2} \qquad (1)$$

$$[Br_2]^{-1/2} = {}^{1}/_{2}kt + [Br_2]_0^{-1/2} \qquad (2)$$

When the temperature was increased from 35° to 45°, the rate of bromine disappearance increased about 50%. When the light intensity was quadrupled at 35°, a 25% increase in rate was observed.

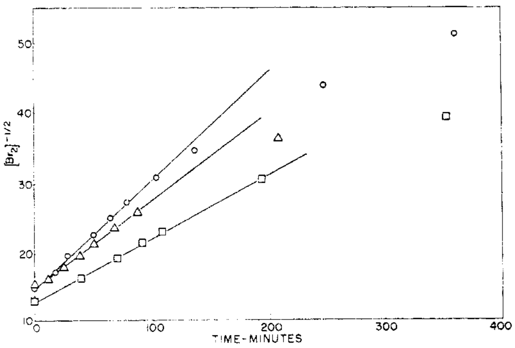

FIG. 1.—PLOT OF $[Br_2]^{-1/2}$ *versus* TIME.

The curvatures of the integrated plots became apparent somewhat earlier (60–70%) in these faster reactions. The rate constants in Table I were calculated from the slopes of the straight portions of the integrated plots.

The solutions used in the rate study were in equilibrium with the atmosphere. The rate was not studied as a function of oxygen concentration.

TABLE I

RATE OF PHOTOBROMINATION OF 2-PHENYLETHENE-1-SULFONYL CHLORIDE IN CARBON TETRACHLORIDE

T, °C.	d, cm.[a]	k, l.$^{1/2}$ moles$^{-1/2}$ min.$^{-1}$	Av. dev.[b]
35	33	0.198	0.010
35	15	.248	.010
45	33	.304	.012

[a] Distance from center of light bulb to center of flask. [b] Four runs were made for each set of conditions.

Bromination in acetic acid. Products. The dark reaction in acetic acid at room temperature was negligibly slow. However, at 55° in the dark, about 75% of the bromine reacted in 24 hours, though about two weeks was required for complete reaction.

Under fluorescent lights at room temperature, 87% of the bromine reacted in 24 hours if the flask had been cleaned with chromic acid before use; the reaction was complete in 7 days. With ordinary washing, however, only 66% reacted in 24 hours, and two weeks elapsed before completion. Deoxygenation by repeated freezing, thawing, and pumping increased the rate only slightly.

When the flask was illuminated with a spotlight, two hours were required for complete decolorization, either at room temperature or at 57°.

In each of the above experiments, the solvent was removed at room temperature and the two-phase residue was pumped for 24 hours at 1 mm. The upper phase, about 5–15% of the weight, was largely water-soluble and acidic; it was considered to be a sulfonic acid derived by hydrolysis of I or II by the water normally present in glacial acetic acid. The water-insoluble lower layer comprised 85–95% of the weight of the residue and contained only traces of acidic material. Samples from each lower layer were treated with liquid ammonia in ether to convert II to IIIb. From each run, approximately 50% of the starting I appeared as IIIb. Usually about 25% of the I could be isolated as IV and V. The product composition was not significantly altered by removal of oxygen.

It appears that the reaction conditions have much less effect upon product composition in acetic acid than in carbon tetrachloride. The effect of oxygen on the reaction in acetic acid was not studied from the standpoint of product composition; the solutions used were prepared from acetic acid in equilibrium with the atmosphere. The effect of oxygen upon the rate was very small, however, though slight retardation was detected.

Photobromination in acetic acid. Rate study. The kinetics in carbon tetrachloride were not studied further because of the pronounced effect of oxygen and the well-known[4] prominence of surface effects upon the halogenation of olefins in this solvent. Since these variables were found to be less important in acetic acid, it was used in further rate measurements. The solutions were in equilibrium with the atmosphere.

In the carbon tetrachloride runs, the concentrations of bromine used were so small that the incident light was incompletely absorbed; thus the variation in rate with changing light intensity was chiefly a function of the extent of light absorption. In acetic acid, a large excess of bromine was employed to insure complete absorption of the active radiation. However, the reaction could not be followed by measuring the bromine decrease, since the percentage change would have been very small, and bromine in acetic acid does not obey Beer's Law.[5] Solutions of I in isoöctane obeyed Beer's Law; λ_{max} 2737 Å, ϵ 21.2 × 10^3. For convenience, the analytical wave-length was selected as 2700 Å, where ϵ 19.9 × 10^3. The absorptions of II, IV, and V at this wave-length were small and did not interfere.

The reaction in acetic acid began rapidly[6] but

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[4] Robertson, Clare, McNaught, and Paul, *J. Chem. Soc.*, 335 (1937).

[5] Child and Walker, *Trans. Faraday Soc.*, **34**, 1506 (1938).

[6] The induction period apparent in early experiments was eliminated by thorough cleaning of the reaction vessel. The initial rates were not reproducible unless the flask was steamed out after cleaning with chromic acid.

fell off rapidly as well to a very low value at about 50% reaction. Rate measurements therefore were confined to the *initial* rate of disappearance of I, as determined by extrapolating to zero time the plot of optical density *vs.* time. The initial rates at varying concentrations of I and constant $[Br_2]_0$ were plotted *vs.* initial concentration of I, giving a straight line (Figure 2). Thus the *initial* rate is proportional to [I]. The order with respect to bromine was similarly determined to be zero (Figure 3), although the scattering of the points at low relative bromine concentrations makes this conclusion somewhat less certain. The rate depended upon the one-half power of the light intensity, as determined by application of the inverse square law. Quantum yields were not measured. These observations show that Eqn. 3 represents the *initial* rate.

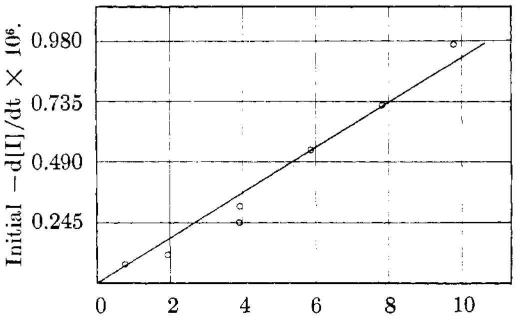

FIG. 2.—PLOT OF INITIAL RATES AT CONSTANT $[Br_2]_0$ *versus* INITIAL I CONCENTRATION.

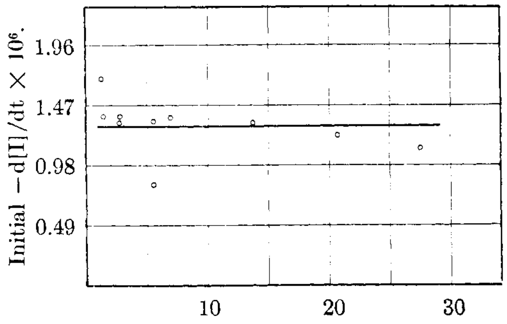

FIG. 3.—PLOT OF INITIAL RATES *versus* INITIAL BROMINE CONCENTRATION.

$$-d[I]/dt = k[I]\phi I_a^{1/2} \qquad (3)$$

where ϕ is the quantum efficiency and I_a the incident light intensity.

The initial rate of the reaction was only slightly dependent upon temperature in the range 20–31° but increased somewhat at 36°.

Robertson, in a series of papers,[7] has shown that ionic halogenations of electron-poor double bonds in acetic acid are often accelerated by salts, notably halides. We observed that added lithium bromide did not promote a dark reaction in acetic acid at room temperature. However, lithium bromide completely inhibited the photobromination. The effect of water was investigated briefly. The results indicated positive catalysis by 12–20% of water. Higher concentrations of water caused decomposition of I to tarry products and sulfur dioxide.

DISCUSSION

Reaction in carbon tetrachloride. The three-halves power dependence upon bromine concentration is similar to that found for the bromination of α-phenylcinnamonitrile by Berthoud and Nicolet.[8] In their work, the three-halves power dependence was noticed only when the bromine concentration was so low that the incident light was not completely absorbed; their reaction became first-order in bromine at higher bromine concentrations where the incident light was completely absorbed. The latter possibility was not tested in our work.

The cleavage reaction appears to parallel the simple addition, indicating that perhaps both proceed through a common intermediate. The effect of oxygen is extremely important in determining the product obtained, as is the light intensity. The following mechanism accounts for the facts as they are now known.

$$Br_2 + h\nu \longrightarrow 2\,Br\cdot \qquad (4)$$

$$PhCH{=}CHSO_2Cl + Br\cdot \longrightarrow \underset{\text{VII}}{PhC\underset{\cdot}{H}CHBrSO_2Cl} \qquad (5)$$

$$\text{VII} + O_2 \longrightarrow \underset{\text{VIII}}{PhC\underset{\mathrm{OO}\cdot}{H}CHBrSO_2Cl} \qquad (6)$$

$$\text{VIII} + Br_2 \longrightarrow \underset{\text{II}}{PhCHBrCHBrSO_2Cl} + O_2 + Br\cdot \qquad (7a)$$

$$\text{VIII} + Br\cdot \longrightarrow \text{II} + O_2 \qquad (7b)$$

$$\text{VII} \longrightarrow PhCH{=}CHBr + \cdot SO_2Cl \qquad (8)$$

$$\cdot SO_2Cl \longrightarrow SO_2 + Cl\cdot \qquad (9)$$

$$PhCH{=}CHBr + Cl\cdot \longrightarrow PhC\underset{\cdot}{H}CHBrCl \qquad (10)$$

$$P\underset{\cdot}{h}CHCHBrCl + Br_2 \longrightarrow \text{IV} + Br\cdot \qquad (11)$$

$$PhCH{=}CHBr + Br_2 \longrightarrow \text{V} \qquad (12)$$

$$Br\cdot + O_2 \longrightarrow BrO_2\cdot \qquad (13)$$

$$2\,BrO_2\cdot \longrightarrow Br_2 + 2\,O_2 \qquad (14)$$

The bromine atom is believed to add to I in the direction shown, since VII should be more stable than the isomeric radical because of resonance in-

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[7] de la Mare and Robertson, *J. Chem. Soc.*, 2838 (1950), give a summary of Robertson's extensive work.

[8] Berthoud, *Helv. Chim. Acta*, **13**, 3851 (1930); Berthoud and Nicolet, *J. chim. phys.*, **25**, 40 (1928).

volving the ring.[9] The formation of the alkylperoxy radical VIII (Eqn. 6) parallels many similar reactions; VIII has been included in the reaction sequence to account for the retardation by oxygen and its effect on products. Eqns. 13 and 14 may be involved at high oxygen concentrations.

The displacement of oxygen from VIII by molecular bromine (Eqn. 7a) appears to be without precedent; it is suggested to provide a chain-carrying radical which the alternative path 7b does not. A choice between Eqns. 7a and 7b could be made when information on chain lengths and quantum yields becomes available.

The alkylperoxy radical VIII is longer-lived than the carbon radical VII from which it is formed, and it provides an opportunity for a bromine molecule or atom to complete the formation of III. In the absence of oxygen, VII dissociates with loss of the sulfur function. Olefin formation by elimination from a radical has been proposed in a similar case.[10] The formation of IV may follow the consecutive steps indicated by Eqns. 8–11, or the first three may be telescoped into a simultaneous process occurring within the solvent cage, following which reaction 11 propagates the chain.

The above mechanism provides a possible explanation of the influence of oxygen upon the rate of photobromination of I and its profound effect upon the nature of the products. An alternative suggestion is that the cleavage products and II are formed by separate paths, the former by an ordinary radical chain which can be inhibited by oxygen (Eqns. 8–12) and the latter by an ionic path (perhaps catalyzed by sulfur dioxide) or a non-chain radical path. A quantitative study of the effect of a range of controlled oxygen concentrations on the products and rate may permit a distinction among the various possibilities.[11]

Reaction in acetic acid. The *initial* rate[13] of photobromination at room temperature is given by Eqn. 3. A possible mechanism is:

$$\mathrm{Br_2 + h\nu \longrightarrow 2\,Br^{\cdot}} \qquad (2\phi \mathrm{I_a}) \qquad (4)$$

$$\mathrm{I + Br^{\cdot} \longrightarrow VII} \qquad (\mathrm{k_2}) \qquad (5)$$

$$\mathrm{VII + Br_2 \longrightarrow II + Br^{\cdot}} \qquad (\mathrm{k_3}) \qquad (15)$$

$$\mathrm{2\,Br^{\cdot} \longrightarrow Br_2} \qquad (\mathrm{k_4}) \qquad (16)$$

Making the usual steady-state approximation that $\mathrm{d[Br\cdot]/dt = d[VII]/dt = 0}$, and that reaction 15 is rate-limiting, this reduces to

$$-\mathrm{d[I]/dt = k_3[VII][Br_2]} = (2\phi \mathrm{I_a/k_4})^{1/2}\mathrm{[I]k_2}$$

or

$$-\mathrm{d[I]/dt = k[I]I_a}^{1/2}$$

This equation agrees with the experimentally observed Eqn. 3. Had a more usual chain-terminating step been assumed instead of Eqn. 16, for example 2 VII → II + I, or 2 VII → 2 I + Br, the steady-state treatment would have led to an expression with first-order dependence on bromine and zero-order on I, contrary to observation.

The reasons for the decrease in rate after the initial reaction are not now understood. The most reasonable explanation is that one of the products of the reaction functions as a chain breaker, most likely at the surface of the vessel. Although the kinetic data might be interpreted in terms of a reversible reaction, the product analyses made on runs which had gone to completion did not disclose detectable amounts of unreacted I; most of the starting material appeared as II, IV, and V.

The relative insensitivity of product composition to conditions suggests that the intermediate radical VII is stabilized by solvation in acetic acid to a considerable extent. Thus oxygen may not be essential to prolong the life of the radical until it can make an effective collision with a bromine molecule.

EXPERIMENTAL[14]

Bromination of 2-phenylethene-1-sulfonyl chloride (I) *in carbon tetrachloride. Dark reaction.* Solutions of I and bromine (each 0.1–0.2 *M*) in carbon tetrachloride were stored in the dark. They were compared visually at intervals with a solution of bromine in carbon tetrachloride of equal concentration. After two days, decolorization was barely perceptible; the bromine color had disappeared completely in 10–20 days. Use of commercial bromine and carbon tetrachloride roughly doubled the rate.

Solutions of I were deoxygenated by bubbling nitrogen through them before and after adding the bromine. The flasks were wrapped in aluminum foil, stoppered, and stored in the dark. No decolorization was apparent in 2 days, judged visually by comparison with a blank standard.

Photobromination of I. A series of runs was made, each with 10.1 g. (0.05 mole) of I from the same batch of material, 8.2 g. (0.051 mole) of bromine from the same bottle, and 200 ml. of carbon tetrachloride from the same lot. The reaction vessels were 300-ml. standard-taper round-bot-

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[9] The limited ability of the sulfonyl group to become involved in resonance is attested by the reluctance of vinylsulfonyl compounds to polymerize, by the failure of the Meerwein reaction with 2-phenylethenesulfonic acid, and by the feeble *ortho-para* directing influence of the sulfonyl group in free radical phenylation of methyl benzenesulfonate. These factors are discussed by Rondestvedt and Blanchard, *J. Org. Chem.*, **21**, in press (1956).

[10] Sah and Brown, *Record Chem. Progress*, **9**, 81 (1948).

[11] The effect of oxygen upon photobrominations of saturated hydrocarbons is notably complex.[12] Low pressures of oxygen *accelerated* the photobrominations of cyclohexane, methylcyclohexane, and isobutane, although high pressures retarded them. The combined effects of oxygen and light were much greater than the sum of the individual effects.

[12] Kharasch, Hered, and Mayo, *J. Org. Chem.*, **6**, 818 (1941).

[13] Since only initial rates were studied, a correlation with product composition cannot be made.

[14] Microanalyses by Anna Griffin in these Laboratories and by Spang Microanalytical Laboratory, Plymouth, Michigan. Spectra were measured in a Beckman Model DU Spectrophotometer in silica cells. Isoöctane was Phillips Spectral Grade; bromine, acetic acid, and carbon tetrachloride were Baker & Adamson Reagent Grade, unless otherwise specified. The preparation of I has been previously described.[15]

tomed Pyrex flasks. After irradiation, the solvent was evaporated at room temperature with a water aspirator, and the residue was pumped at 1 mm. (room temperature) for 2 hours.

In three runs, nitrogen was bubbled through the solution before and after the addition of the bromine. When the flasks were exposed to room fluorescent lights, decolorization of the bromine occurred in 5–15 minutes with evolution of some heat. Gas pressure, with the odor of sulfur dioxide and hydrogen chloride, was evident on removal of the stopper. In two of these runs made in 300-ml. Pyrex flasks, the decolorization occurred first at the surface of the liquid, indicating possibly the presence of a trace of oxygen in the gas phase. To the third run was added enough carbon tetrachloride to fill the flask to the neck before the nitrogen purging; decolorization was practically uniform throughout the solution.

After solvent removal, the residues were treated with 0.05 mole of triethylamine in ether at 0°, washed with dilute acid and water, dried, and distilled.[3,16] There was obtained 50–60% of mixed IV and V (calc'd as IV); a little IIIa was obtained as a higher-boiling fraction which solidified partially (1.5–2.5 g.). The tarry pot residue weighed 2–3 g.

Other experiments were conducted with the solutions in contact with the atmosphere. Under fluorescent lights, decolorization required 7–10 hours. After solvent removal and treatment of the residue with triethylamine, distillation gave 40–50% of a mixture of IV and V, and 18–30% of IIIa after crystallization of the higher-boiling fraction. In a similar run with commercial carbon tetrachloride and commercial bromine, the yield of IIIa was 38%.[17] The crude residue before triethylamine treatment contained 5.65 (duplicate 5.90) % S [calc'd for $C_8H_7Br_2ClO_2S$ (II): S, 8.8.]

When solutions in contact with the atmosphere were irradiated strongly with a 75-watt spotlight or a 150-watt incandescent bulb, decolorization of the bromine was much more rapid. The residues after solvent removal contained no sulfur, and no IIIa could be isolated after triethylamine treatment. The yields of the mixture of IV and V varied from 50–77%.

A run was made in which oxygen was bubbled through the solution of I for 10 minutes before addition of the bromine. Under fluorescent lights, the surface layer decolorized rapidly (15 minutes). When the flask was swirled, this effect was not repeated. Decolorization was complete only after 18 hours. The yield of IIIa was 38%, and of mixed IV and V, 40% calc'd as IV.

In two other experiments, the solutions were saturated with oxygen and a very slow stream of oxygen was bubbled through and allowed to escape against a head of 10–15 mm. of mercury. The first was irradiated only with ceiling fluorescent lights; the second was also exposed to a 75-watt spotlight 9 inches away (center to center). Both runs were maintained at room temperature. The first became pale orange in 28 hours, the second in 3 hours. The residues after solvent removal gave strong tests for peroxide. After treatment with triethylamine, the first gave 20% of IIIa and 36% of mixed IV and V; the second gave no IIIa and 69% of IV and V, both calc'd as IV.

Pure 1,2-dibromo-1-chloro-2-phenylethane (IV) and 1,1,2-tribromo-2-phenylethane (V) were synthesized for reference in quantitative yields by addition of bromine to β-chlorostyrene and β-bromostyrene.[18] Their properties were, respectively, $n^{23}D$ 1.6094 and 1.6346, and b.p. 118–120° (2.8 mm.) and 122–123° (0.8 mm.). The mixtures of IV and V obtained in this work boiled at 120–132° (1–2 mm.). Experiments with pure IV and V showed that neither reacted with triethylamine in ether at 0° in 0.5 hour and that reaction at room temperature was very slow. In contrast, crude II reacted vigorously at 0°.

Bromination of I in acetic acid. Dark reaction. The dark reaction at 36° was shown to be negligible by maintaining a solution 6.25 millimolar in bromine and 1.0 millimolar in I at this temperature for 22 hours. The change in optical density at 2700 Å. was zero within the experimental error. A similar experiment containing also 18.7 millimolar lithium bromide showed no change in 21 hours at 20°.

In another experiment, 5.0 g. (0.025 mole) of I and 4.0 g. (0.025 mole) of bromine in 50 ml. of glacial acetic acid was stored in the dark at 55°. After 24 hours, iodometric titration showed the consumption of 75% of the bromine. After 14 days, the solvent was removed at room temperature and the residue was pumped at 0.1 mm. for 3 hours. The product consisted of two layers, the upper weighing 1.02 g. and the lower 7.87 g. The upper layer darkened fairly rapidly on standing at room temperature; it was largely water-soluble and strongly acidic. The lower layer was pale yellow, water-insoluble, and contained almost no water-soluble acidic material; sulfur was present. Analysis of the lower layer (C, 29.41; H, 2.35) indicated that it was a mixture of II with IV and/or V.

Bromination of I in acetic acid. Moderate light. A solution of 5 g. (0.025 mole) of I and 5 g. (0.031 mole) of bromine in 50 ml. of acetic acid in a stoppered round-bottomed flask was kept under fluorescent lights. After 24 hours, 66% of the bromine had been consumed (iodometry). After 14 days, the volatiles were removed at room temperature (0.1 mm.), leaving two phases (the upper 5%, the lower 95% by weight) with properties similar to those in the preceding section. A sample of the lower layer was treated with excess liquid ammonia in dry ether, giving 41% (based on I) (after crystallization from water) of IIIb, m.p. 131–132°, identical with an authentic sample.[3] Another sample of the lower layer was heated for several hours with aqueous sodium hydroxide solution. Half of the material did not dissolve; the insoluble portion did not contain sulfur (permanganate oxidation), but the soluble portion did. Another sample of the lower layer was subjected to short-path distillation at 80° (0.2 mm.); 50% of the weight distilled as a mixture of IV and V, $n^{23}D$ 1.6220, containing no sulfur.

In a similar experiment, the reaction flask was cleaned before use with dichromate-sulfuric acid mixture, rinsed and dried at 120°. The reaction consumed 87% of the bromine in 24 hours. Apart from the difference in rate, the products were almost identical.

Bromination of I in acetic acid. High light intensity. A solution of 5 g. (0.025 mole) of I and 4 g. (0.025 mole) of bromine in 50 ml. of acetic acid was irradiated with a 75-watt spotlight three inches from the flask. The temperature rose to 57°. Decolorization occurred first at the surface of the solution, which was swirled periodically during the 2 hours required for complete decolorization. Removal of the solvent gave two phases similar to those obtained above. In another experiment in more dilute solution, the infrared rays were screened out by a copper chloride filter; with a reaction temperature of 20°, decolorization was complete in 2 hrs. The products were similar to those above.

Chlorination of I in acetic acid. A stream of chlorine was bubbled for one hour through a solution of I in acetic acid at room temperature. Room lights were on during this experiment. After standing overnight, the solvent was removed *in vacuo* leaving a colorless oil whose analysis corresponded

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(15) Rondestvedt and Bordwell, *Org. Syntheses*, **34**, 85 (1954).

(16) In another run, an attempt to distill the residue without triethylamine treatment resulted in very extensive decomposition.

(17) The 82% yield reported previously[3] was obtained with a different batch of I and different lots of commercial carbon tetrachloride and bromine. A little iodine had also been added. Four other runs made at that time without iodine gave yields of 65–76% of IIIa. The discrepancy between those earlier results and the present experiments may have resulted from trace impurities or from some other unknown factor.

(18) Biltz, *Ann.*, **296**, 272 (1897).

to an equimolar mixture of VI and 1,2-dichloro-2-phenylethane-1-sulfonyl chloride.

Anal. Calc'd for $C_8H_7Cl_3$: C, 45.85; H, 3.37. Calc'd for $C_8H_7Cl_3O_2S$: C, 31.44; H, 2.31. Found: C, 38.77; H, 2.77.

Chlorination of I in carbon tetrachloride. A solution of 10.1 g. (0.05 mole) of I in 125 ml. of carbon tetrachloride was treated with chlorine until the weight increase was 3.6 g. (0.05 mole). There was no change in the pale green color on standing under fluorescent lights for 8 hours, but when the flask was irradiated with an ultraviolet lamp, the mixture rapidly came to a boil. The mixture was cooled and irradiated for two hours, whereupon the color of chlorine disappeared. The solvent was evaporated and the residue was distilled. The product (VI) weighed 9.0 g., 86%, b.p. 84–85° (1.4 mm.);[19] sulfur was absent.

Anal. Calc'd for $C_8H_7Cl_3$: C, 45.86; H, 3.37; Cl, 50.77. Found: C, 45.36; H, 3.55; Cl, 49.47.

In a second experiment, the lamp was kept far enough away so that the flask temperature did not exceed 35°. The chlorine color disappeared in 3 hours, and the yield of VI was 8.7 g. In both experiments, there was only a trace of undistillable residue, indicating that the dichloride of I could not have been present in appreciable amount.

Bromination of I in carbon tetrachloride. Rate study. The solutions were prepared in 25 ml. Pyrex volumetric flasks. They were clamped in a water thermostat (±0.05) made from a Pyrex jar and illuminated through the wall with a 50-watt incandescent bulb. After verifying the fact that solutions of bromine in carbon tetrachloride obeyed Beer's Law over the concentration range of interest, samples were withdrawn at intervals and the bromine concentration was determined spectrophotometrically at 4360 Å.

Bromination of I in acetic acid. Rate study. A large Pyrex test tube[20] with a standard taper joint was clamped in a glass-walled thermostat. The solution was stirred through a Trubore bearing with a spiral stirrer in the ascending direction (stirring was essential for reproducible results). The same light bulb was used for all runs in a series, and its output was held constant with a constant-voltage transformer; the output was checked periodically with a barrier-layer cell and a microammeter.

The dependence upon light intensity was established without a thermostat, since the temperature dependence is very small near room temperature. Checks showed only a small variation in temperature as the light source was moved from 37 cm. to 10 cm. (center of bulb to center of reaction vessel). The product of initial rate and distance was constant for *d* from 37 cm. to 15 cm., as expected for $I_a^{1/2}$ dependence and the inverse square law. A sharp increase in rate appeared at $d = 10$ cm.

Analysis for the extent of reaction was made by diluting aliquots of the solution with isoöctane, allowing the mixture to stand several minutes until the bromine had been consumed by reaction with the isoöctane (or impurities in it), and measuring the optical density at 2700 Å. The optical densities were plotted against time and extrapolated to zero time to determine the initial rate.

It was demonstrated that the further photobromination of IIIa was very much slower than the photobromination of I. The difference is at least two powers of ten, although accurate results were not sought. The oxygen effect was not investigated.

Acknowledgment. The authors are indebted to Professor Richard B. Bernstein for many helpful suggestions concerning experimental methods, and to Drs. Frank R. Mayo and Glen A. Russell for stimulating discussions.

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[19] Biltz, *Ann.*, 296, 267 (1897), reported b.p. 134° (19 mm.) for VI.

[20] The vessel was cleaned by soaking for 8 hours in chromic acid solution. Then it was rinsed thoroughly with distilled water and steamed for at least four hours by passing steam into the inverted tube. In the early work, in which Alconox was used for cleaning, followed by water rinsing, the results were poorly reproducible.