chloroform or less polar solvents. Chromatographic purification always lead to the formation of the two geometrical isomers.

**Method B.**—The selenadiazole was dissolved in 10% KOH or potassium ethoxide in ethanol. The reaction product was purified as described in method A.

**2,ω-Di-*tert*-butyl-1,4-diselenafulvene.**—4-*tert*-Butyl-1,2,3-selenadiazole (0.5 g, 2.6 mmol) was dissolved in 10 ml of 95% ethanol and a pellet of KOH was added. After the gas evolution had ceased water was added and extracted with chloroform. The chloroform layer after drying was evaporated to yield 0.3 g (72%) of an oil: nmr ($CCl_4$) 6.45 (s, 1 H), 5.90 (s, 1 H), 1.20 (s, 9 H), 1.10 (s, 9 H); upon standing for some times 6.45 (s, 0.5 H), 6.44 (d, $J$ = 1.5 Hz, 0.5 H), 5.97 (d, $J$ = 1.5 Hz, 0.5 H) 5.90 (s, 0.5 H), 1.29 (two lines, 9 H), 1.10 (two lines, 9 H). Repeated recrystallization from acetone gave a product: mp 78–80° (*Anal.* Calcd for $C_{12}H_{20}Se_2$: C, 44.72; H, 6.21. Found: C, 44.81; H, 6.02.); nmr ($CCl_4$) 6.44 (d, $J$ = 1.5 Hz, 1 H) 5.97 (d, $J$ = 1.5 Hz, 1 H), 1.21 (s, 9 H) 1.10 (s, 9 H); mol wt (mass spectrum) *m/e* 324.

**2,ω-Diphenyl-1,4-diselenafulvene.**—4-Phenyl-1,2,3-selenadiazole (2.2 g, 0.01 mol) was dissolved in about 15 ml of ethanol, and a few pellets of KOH were added. Upon heating the solution slightly, gas evolution commenced. Yellowish crystals began to separate when gas evolution ceased. These crystals, ir (KBr) 912 (w), 900 (w), 890 (m), 821 (w), 846 (w), 840 (m), 835 (s), 692 (m), 512 $cm^{-1}$ (m) (yield 1.5 g, 90%; another 0.1 g of material could be obtained from the mother liquor by trituration with water), had mp 139–140° and upon cooling and reheating melted at 219–220°: ir (KBr) 890 (m), 832 (m), 820 (m), 735 (s), 682 (s), 510 $cm^{-1}$ (s); uv (EtOH) 340 nm ($\epsilon$ 1.8 × $10^4$) (*Anal.* Calcd for $C_{16}H_{12}Se_2$: C, 53.04; H, 3.32. Found: C, 52.85; H, 3.06.); mol wt (mass spectrum) *m/e* 364.

**2,ω-Diisopropyl-1,4-diselenafulvene.**—4-Isopropyl-1,2,3-selenadiazole (1.0 g, 5.7 mmol) was dissolved in 10 ml of 95% ethanol, and a few pellets of KOH were added. After gas evolution had ceased, water was added and the solution was extracted with chloroform. From the chloroform extracts 0.6 g (79%) of an oil was isolated. The oil was purified on silica gel plates using petroleum ether as solvent, nmr shown in Figure 1, mol wt (mass spectrum) *m/e* 296. The nmr of the oil without purification on silica gel and obtained immediately after the reaction is shown in Figure 2.

**Potassium 2-Phenylethyneselenolate.**—4-Phenyl-1,2,3-selenadiazole (0.5 g, 2.4 mmol) was added to a solution of 50 mmol of potassium ethoxide in 50 ml of dioxane containing 2 ml of ethanol. After the gas evolution had ceased the precipitate was filtered under a dry atmosphere and washed with dry ether to give the white potassium salt, ir (KBr) 2200 $cm^{-1}$, uv (EtOH) 308 mm ($\epsilon$ 2.1 × $10^4$). This salt, which was always formed contaminated with, apparently, some potassium ethoxide (the weight of material isolated was always more than the theoretically calculated amount and the percentage of potassium in the sample was variable, but always in excess of that calculated) rapidly turned yellow on standing in moist air. Dissolution of this salt in 10 ml of ethanol gave 0.42 g (99% based on 4-phenyl-1,2,3-selenadiazole) of III, mp 139–140°.

**Registry No.**—*cis*-III (R = Bu), 36912-13-7; *trans*-III (R = Bu), 36912-17-1; *cis*-III (R = Ph), 36912-14-8; *trans*-III (R = Ph), 36912-18-2; *cis*-III (R = *i*-Pr), 36912-15-9; *trans*-III (R = *i*-Pr), 36912-16-0; potassium 2-phenylethyneselenolate, 36928-61-7; 1,2,3-selenadiazole, 26223-16-5.

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# Sensitized Photolyses of DDT and Decyl Bromide

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*Received May 5, 1972*

The photolysis of alkyl halides can be sensitized by aromatic amines in oxygenated or degassed solutions. The photoproducts from irradiation of diethylaniline in the presence of decyl bromide in cyclohexane are decane (22.7%), *N*-ethylaniline (3.6%), *o*-decyl-*N*,*N*-diethylaniline (48.5%), *p*-decyl-*N*,*N*-diethylaniline (30.8%), and diethylaniline hydrobromide (88%). Similar yields are formed in solvents methanol, dimethylformamide, and benzene and the quantum yields for decyl bromide disappearance are similar to the value of 0.19 found for methanol solution. This photolysis is not quenched by oxygen or piperylene and decyl bromide photolysis is not sensitized by benzophenone. This implicates the excited singlet state of diethylaniline as the first reactive intermediate. A mechanism involving decyl radicals is proposed. Diethylaniline also sensitizes DDT degradation. In aerated methanol the following photoproducts are formed: DDD, DDE, DDCO, diethylaniline hydrochloride, methyl 1,1-bis(*p*-chlorophenyl)acetate, *cis*- and *trans*-1,1,4,4-tetrakis(*p*-chlorophenyl)-2,3-dichloro-2-butene, 1,1-bis(*p*-chlorophenyl)-2-(*p*-diethylaminophenyl)-2-methoxyethylene, and 1,1-bis(*p*-chlorophenyl)-2,2-bis(*p*-diethylaminophenyl)ethylene. Mechanistic hypotheses involving the 2,2-bis(*p*-chlorophenyl)-1,1-dichloromethyl radical are given. It is shown that in degassed solutions of DDT in ethanol or cyclohexane a radical chain reaction is initiated by 310-nm light which efficiently converts DDT to DDD. This reaction can be inhibited by dibutyl sulfide or hexyl mercaptan, and is quenched by oxygen. Oxygen quenching may explain the inefficiency of DDT degradation by sunlight.

It has been observed that aromatic amines can induce the photodecomposition of alkyl halides.[1-4] It seemed that this process might be applicable to halogenated pesticide degradation. We have, therefore, initiated a study of pesticide photolyses with particular attention to sensitization. It was hoped that new designs for degradable pesticides[5] and information about natural degradation pathways would result.

This paper reports results which enucleate this problem. Thus we have explored the feasibility of degrading the persistent pesticide DDT with several photosensitizers both under air and under nitrogen and we have studied the photolysis of a simple alkyl halide in order to gain more mechanistic insight into the processes available to halogenated pesticides.

The photosensitization of pesticide degradation has not escaped attention by other chemists. Casida and Ivie[6] placed mixtures of known photosensitizers and pesticides on silica gel and found that several pesticides, including halogenated compounds, were degraded in sunlight. They also investigated the solar decomposition of chlorinated pesticides on bean leaves as accelerated by rotenone, triphenylamine, and other insecticides.

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(1) L. L. Miller and R. S. Narang, *Science*, **169**, 368 (1970).

(2) W. C. Meyer, *J. Phys. Chem.*, **74**, 2118 (1970).

(3) E. A. Fitzgerald, P. Wuelfing, and H. H. Richtol, *ibid.*, **75**, 2737 (1971).

(4) M. Kondo, M. R. Ronayne, J. P. Guarino, and W. H. Hammill, *J. Amer. Chem. Soc.*, **86**, 1297 (1964).

(5) H. J. Liu, P. J. Silk, and J. Unger, *Can. J. Chem.*, **50**, 55 (1972).

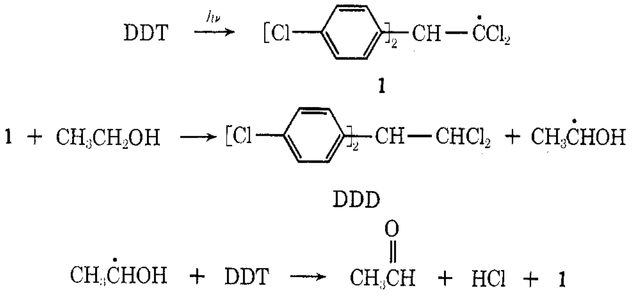
(6) G. W. Ivie and J. E. Casida, *Science*, **167**, 1620 (1970); G. W. Ivie and J. E. Casida, *J. Agr. Food Chem.*, **19**, 405 410 (1971).

The sensitized photodecomposition of chlorinated cyclodienes has received considerable attention.[7-10] The reaction can be sensitized by transfer of triplet energy and results primarily in photoisomerization. Other chlorinated pesticides which have been decomposed by photosensitization include 2,4-dichlorophenol.[11]

The direct photolysis of DDT at 254 nm has been studied by several groups.[12-14] An extensive elucidation of the products formed during irradiation in oxygenated methanol has been performed by Plimmer and coworkers.[14] Some 17 products were identified, most of which directly involved trapping of radical intermediates by oxygen. A mechanistic rationale for several of these products was advanced which involved initial cleavage of a carbon–chlorine bond. This scheme followed an earlier mechanism suggested[13] for the formation of DDD, DDE, and 4,4′-dichlorobenzophenone (DDCO) from DDT during photolysis at 254 nm. In that study radical scavenging results were obtained which indicated the unimportance of chain processes during photolysis in hexane and the precursorial role of radical **1** to DDD. These schemes are, however, largely speculative and the photophysical chemistry involved has not received attention.

## Results and Discussion

**DDT Photochemistry.**—The photolysis of DDT at 310 nm in a nitrogen atmosphere affords only DDD and HCl. The reaction in either ethanol or cyclohexane seems to involve a radical chain mechanism. This mechanism was suggested by Sherman[15] for $\gamma$ radiations of DDT in alcohol and is similar to photoinitiated chain reactions between amines and carbon tetrachloride.[16] Addition of hexyl mercaptan ($5 \times 10^{-3}$ $M$) to an irradiation of $10^{-3}$ $M$ DDT in ethanol slowed the rate by about a factor of 10. DDD was still the product. This behavior has been taken as evidence for inhibition of a DDT–alcohol chain reaction[15] *via* the following chain transfer and termination steps.



$$1 + RSH \longrightarrow DDD + RS\cdot$$

$$2RS\cdot \longrightarrow RSSR$$

It seems likely that this is also involved here, since the above chain reaction explains the stability of DDD. In contrast to DDT, reaction of ethanol radicals with DDD should not give chlorine atom transfer, but instead hydrogen atom transfer in analogy with chloroform, if it reacts at all. Thus, DDD is not dechlorinated.

$$DDD + CH_3\dot{C}HOH \longrightarrow 1 + CH_3CH_2OH$$

There is, however, an additional inhibition mechanism open to hexyl mercaptan, since sulfur compounds can quench excited states.[17] We found DDT photolysis to be slowed by a factor of about 3 by addition of $10^{-3}$ $M$ dibutyl sulfide. This sulfide is not a good radical scavenger and demonstrates the duality of quenching mechanisms. This study has reconfirmed that such drastic mercaptan inhibitory effects are not noted if DDT is photolyzed in hexane[13] or in ethanol at 254 nm. There is apparently more direct photolysis occurring under these conditions and the products are more complex.[13,14]

We find that, while photolysis at 310 nm is quenched by oxygen or by $5 \times 10^{-2}$ $M$ piperylene, photolysis at 254 nm is not quenched by oxygen.[14] This again indicates the wavelength dependence of DDT photochemistry. There are two bands in the absorption spectrum of DDT and it appears that photolysis at 254 nm involves a singlet after excitation in the band $\lambda_{max}$ 256 nm while 310-nm photolysis yields a triplet after excitation in the band $\lambda_{max}$ 270 nm.

Quenching of solar wavelength photochemistry by oxygen is an important discovery, since it may explain the long lifetime of DDT in the environment. DDT absorbs solar light and is photoreactive, but the reaction can be quenched by atmospheric oxygen.

**DDT–Diethylaniline Photochemistry.**—An initial goal of this research was to sensitize DDT photolysis in air with light of solar wavelengths. Unfortunately, sensitization by triplet energy transfer is generally ineffective in the presence of oxygen and indeed benzophenone does not effect DDT decomposition in undegassed samples. It has been found, however, that a variety of aromatic amines are effective sensitizers in air for alkyl halides including DDT.[1] The reaction of DDT and diethylaniline at 310 nm in methanol was chosen for more careful investigation. This reaction in air has a quantum yield of 0.30 at conversions of 5–15%. Longer irradiation times will destroy more than 85% of the DDT but the rate slows down. This may be related to the fact that the absorptivity of the reaction mixture at 310 nm is essentially invariant during the reaction. Diethylaniline is being consumed, but the products absorb at this wavelength and may account for the apparent quantum yield decrease with time.

The following decomposition products from an 8-hr, 310-nm irradiation of DDT (12 g) and diethylaniline (12 g) in 500 ml of methanol were identified by glc retention times and mass spectra or by chromatographic separation and spectral characterization: DDD, DDE, DDCO, diethylaniline hydrochloride, methyl 1,1-

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(13) A. R. Mosier, W. D. Guenzi, and L. L. Miller, *Science*, **164**, 1083 (1969).

(14) J. R. Plimmer, U. I. Klingebiel, and B. E. Hummer, *ibid.*, **167**, 67 (1970).

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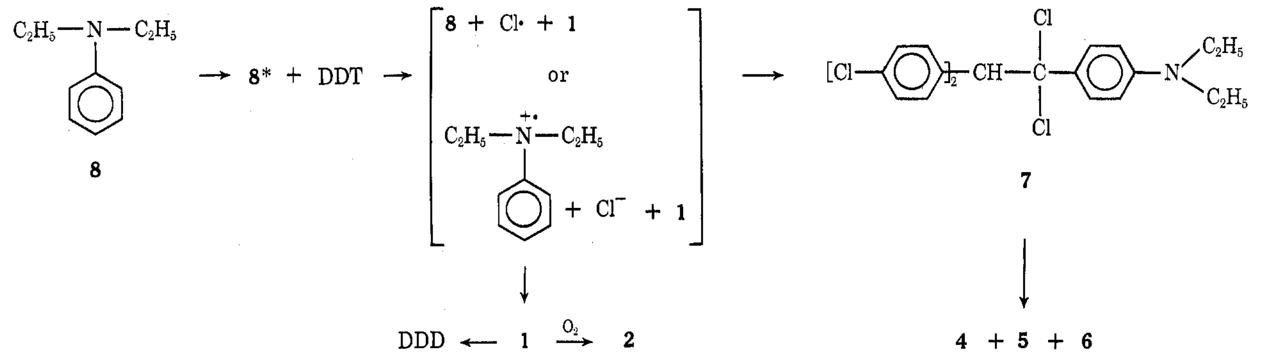
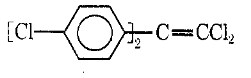
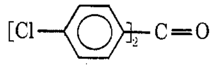
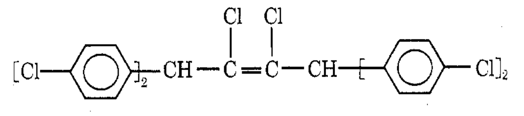


(1)

bis(*p*-chlorophenyl)acetate (**2**), *cis*- and *trans*-1,1,4,4-tetrakis(*p*-chlorophenyl)-2,3-dichloro-2-butene (**3**), $\alpha,\alpha$-bis(*p*-chlorophenyl)-*p*-diethylaminoacetophenone (**4**), 1,1-bis(*p*-chlorophenyl)-2-(*p*-diethylaminophenyl)-2-methoxyethylene (**5**), and 1,1-bis(*p*-chlorophenyl)-2,2-bis(*p*-diethylaminophenyl)ethylene (**6**).


DDE


DDCO


*cis*- and *trans*-**3**

DDE, DDD, and ester **2** are the products present in highest analyzable yield, since separation of the other components is extremely tedious. A combination of glc and nmr analysis of an unchromatographed product mixture indicated the yields in Table I based on the initial amount of DDT. Considering the other products recovered, about 70% of the reacted DDT is accounted for. DDD and DDE are not stable to the reaction conditions, as demonstrated by independent photolyses in the presence of diethylaniline. Therefore, they do not build up during the reaction.

Table I

Product Yields[a] from Diethylaniline–DDT Photolysis in Methanol

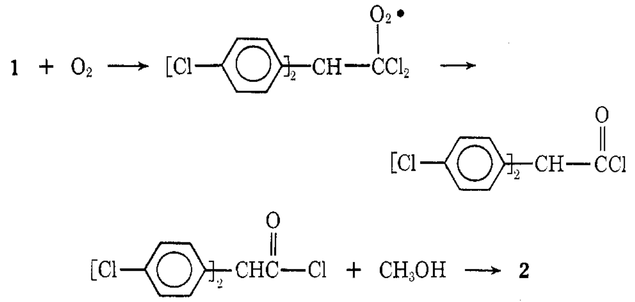
| Time, hr | % DDT consumed | % DDD | % DDE | % **2** |
|---|---|---|---|---|
| 0.5 | 22 | 5 | 2 | 3 |
| 1 | 37 | 6 | 5 | 6 |
| 2 | 54 | 6 | 9 | 9 |
| 7 | 72 | 6 | 8 | 23 |

[a] Yields based on the initial amount of DDT; 0.32 mmol of DDT and 0.64 mmol of diethylaniline in 4 ml of methanol were irradiated in each of four tubes.

Two dimeric compounds were isolated. One of these, mp 235°, had the same properties as a compound formed in the direct photolysis of DDT at 254 nm.[13] An isomeric compound, mp 278°, with an essentially similar mass spectrum was also isolated. These products are *cis*- and *trans*-**3**.

Only limited mechanistic conclusions can be drawn about this process because of the complexity of the reaction products and the unelucidated role of oxygen and chain reactions. It is suggested that since the reaction proceeds in air and is not quenched by piperylene ($10^{-2}$ *M*), an excited singlet diethylaniline (**8***) is involved. **8*** can produce **1** by reaction with DDT and this radical can then lead to the observed products *via* hydrogen abstraction, disproportionation, reaction with oxygen, or coupling (eq 1).

Transformation of **1** into DDD, DDE, and DDCO may involve previously proposed pathways.[13] The formation of ester **2** seems to involve oxygen and methanol and may be related to the chemistry observed in the irradiation of aromatic amines and chloroform in air.[3,18] Electron transfer was invoked in this reaction followed by trapping of dichloromethyl radicals by oxygen to produce phosgene. The analog for DDT would be



If peroxy radicals are involved, the complexity of the reaction is necessarily increased, since these radicals can in turn produce alkyl and alkoxy radicals, initiate chain reactions, and dimerize.

Three products involve coupling between diethylaniline and DDT in analogy with results found for the simple alkyl halide, decyl bromide. These may arise *via* dihalide **7**, which will be extremely labile. Photochemically it could lead to substitution of a second diethylaniline moiety, thus compound **6**, or to **4** by reaction with oxygen. The diethylaniline function in **7** also activates the halides toward chemical reaction[19] and **5** could be formed by methanolysis.

It is important to iterate that the reaction of aromatic amines with DDT is not quenched by oxygen and could provide interesting environmental chemistry. This reaction is general for organic halides and should, therefore, be applicable to a variety of pesticides. It has been shown, for example, that triphenylamine sensitizes degradation of Dieldrin and Aldrin in air.[20]

**Sensitized DDT Photolysis in Degassed Solution.—**

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[18] See K. Thomas, C. Huybrechts, and J. Olbregts, *Trans. Faraday Soc.*, **63**, 1647 (1967), and A. T. Chapman, *J. Amer. Chem. Soc*, **54**, 3852 (1932), for photolytic mechanisms of acyl chloride formation from oxygen and trichloromethyl groups.

[19] S. Patai, Ed., "The Chemistry of the Carbonyl Group," Wiley, New York, N. Y., 1966, p 182.

[20] Unpublished work in these laboratories by Mr. Thomas Rogers.

Sensitization of DDT photolysis is extremely interesting. We find that in degassed solution triplet sensitizers with $E_T \geq 59$ kcal/mol effectively sensitize the decomposition of DDT to DDD, while those with $E_T \leq 53$ kcal/mol do not. The sensitizers used were benzophenone, diethylaniline, phenanthrene, 2-acetonaphthone, pyrene, biphenyl, fluoren-9-one, and 7*H*-benz[*d*,*e*]anthracen-7-one. In each case the reaction was run with $10^{-3}$ *M* DDT in *degassed* ethanol at either 350 or 310 nm and the sensitizer absorbed >95% of the light. The same results were obtained in cyclohexane solvent. These data are characteristic of triplet energy transfer. It seems likely that sensitization initiates a chain reaction and that the initiation step could involve an acceptor with $E_T \cong 56$ kcal/mol. A problem with this interpretation is that DDT should not have a triplet with that low an energy and, if it did, it should not decompose to give radical **1**. The carbon–chlorine bond energy is about 70 kcal/mol and, if only 56 kcal/mol are available from the sensitizer, the reaction requires too much extra thermal energy to be effective from a short-lived excited state. More important is the fact that the phosphorescence spectrum of DDT[21] indicates a triplet with $E_T \cong 70$ kcal/mol. This is exactly what is expected from a *p*-chlorotoluene moiety and the carbon trichloride group is expected to be even higher in energy, since benzophenone triplets are not quenched by carbon tetrachloride. Involvement of a DDE impurity was suspected, but DDE photolysis is not sensitized by benzophenone and addition of a little DDE to DDT does not change the reaction rate. A direct generation of radicals from attack on solvent seems improbable, since phenanthrene is an effective sensitizer even in cyclohexane. Singlet energy transfer is also ruled out since it is endothermic for almost all the sensitizers used. Attempted purification of the DDT by recrystallization or zone refining did not change the behavior at all. The nature of initiation by triplet sensitizers, therefore, remains obscure.

Casida and Ivie[6] have previously evaluated the feasibility of sensitizing pesticide photolyses on silica gel tlc plates. It was found that DDT was effectively sensitized by triphenylamine and carbazole and less efficiently sensitized by dibenzothiophene, fluorene, anthraquinone, stilbene, and pyrene. Many other sensitizers, including benzophenone, were ineffective. Comparison of these results with those in solution or on bean leaves[6] indicates that the tlc plate technique is not very informative. It seems likely that the photochemistry of the *adsorbed* sensitizers is important in the latter.

**Sensitized Decyl Bromide Photolysis.**—In order to demonstrate the generality of the photoreaction between aromatic amines and organic halides, several simple halides were decomposed by diethylaniline and 310-nm light in undegassed solutions. Several examples were cited previously[1] and we have shown that *n*-butyl bromide, chloride, and iodide, as well as *tert*-butyl bromide, are destroyed under these conditions. The photoproducts from decyl bromide (**9**) and diethylaniline at 310 nm were investigated as a model system. Most runs were made in closed but not degassed tubes. Glc revealed that a very similar product mixture resulted in solvent methanol, dimethylformamide, benzene, or cyclohexane (Table II). The presence of air or triethylamine also had little effect. The samples were stable in the dark and the individual components did not photolyze alone. Decane (**10**), *N*-ethylaniline (**11**), *o*-decyl-*N*,*N*-diethylaniline (**12**), and *p*-decyl-*N*,*N*-diethylaniline (**13**) were measured by glc. Hydrogen bromide was measured as diethylaniline hydrobromide (**14**). Decane and *N*-ethylaniline were identified by glc retention times and mass spectra. *o*- and *p*-decyl-*N*,*N*-diethylaniline were collected by glc and identified spectrally. Also *p*-decyl-*N*,*N*-diethylaniline was independently synthesized for comparison. The differences in the nmr spectra of these isomers were considered as evidence for their structure. In the ortho isomer the diethylamine group is twisted out of the plane of the ring, causing the aromatic proton signal to collapse to a singlet[22] and the quartet due to the methylene protons to be deshielded.[23]

TABLE II

PRODUCTS OF PHOTOLYSIS OF DECYL BROMIDE AND DIETHYLANILINE

| | Product yields,[a] % | | | | |
|---|---|---|---|---|---|
| Solvent | 10 | 11 | 12 | 13 | 14 |
| Methanol[b] | 8.7 | 1.8 | 51.0 | 33.4 | 63 |
| Dimethylformamide | 13.5 | 2.7 | 56.8 | 28.2 | 69 |
| Benzene | 15.0 | 2.5 | 49.2 | 30.6 | 83 |
| Cyclohexane | 21.7 | 3.6 | 48.5 | 30.8 | 88 |

[a] Yields based on decyl bromide consumed after 36 hr of photolysis. The original solution was 0.345 *M* in decyl bromide and 0.725 *M* in *N*,*N*-diethylaniline. This photolysis in DMF consumed 40% of the decyl bromide. [b] Triethylamine (0.65 *M*) or degassing by freeze–thaw did not significantly change these yields.

One mechanism which accommodates the above products is indicated in eq 2. The diethylaniline, **8**, absorbs all the light at 310 nm indicating an excited state of **8** is involved. Any ground state complexing between **8** and **9** should be weak and, indeed, uv spectrometry shows no evidence for a complex when decyl bromide is added to diethylaniline. The reactive excited state of **8** seems to be a singlet.[19,24] The obvious alternative pathway *via* the triplet is eliminated because the reaction of $10^{-3}$ *M* decyl bromide in degassed benzene is not quenched by $10^{-2}$ *M* piperylene nor by oxygen and is not sensitized by benzophenone. The latter is not surprising, since the alkyl bromide excited state energies should be high.

The products are easily rationalized in terms of this mechanism. Thus, decane seems diagnostic for decyl radicals. Coupling between decyl radicals and diethylaniline cation radicals explains the formation of products **12** and **13** and especially accounts for the preferred formation of the ortho, para isomers. Attack on neutral diethylaniline by decyl radicals should not be nearly so selective. It seems that an initial

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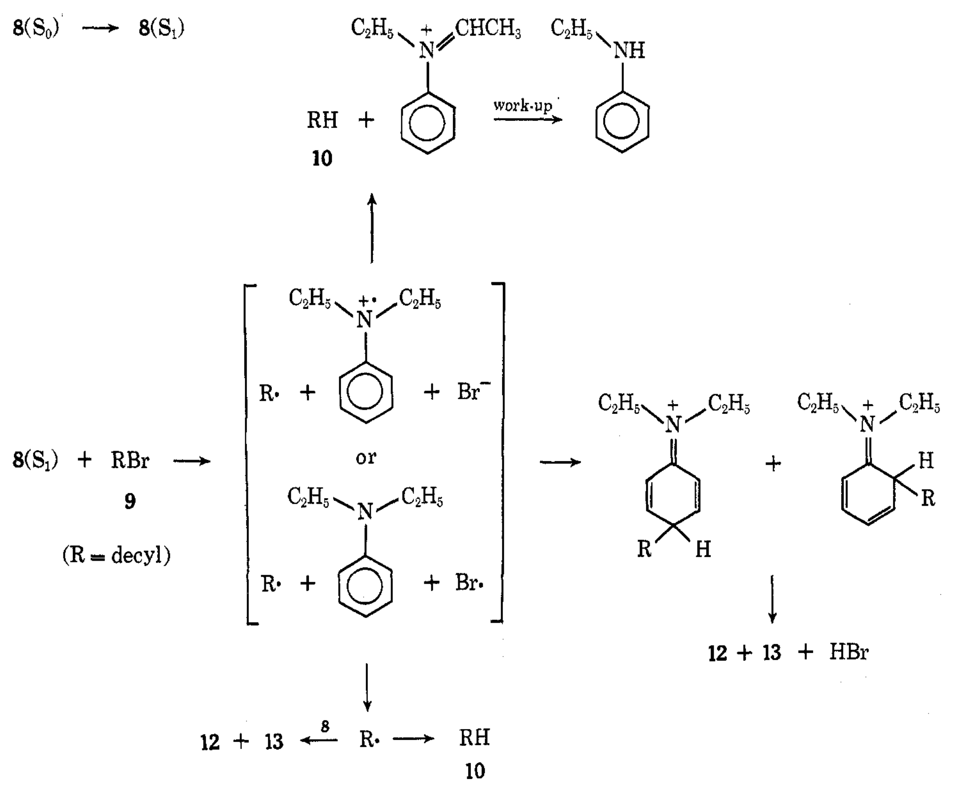
[21] H. A. Moye and J. D. Winefordner, *J. Agr. Food Chem.*, **13**, 516 (1965); emission spectra were also recorded by Dr. C. M. O'Donnell with careful attention to the undetected possibility of a long-wavelength component. The band is, however, extremely broad in comparison to that of *p*-chlorotoluene or chlorobenzene and extends into the region where a 56 kcal/mol triplet would be observed.

[22] W. F. Reynolds and T. Schaefer, *Can. J. Chem.*, **41**, 2339 (1963).

[23] L. Yamaguchi and S. Brownstein, *J. Phys. Chem.*, **67**, 525 (1963).

[24] Other electron transfers *via* excited singlets have been demonstrated. See, for examples, W. Ware and H. P. Richter, *J. Chem. Phys.*, **48**, 1595 (1968); H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1963); G. R. Seely, *J. Phys. Chem.*, **69**, 2779 (1965).



(2)

complex between $8(S_1)$ and **9** must primarily collapse to form **12** and **13** and perhaps **10** before dissociation in order to account for the high yields of coupled products. Free decyl radicals will be rapidly scavenged by oxygen or solvent in competition with coupling. The nature of the initial complex is not known, but is presumed to be similar to that described in similar reactions[25,26] which have been studied by emission spectroscopy and quantitative quenching experiments. The photolysis of mixtures of dimethylaniline and chlorobenzene,[25] for example, produces emission from a species containing both reactants, as well as photoproducts suggestive of charge transfer.

Solvent effects on photoreactions involving electron transfer are of considerable current interest.[27,28] In the present case, the quantum yield for decyl bromide disappearance is rather insensitive to solvent polarity. The relative rates are, cyclohexane, 1.0; benzene, 1.5; methanol, 1.5; dimethylformamide, 1.8. This is perhaps unexpected if the complex involves charge transfer, but, since the singlet may react at near diffusion controlled rates, and because we are measuring the overall quantum yield, the rate data may be irrelevant to mechanistic conclusions without further information.

Since a chain reaction was implicated in some of the DDT chemistry, we have checked this possibility for the reaction between **8** and **9** in methanol. Addition of butyl mercaptan to this photolysis mixture did not substantially change the quantum yield for decyl bromide disappearance of 0.19. It did, however, increase the yield of decane by several per cent. This rules out a chain mechanism, since the radical scavenger would have slowed the overall reaction rate. The difference between the decyl bromide and DDT reactions lies in two factors. One is the relative instability of decyl radicals compared to DDT radical, **1**. The latter is readily formed from DDT and can propagate chain reactions in suitable media. Other differences are due to the aromatic moiety of DDT, which provides a chromophore for direct photolysis and quenchable excited states.

## Experimental Section

**Materials.**—DDT was 99%+ 2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane. Some of this material was also purified by recrystallization and some was zone refined without changing the observed chemistry. Methanol, ethanol, benzene, dimethylformamide, and cyclohexane were reagent grade materials used without purification. Diethylaniline was purified by distillation under nitrogen. Triplet sensitizers were from the J. T. Baker kit and were not purified.

**Photolyses.**—A Rayonet reactor equipped with a bank of 16 254-, 310-, or 350-nm lamps was employed. Except for one large-scale reaction run in a flask and 254-nm photolyses, the samples were held in Pyrex tubes in a merry-go-round apparatus. Degassing was accomplished by a 5 min nitrogen flush or by five freeze–thaw cycles at 0.005 mm.

**Glc Analysis.**—A F & M Hewlett-Packard Model 5750 gas chromatograph equipped with a flame ionization detector was used. Other samples in which DDD was the major (>90%) product were assayed on a Bendix Model 2110 chromatograph with an electron capture detector. The column employed there was Teflon-lined aluminum tubing, 6 ft × 0.25 in., packed with 5% OV-1 on Chromosorb W (60/80 mesh).

**Photolysis of DDT.**—DDT (70.9 mg, 0.005 mmol) in EtOH (200 ml) was irradiated in capped Pyrex tubes (5-ml aliquots). Degassing of samples consisted of a 5-min nitrogen flush or five freeze–thaw cycles at 0.005 mm. Oxygen gas was bubbled through the samples for 5 min before irradiation in the oxygen quenching experiments. In sensitizer experiments the sensitizer concentration was controlled so as to absorb >95% of the irradiation. Glc analysis at 175°, was accomplished by comparing retention times with those of authentic samples.

**Photoproducts from DDT and Diethylaniline.**—DDT (12 g, 33.9 mmol) and diethylaniline (12 g, 80.5 mmol) in methanol (500 ml) were irradiated in Pyrex tubes using a merry-go-round

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for 8 hr. Concentration of the reaction mixture and chromatography on a silica gel column (400 g) was performed, and 1-l. to 1500-ml fractions were collected with the following solvents: fraction A and B with Skellysolve H (SSH), C with $CCl_4$–SSH (1:1), D with $CCl_4$, E with $CCl_4$–benzene (1:1), F with benzene, G with $CHCl_3$, and H with $CHCl_3$ and methanol (9:1). These fractions were concentrated on a rotary evaporator at 40–70°, transferred to 10-ml vials with acetone, and kept at 5° until further analysis.

**Fraction A.**—Glc analysis on column 1, a 6 ft × 0.25 in. glass column packed with 10% DC-200 and 15% QF-1 on Chromosorb W (60/80 mesh), at 228°, showed three major peaks with retention times identical with those of authentic samples of DDE, DDD, and DDT.

**Fraction B.**—When acetone was added to the concentrate of fraction B, a white solid separated and was filtered. Glc analysis of the filtrate showed the presence of DDT, DDD, and DDE, while the white solid would not elute from column 1. It was recrystallized from benzene and dried. Its nmr spectrum was identical with one reported by Mosier[13] for one isomer of **3** and showed a singlet at $\delta$ 6 (1 H) and an AA′BB′ multiplet at 7.25 (8 H). The mass spectrum showed a molecular ion of *m/e* 564 (abundance 2.3%) with M, M + 2, M + 4, M + 6, and M + 8 peaks in the ratio 1.0:1.86:1.61:0.74:0.17, indicating the presence of six chlorine atoms. Other prominent ions were *m/e* 235 (100), with M, M + 2, M + 4, in the ratio 1.0:0.69:0.12, and *m/e* 165 (35.3). It melted at 235° (lit.[13] mp 232°).

**Fraction C.**—Glc analysis showed that this fraction contained small amounts of DDT, DDD, and DDE.

**Fraction D.**—It was rechromatographed on a silica gel column (60 g), using SSH, $CCl_4$, and benzene. Several compounds were isolated, one being a white solid, insoluble in acetone. It was crystallized from benzene and melted at 278°. Its nmr spectrum showed a broad singlet at $\delta$ 5.5 (1 H) and an AA′BB′ quartet (8 H) with $\delta_a$ 7.2, $\delta_b$ 7.6, and $J_{ab} = 10$ Hz. Its mass spectrum gave a parent ion (2.1%) of *m/e* 564 with M, M + 2, M + 4, M + 6, and M + 8 ions in the ratio 1.0:1.95:1.62:0.67:0.19, which is indicative of six chlorines. Other prominent ions were *m/e* 235 (100), with M, M + 2, and M + 4 in the ratio 1.0:0.61:0.11, and *m/e* 165 (47.8). It is identified as an isomer of **3**.

A second compound gave an nmr spectrum with three singlets at $\delta$ 3.8 (3 H), 4.9 (1 H), and 7.3 (8 H). Its mass spectrum showed a molecular ion with *m/e* 294 with M, and M + 2 ions in the ratio 1.5:1. The prominent mass spectral peaks are *m/e* (rel intensity) 296 (13), 294 (20), 237 (66.5), and 235 (100). The ir spectrum showed a strong peak at 1735 $cm^{-1}$. This compound is identified as methyl 1,1-bis(*p*-chlorophenyl)acetate (**2**) by matching its spectra with literature reports.

A yellow solid was also obtained that had an nmr spectrum with a triplet at $\delta$ 1.1 (6 H), a singlet imposed on a quartet at 3.3 (7 H), and a multiplet at 6.8 (12 H). Mass spectrometry gave a molecular ion of *m/e* 425 with M, M + 2, and M + 4 peaks in the ratio 1.2:0.9:0.11, indicating the presence of two chlorine atoms. Other prominent peaks are *m/e* 412, 410, 384, 382, 340, 338, 275, 274, 272, 239, 199, 170, 164, 163, 162, 133, 105, 104, 91, 77, and 49. This compound was identified as **5**. A dirty white solid was isolated, which was recrystallized from EtOH and gave an nmr spectrum which had only an AA′BB′ quartet centered at $\delta$ 7.6. Its mass spectrum gave a molecular ion of *m/e* 250 with M and M + 2 in the ratio of 1.5:1, indicating the presence of two chlorine atoms. The major mass spectral peaks at *m/e* (rel intensity) 252 (28.6), 250 (43.6), 139 (100). Its ir and nmr spectra and mp matched with an authentic sample of 4,4′-dichlorobenzophenone (DDCO).

**Fraction E.**—It was rechromatographed on a silica gel column (60 g), with SSH, $CCl_4$, and benzene. One major component was obtained and recrystallized from benzene. White crystals (mp 114°) were obtained and these gave nmr spectra with a triplet at $\delta$ 1.3 (6 H), a quartet at 3.16 (4 H), and AA′BB′ quartet at 6.4 (2 H), 7.7 (2 H), and a singlet at 7.3 (8 H). Its mass spectrum gave a molecular ion of *m/e* 411 with M and M + 2 in the ratio 1.4:0.9. The ir spectrum showed a strong band at 1665 $cm^{-1}$. This compound is identified as $\alpha,\alpha$-bis(*p*-chlorophenyl)-*p*-diethylaminoacetophenone.

*Anal.* Calcd for $C_{24}H_{23}Cl_2NO$: C, 69.95; H, 5.58; Cl, 16.99. Found: C, 69.71; H, 5.75; Cl, 16.99.

**Fraction F.**—A yellow solid had separated on standing and it was filtered off and crystallized from a 1:1 mixture of benzene and methanol. Yellow crystals were obtained (mp 253°) which gave a nmr spectrum with a triplet at $\delta$ 1.2 (12 H), a quartet at 3.3 (8 H), and a multiplet centered at 6.8 (16 H). Its mass spectrum showed a molecular ion of *m/e* 542 with M and M + 2 peaks in the ratio 1.4:0.9, required for two chlorine atoms. It is identified as 1,1-bis(*p*-chlorophenyl)-2,2-bis(*p*-diethylaminophenyl)ethylene.

*Anal.* Calcd for $C_{34}H_{36}Cl_2N_2$: C, 75.4; H, 6.62. Found: C, 74.31; H, 6.69.

**Fraction G.**—The solution was evaporated to dryness. Ether was added to the dark brown mass and a brown solid separated out. After filtering and recrystallizing it from carbon tetrachloride, it was identified as diethylaniline hydrochloride by matching its nmr and ir spectra and melting point with those of an authentic sample.

**Quantitative Analysis of DDT–Diethylaniline Products.**—DDT (1.416 g, 3.99 mmol) and DEA (1.2 g, 8.05 mmol) were dissolved in methanol (total volume 50 ml). Seven 4-ml aliquots of this solution were placed in Pyrex tubes and irradiated for different lengths of time. The concentrations of DDT, DDD, DDE, DDCO, and **2** were followed by glc on column 1 at 228°. Only about 1% of DDCO was formed. It was not possible to separate DDE and methyl 1,1-bis(*p*-chlorophenyl)acetate so that the latter was measured by nmr in $CDCl_3$ with an internal standard.

**Identification of Photoproducts of Decyl Bromide and Diethylaniline Reaction.**—Decyl bromide (5.75 g, 27.2 mmol) and diethylaniline (10 g, 67 mmol) in DMF (160 ml) were irradiated in Pyrex tubes for 44 hr. Water was added to the reaction mixture which was then extracted with ether. The water-soluble portion contained diethylaniline hydrobromide as identified by nmr, ir, and melting point. The ether extract was washed with dilute HCl and again with water. The HCl extract was neutralized with dilute NaOH and extracted with ether. After washing with water it was dried over magnesium sulfate and analyzed by glc using a Teflon-lined aluminum column, 6 ft × 0.25 in., packed with 10% DC-200 on Chromosorb Q. It showed a peak with a retention time identical with that of *N*-ethylaniline on several columns. Glc of the neutral material used temperature programming. After injection, the temperature was held at 130° for 10 min and raised at the rate of 10°/min to 230°. Five major peaks with retention times of 3.16, 15.6, 21.8, 28, and 33.2 min appeared. The peak with a retention time of 15.6 min was due to decyl bromide.

The peak with a retention time of 3.6 min and a molecular ion at *m/e* 142 is due to *n*-decane, as shown by comparison of its nmr spectrum and glc retention time with those of authentic sample. The compound with a retention time of 33.2 min had a mass spectrum with a molecular ion of *m/e* 289 and major peaks of 289 (22), 274 (100), 134 (40), 105 (10), and 91 (14). The nmr spectrum showed a multiplet at $\delta$ 7.0–6.2 (4 H), a quadruplet at 3.2 (4 H), 2.3 (2 H), and 1.4–0.08 (25 H). This was identified by comparison of nmr and glc retention time with those of authentic *p*-decyl-*N*,*N*-diethylaniline. The compound with retention time 28.0 min had a mass spectrum with major peaks at *m/e* (rel intensity) 289 (1), 274 (2), 218 (50), 134 (17), 105 (22), 92 (95), 91 (100); nmr $\delta$ 9.70 (s, 4), 2.87 (q, 4), 2.6 (q, 2), and 1.4–0.8 (q, 25). This was identified as *o*-decyl-*N*,*N*-diethylaniline.

**Solvent Effects on Decyl Bromide–Diethylaniline Photolysis.**—Decyl bromide (7 g, 34.5 mmol), diethylaniline (10 g, 72.5 mmol), and a dodecanol standard (6 ml) were mixed. Four 5-ml aliquots of this solution were taken in Pyrex tubes, and to each of these was added 15 ml of one of the following solvents: DMF, methanol, benzene, and cyclohexane. These were irradiated for 36 hr, followed by glc analysis. After glc analysis, solutions were concentrated and extracted with dry ether. The solid left after ether extraction was diethylaniline hydrobromide, which was weighed to determine the amount of hydrogen bromide evolved.

***p*-Decyl-*N*,*N*-diethylaniline.**—1-Phenyldecane (6 ml) was added dropwise to a mixture of 5 ml of 70% $HNO_3$ and 6 ml of concentrated $H_2SO_4$ at 5°. This mixture was then neutralized with cold aqueous sodium hydroxide and extracted with ether. The ether soluble material had an nmr spectrum consistent with a mixture of nitrated decyl bromides. This material was reduced with tin (9 g) and concentrated hydrochloric acid (25 ml) on a steam bath for 45 min. Addition of aqueous sodium hydroxide and ether gave an ether soluble material with nmr $\delta$ 6.9–6.3 (m, 3.5), 3.4 (s, 2), 2.5–2.2 (m, 2), and 1.4–0.8 (m, 19). This material was not purified since the above nmr looked like primarily *p*-decylaniline (a poorly resolved AA′BB′ quartet in the aromatic region). This product (1 ml) was treated with 4 ml of ethyl bromide in a sealed tube at 130° for 19 hr. After cooling, the contents of the tube were neutralized with aqueous sodium hydroxide and extracted with ether. The ether extract was dried with magnesium sulfate. Glc showed three components, two with retention times identical with those obtained from the photolysis of decyl bromide and diethylaniline. The mixture was chromatographed on acid-washed alumina with Skellysolve H as the eluent. The major component had an nmr spectrum with an AA'BB' quartet centered at $\delta$ 6.65 (4, $J$ = 9 Hz), 3.25 (q, 4, $J$ = 8 Hz), 2.4 (m, 2), 1.2–0.9 (m, 25).

*Anal.* Calcd for $C_{20}H_{35}N$: C, 83.0; H, 12.1. Found: C, 83.4; H, 11.9.

**Photolysis of *n*-BuI, *n*-BuBr and *n*-BuCl with Dimethylaniline.**—Solutions of *n*-BuI, *n*-BuBr, and *n*-BuCl in benzene were prepared such that these contained 0.01 mol of halide, 0.03 mol of DMA, and 1.5 ml of toluene and the total volume was 10 ml. These solutions were irradiated for 96 hr. The progress of the reaction was followed by nmr, and it was shown that 27% of *n*-BuBr, 12% of *n*-BuCl, and 10% of *n*-BuI had reacted.

**Quantum Yields.**—The following solutions were prepared: benzophenone (0.91 g) and benzhydrol (0.92 g) in benzene (50 ml); DDT (1.41 g) and diethylaniline (1.2 g) in methanol (net volume 100 ml); and decyl bromide (1.105 g), diethylaniline (1.49 g) and dodecanol (1 ml) in methanol (total volume 25 ml). The uv spectrum of the benzophenone and benzhydrol solution was recorded by diluting 0.5 ml of this solution to 10 ml with benzene. Two 5-ml aliquots and two 7-ml aliquots of this solution were taken in identical Pyrex tubes with long stems. These tubes were degassed by three freeze–thaw cycles to 0.005 mm and sealed *in vacuo*. Three 5-ml aliquots of the DDT solution were taken in Pyrex tubes which were similar to the actinometer tubes. These were photolyzed with two actinometer tubes containing 5 ml of solution for 5 min. The amount of DDT reacted was determined by glc on column 1 at 240° using triphenylmethane as an internal standard which was added after irradiation. The per cent of DDT lost in three tubes was 12.24, 12.2, and 12.4. The per cent benzophenone reacted was determined by recording the uv spectrum of the irradiated solution after diluting 0.5 ml of this solution to 10 ml; the percentage lost was 7.5 and 7.5. The quantum yields were calculated for disappearance of DDT as 0.30, 0.30, and 0.31. Two 7-ml aliquots of the decyl bromide solution prepared above were placed in Pyrex tubes. These were irradiated along with two actinometer tubes (containing 7 ml of solution) for 30 min. The loss of benzophenone was determined as 23.5% in both tubes and of decyl bromide by glc, which was 6.3 and 6.5%. Quantum yields for the reaction were 0.19 and 0.20.

**Registry No.**—*cis*-**3**, 36954-66-2; *trans*-**3**, 36954-67-3; **5**, 36955-24-5; DDT, 50-29-3; diethylaniline, 91-66-7; decyl bromide, 112-29-8; $\alpha,\alpha$-bis(*p*-chlorophenyl)-*p*-diethylaminoacetophenone, 36955-25-6; 1,1-bis(*p*-chlorophenyl)-2,2-bis(*p*-diethylaminophenyl)ethylene, 36955-26-7; *p*-decyl-*N*,*N*-diethylaniline, 36955-27-8; *o*-decyl-*N*,*N*-diethylaniline, 36955-28-9.

**Acknowledgment.**—This research was supported by the Colorado Agricultural Experiment Station. This is report no. 1614.

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# The Free-Radical Bromination of Bromobutane with Bromotrichloromethane

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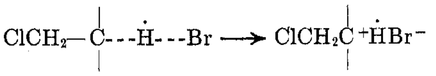
*Received July 11, 1972*

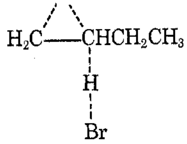
The photolytic bromination of 1-bromobutane with bromotrichloromethane was studied at three different temperatures. Product ratios were observed to be independent of per cent conversion with products resulting from $\beta$-hydrogen abstraction predominating. This result is discussed in terms of the stabilization of the $\beta$ radical by a bromo substituent. A rearrangement product, 2-bromobutane, was also observed and a 1,2 bromine migration in the radical intermediate is proposed to account for its formation.

A large amount of work has dealt with the selectivities of hydrogen atom abstraction from hydrocarbons.[1] Some of the more interesting observations have resulted from studies in which alkyl halides serve as the hydrogen donor.[2-8] These systems are complicated by the effects of the halogen, which could potentially either stabilize or destabilize nearby radical centers. Studies of the photolytic bromination of alkyl chlorides with bromine have shown that a position $\beta$ to the chlorine substituent is deactivated toward hydrogen abstraction.[3,4] This has been attributed to the polar effect of the electronegative substituent. The electronegative bromine atom is apparently repelled by the decreased electron density adjacent to the chlorine. This can be explained by including in the transition state for hydrogen abstraction an appropriate resonance structure showing some polar contribution to the radical reaction.



$$\mathrm{ClCH_2{-}C{-}{-}{-}\dot{H}{-}{-}{-}Br} \longrightarrow \mathrm{ClCH_2C^{+}\dot{H}Br^{-}}$$

A more complicated situation obtains in alkyl bromides. If 1-bromobutane is photolytically brominated using $Br_2$ as the halogen source, 1,2-dibromobutane is the predominant product.[4] The polar effect has apparently been superseded by a stronger stabilizing influence of the bromo substitutent. Many authors have attributed this effect to a bridged radical species in which the neighboring bromine can anchimerically assist hydrogen abstraction from a $\beta$ position.[3-9] This bridged radical intermediate postulation is supported by the observed retention of optical activity when optically active 1-bromo-2-methylbutane is halogenated under the same conditions.[9]



An alternative explanation has recently been pro-

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