vacuo; the residue was crystallized from methanol as the bromide, yield 0.3 g. (67%). Recrystallization afforded pale orange needles, m.p. 323–324° (S.T.), which on analysis appeared to be associated with over 2 moles of water which could not be completely removed by drying *in vacuo* at 140°.

The **perchlorate** crystallized from methanol–acetonitrile as orange needles: m.p. 295–296° (S.T.) dec.; λ_{max} mμ (log ϵ) 206 (4.47), 228 (4.56), 248 sh (4.30), 278 (4.43), 298 (4.52), 308 (4.54), 317 (4.38), 345 sh (3.91), 366 (3.76), 388 sh (3.92), 406 (4.07), 415 (4.02), and 454 sh (3.32).

Anal. Calcd. for $C_{22}H_{16}ClNO_4$: C, 67.09; H, 4.10; N, 3.69. Found: C, 67.00; H, 4.19; N, 3.64.

Naphtho[2,1-*a*]phenanthridizinium (IVa) Perchlorate.—The quaternization of 0.8 g. of 1-(2-naphthyl)isoquinoline with 0.46 g. of chloroacetaldoxime was carried out in 8 ml. of tetramethylene sulfone in 14 days at room temperature. The oil which precipitated on addition of ethyl acetate could not be obtained solid. The iodide and perchlorate salts likewise appeared to be oils.

The crude chloride was refluxed for 22 hr. in 20 ml. of concentrated hydrochloric acid. Worked up in the usual way, 0.5 g. (51%) of crystalline material was obtained. The yellow prisms, m.p. 322–323° (S.T.), appeared to be hydrated and could not be made anhydrous by heating at 140°.

The **perchlorate** prepared from the chloride in the usual way, crystallized from methanol–acetonitrile as orange needles: m.p. 266–269° (S.T.) with previous darkening and softening; λ_{max} mμ (log ϵ) 206 sh (4.46), 227 (4.64), 258 sh (4.33), 278 (4.43), 294 sh (4.47), 305 (4.53), 310 sh (4.52), 325 (4.40), 370 (3.80), 391 (4.03), 409 (4.16), and 455 sh (3.34).

Anal. Calcd. for $C_{21}H_{14}ClNO_4$: C, 66.40; H, 3.72; N, 3.69. Found: C, 66.75; H, 3.68; N, 3.91.

1-Acetonyl-1-azafluoranthene Bromide (V).—The quaternization of 1 g. of 1-azafluoranthene with 1 g. of bromoacetone was carried out in boiling acetone (3 hr.). The product, 1.6 g. (80%), on recrystallization from methanol–ethyl acetate gave orange prisms, m.p. 241° dec.

Anal. Calcd. for $C_{18}H_{14}BrNO \cdot 0.5H_2O$: C, 61.90; H, 4.33; N, 4.01. Found: C, 61.51; H, 4.22; N, 4.09.

The **perchlorate** crystallized from methanol as orange needles, m.p. 213.5–214.5°.

Anal. Calcd. for $C_{18}H_{14}ClNO_5$: C, 60.00; H, 3.92; N, 3.89. Found: C, 60.24; H, 3.96; N, 4.05.

7-Acetonyl-7-azafluoranthene Bromide (VI).—The quaternization of 7-azafluoranthene was carried out as in the case of the 1 isomer, affording 1.4 g. (79%) of product. It crystallized from methanol–ethyl acetate as pale yellow prisms, dec. pt. >250°.

Anal. Calcd. for $C_{18}H_{14}BrNO$: C, 63.53; H, 4.15; N, 4.12. Found: C, 63.72; H, 4.21; N, 4.30.

The **perchlorate** was obtained from methanol as pale yellow prisms, m.p. 255–255.5°.

Anal. Calcd. for $C_{18}H_{14}ClNO_5$: C, 60.00; H, 3.92; N, 3.89. Found: C, 59.90; H, 3.63; N, 4.05.

Attempted Cyclization of V and VI.—The conditions tried for cyclization varied from heating on the steam bath with 48% hydrobromic acid to heating with polyphosphoric acid at 240° for 20 hr. Even under the most drastic conditions, where severe decomposition was observed, samples showed the carbonyl absorption in the infrared characteristic of the starting material.

Photosensitized Cycloaddition of Haloethylenes and 1,3-Dienes*

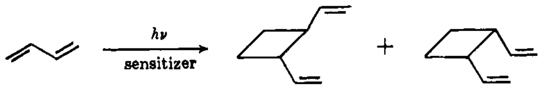
NICHOLAS J. TURRO[1] AND PAUL D. BARTLETT

The Converse Memorial Laboratory, Harvard University, Cambridge, Massachusetts 02138, and the Department of Chemistry, Columbia University, New York, New York 10027

The photosensitized cycloaddition reactions of a number of 1,3-dienes and haloethylenes has been investigated. The formation of four-membered rings is invariably the predominant path of reaction in all the cases studied, although six-membered ring formation (Diels–Alder reaction) is competitive on occasion. The results are consistent with the attack of the triplet diene on haloethylene to form a biradical which rapidly cyclizes to products.

Photosensitized cycloaddition reactions to form cyclobutanes have long been known.[2] Although direct irradiation of suitably activated ethylenes often results in cyclobutane formation, the factors which direct the course of these reactions are not clear in most cases.[2,3] On the other hand, photosensitized dimerization of conjugated dienes is believed (a) to proceed *via* attack of a triplet diene on an unactivated diene and (b) to follow the rule that the products are determined by formation of the most stable biradical intermediate. This means that the predominant (often the exclusive) products formed may be predicted with remarkable accuracy merely by inspecting all of the possible biradical intermediates and then noting how resonance and inductive effects contribute to the stabilities of these intermediates. If one biradical is expected to be appreciably more stabilized than the others, we may expect the product of cyclization of this intermediate to predominate.

For example, the photosensitized dimerization of butadiene[4] results in a 98% yield of the dimers **1** and **2**, in a relative yield of 3 to 1. No 1,3-divinylcyclobutane (**3**) can be detected.



1 **2** (1)

The thermal cycloaddition reactions of a number of 1,3-dienes and fluoro olefins also yield products which closely follow the biradical postulate.[5,6] Thus, 1,1-dichloro-2,2-difluoroethylene (1122) yields only the adduct **4** when a solution of 1122 and butadiene is heated at 80°. The adduct **5** cannot be detected. In view of the formal similarities of the factors which

---

* To Professor Louis F. Fieser.

(1) National Science Foundation Postdoctoral Fellow 1963–1964; visiting scientist, Dow Chemical Co., Eastern Research Laboratory, summer 1964; to whom communications should be sent at Columbia University.

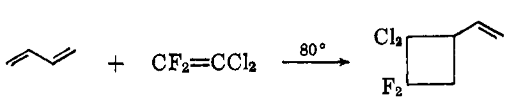
(2) (a) For reviews, see A. Schönberg, "Präparative Organische Photochemie," Springer-Verlag, Berlin, 1958; (b) A. Mustafa, *Chem. Rev.*, **51**, 1 (1952); (c) P. deMayo, *Advan. Org. Chem.*, **2**, 367 (1960); (d) P. deMayo and S. T. Reid, *Quart. Rev.* (London), **15**, 393 (1961); (e) C. R. Masson, V. Boekelheide, and W. A. Noyes in "Technique of Organic Chemistry," Vol. II, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 257; (f) G. O. Schenck and R. Steinmetz, *Bull. soc. chim. Belges*, **71**, 781 (1962); (g) G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963); (h) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin Co., New York, N. Y., 1965.

(3) For recent investigations of the mechanism of photochemical cycloadditions, see (a) G. W. Griffin, A. F. Villturo, and K. Furukawa, *J. Am. Chem. Soc.*, **83**, 2725 (1961); (b) J. Bregman, K. Osaki, G. M. J. Schmidt, and F. I. Sonntag, *J. Chem. Soc.*, 2021 (1964); (c) P. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.*, **86**, 963 (1964); (d) E. J. Corey, R. B. Mitra, and H. Uda, *ibid.*, **86**, 485, 5570 (1964).

(4) G. S. Hammond, N. J. Turro, and H. Fischer, *ibid.*, **83**, 4674 (1961); N. J. Turro, Ph.D. Thesis, California Institute of Technology, 1963.

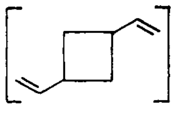
(5) J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, (1962).

(6) P. D. Bartlett, L. K. Montgomery, B. Seidel, and K. Schueller, *J. Am. Chem. Soc.*, **86**, 616, 622, 628 (1964).

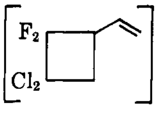


4 (2)

direct the photosensitized dimerization of dienes[4,7-10] and the thermal cycloaddition[5,6] of 1122 and dienes it was desirable to examine the photosensitized cycloaddition reactions of conjugated 1,3-dienes and halo olefins.



3

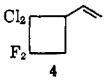
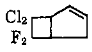
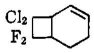
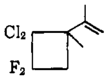
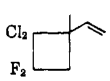
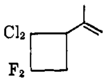


5

Photosensitized Cycloaddition of 1,1-Dichloro-2,2-difluoroethylene and Dienes.—The thermal cycloaddition of 1,1-dichloro-2,2-difluoroethylene (1122) with 1,3-dienes occurs smoothly at 80°. The photosensitized cycloaddition of 1122 and a number of 1,3-dienes is effected by irradiation (through Pyrex) of a solution containing sensitizer, 1,3-diene, and a tenfold excess of 1122 at 0–25° (see Table I). Diene dimerization accompanies cross cycloaddition but the dimer of 1122 could not be detected by vapor phase chromatographic (v.p.c.) analysis. The quantum yields for cycloaddition of 1,3-cyclohexadiene and 1122 (photosensitized by various sensitizers) are given in Table II. The quantum yield for photosensitized cycloaddition of 1122 and 1,3-butadiene (benzophenone as sensitizer) is approximately 0.001. The linear dienes are in general less reactive toward photosensitized cross cycloaddition than toward self-dimerization. The quantum yields for cross addition *vs.* 1,3-diene dimerization as a function of concentration of diene with benzophenone as sensitizer are given in Table III. The relative ratios of the cross adduct pairs **6**–**7**, **8**–**9**, and **11**–**12** are 2:1, 24:1, and 55:45, respectively. The structures of all cycloadducts (except for the isomers of gross structure **13**) were established by comparison of their n.m.r. spectra and v.p.c. retention times with those of authentic materials.

TABLE I

PHOTOSENSITIZED CYCLOADDITION[a] OF 1122 TO VARIOUS DIENES

Diene	Cross adducts formed[b]		% yield[b]	Ratio
Butadiene	 4		40	... ...
Cyclopentadiene	 6	 7	90	2:1
Cyclohexadiene	 8	 9	75	24:1
2,3-Dimethylbutadiene	 10		81	...
Isoprene	 11	 12	47	55:45

[a] Benzophenone as sensitizer, tenfold excess of 1122, no solvent. [b] The only products detectable by v.p.c. analysis of the cross adducts and diene dimers. The yield given is the percentage of products detectable by v.p.c. analysis. Diene dimers account for the remainder.

TABLE II

QUANTUM YIELDS FOR THE CYCLOADDITIONS OF CYCLOHEXADIENE AND 1122[a] WITH VARIOUS SENSITIZERS

Sensitizer	Quantum yields Cross addition	 Dimerization	 Blank (dimers)
Benzophenone	0.50	0.16	0.30
2-Acetonaphthone	0.49	0.17	0.30
Fluorenone	0.04	0.01	0.20

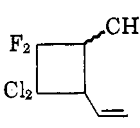
[a] 1,1-Dichloro-2,2-difluoroethylene in tenfold excess.

TABLE III

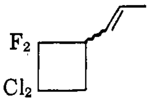
QUANTUM YIELDS FOR THE BENZOPHENONE-PHOTOSENSITIZED CYCLOADDITION REACTIONS OF CYCLOHEXADIENE AND 1122

Concentration of diene, *M*	Quantum yields Cross addition	 Dimerization	 Blank (dimers)
0.157	0.41	0.23	0.40
0.080	...	0.16	0.31
0.063	0.41	0.085	...
0.037	0.36	0.025	0.30

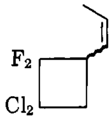
An attempt was made to study the stereochemistry of photosensitized cycloaddition of 1122 to 1,3-pentadiene and 2,4-hexadiene. However, these studies were complicated by simultaneous cycloaddition and *cis*–*trans* isomerization of the diene. Two products were isolated from the photosensitized cycloaddition of 1,3-pentadiene and 1122 which are not formed in the thermal cycloaddition of these compounds, and whose n.m.r. spectra suggest that these compounds are isomers which possess the gross structure **13**. This was the only instance in which other adducts, in addition to those produced thermally, were observed in the photosensitized cycloadditions. The adducts **14** and **15** were formed as the major products, however.



13



14



15

A number of compounds are effective in sensitizing these cycloadditions with similar results. The major requirement appears to be that the triplet energy of the sensitizer be greater than about 53 kcal./mole. No appreciable solvent (acetonitrile, ether, cyclohexane, methanol) effect was noted on the rate of cycloaddition and the relative ratio of products formed.

Unsuccessful attempts were made to photosensitize the addition of simple ethylenes such as cyclohexene and cyclopentene to 1122 (acetophonone as sensitizer). The main reaction, however, was cycloaddition with sensitizer to form oxetanes.

Photosensitized Cycloaddition of 1,1-Dichloroethylene and Dienes.—1,1-Dichloroethylene is relatively inert toward thermal cycloaddition reactions.[5,11] The

---

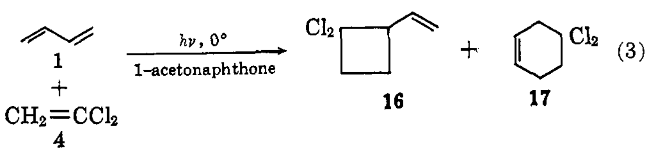
(7) N. J. Turro and G. S. Hammond, *J. Am. Chem. Soc.*, **84**, 2841 (1962).

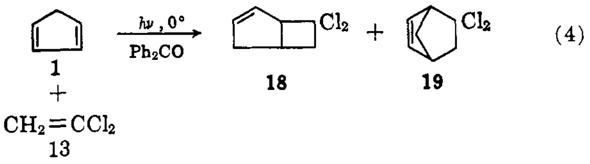
(8) G. S. Hammond and R. S. H. Liu, *ibid.*, **85**, 477 (1963).

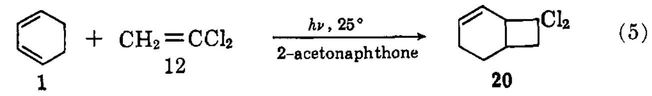
(9) G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963).

(10) D. Valentine, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 5202 (1964).

(11) R. E. Tidov, *Chem. Abstr.*, **47**, 6596*g* (1953); J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Am. Chem. Soc.*, **76**, 5692 (1954).





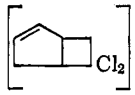


course of photosensitized cycloadditions of 1,1-dichloroethylene and three dienes are given in eq. 3–5.

The approximate molar ratio of haloethylene to diene employed is listed under the respective compounds in the equations. Analysis of reaction mixtures by v.p.c. showed that cross adducts are formed in 20, 80, and 70% yields in the case of butadiene, cyclopentadiene, and cyclohexadiene, respectively. Three dimers are formed from each diene used and the ratios of these dimers in the reaction mixtures were the same in the presence and absence of halo olefin. No dimers of 1,1-dichloroethylene could be detected in the reaction mixtures. The ratio **16**:**17** was 9:1 and the ratio **18**:**19** was 3:2.

Compounds **16** and **17** were only preliminarily examined and their structures were assigned on the basis of their n.m.r. spectra. The n.m.r. of **16** shows a typical vinyl progression from 6.3 to 4.9 p.p.m. (three protons), a pair of doublets (one proton) centered at 3.58 (J = 7 c.p.s.) and 3.28 p.p.m. (J = 7 c.p.s.), and complex multiplets from 3.0 to 2.5 (two protons) and from 2.3 to 1.8 p.p.m. (two protons). The minor adduct **17** shows a broad multiplet centered at 5.5 p.p.m. (two protons) and broad singlets at 2.8 (two protons) and 2.3 p.p.m. (four protons).

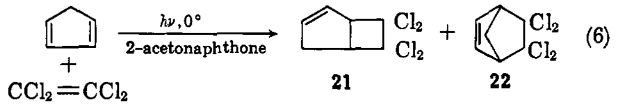
Compounds **18** and **19** are isomeric (mass spectrum, m/e 162, $C_7H_8Cl_2$). The n.m.r. spectrum of **19** was identical with that of 5,5-dichloronorbornene.[12] The infrared spectrum of **19** possesses a C=C absorption at 1570 cm.$^{-1}$ (norbornene 1560 cm.$^{-1}$) and =C—H absorption at 3058 cm.$^{-1}$ (norbornene 3054 cm.$^{-1}$). The n.m.r. spectrum of **18** shows a broad singlet at 6.05 p.p.m. (two protons), a broad multiplet at 4.10 p.p.m. (one proton), a complex multiplet of at least seven peaks at 3.35–2.80 p.p.m. (three protons), and a set of four peaks from 2.40 and 2.72 p.p.m. (two protons). The infrared spectrum of **18** shows C=C absorption at 1603 cm.$^{-1}$ (cyclopentene 1603 cm.$^{-1}$) and =C—H absorption at 3048 cm.$^{-1}$. The base peaks in the mass spectra of **18** and **19** are both at m/e 80 (loss of $C_2H_2Cl_2$). The location of the chlorine atoms in **18** is not rigorously defined by these spectra, but the single proton absorption at 4.10 p.p.m. suggests a hydrogen on a carbon atom both allylic and adjacent to a *gem*-dichloro group, *i.e.*, structure **18** rather than **18a**.

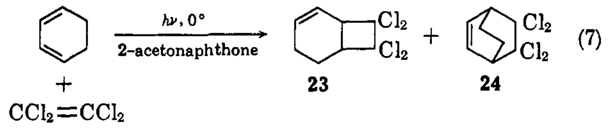


18a

The mass spectrum of compound **20** shows a molecular ion at m/e 176 ($C_8H_{10}Cl_2$) and base peak at m/e 80 (loss of $C_2H_2Cl_2$). The n.m.r of **20** shows a multiplet centered at 6.0 p.p.m. (two protons), a broad band at 3.6 p.p.m. (one proton), a complex multiplet from 3.2 to 2.5 p.p.m. (three protons), and a broad absorption from 3.5 to 2.0 (two protons) and 1.9 to 1.5 p.p.m. (two protons). The infrared spectrum of **20** shows a C=C absorption at 1640 cm.$^{-1}$. On the basis of these data and analogy to other photoadducts **20** is assigned the structure of the bicyclo[4.2.0]octene shown.

Photosensitized Cycloaddition of Tetrachloroethylene and Cyclic Dienes.—Tetrachloroethylene is extremely inert toward thermal cycloaddition reactions. The photosensitized cycloaddition of tetrachloroethylene (in sixfold excess) and cyclopentadiene or cyclohexadiene proceeds smoothly as shown in eq. 6 and 7.





Analysis of reaction mixtures by v.p.c. showed that cross adducts were formed in 55 and 30% yield in the case of cyclopentadiene and cyclohexadiene, respectively. The ratio **21**:**22** was 3:2 and the ratio **23**:**24** was about 20:1. No dimer of tetrachloroethylene was detected in the reaction mixture.

The mass spectra of **21** and **22** both exhibit molecular ions at m/e 230 ($C_7H_2Cl_4$) and base peaks at m/e 76 (loss of C_2Cl_4). The n.m.r. spectrum of the major adduct **21** shows a pair of broad bands possessing some unresolved fine structure and centered at 6.15 and 5.9 p.p.m. (two protons), a band at 4.3 p.p.m. (one proton), a triplet (J = 7 c.p.s.) centered at 3.88 p.p.m. (one proton), and a complex multiplet centered at about 2.9 p.p.m. (two protons). The infrared spectrum of **21** shows a C=C absorption at 1605 cm.$^{-1}$ (cyclopentene 1603 cm.$^{-1}$).

The n.m.r. spectrum of the minor adduct **22** shows a triplet (J = 2 c.p.s.) centered at 6.45 p.p.m. (two protons), a sharp multiplet (quartet?) centered at 3.75 p.p.m. (two protons), and a quartet centered at 2.38 p.p.m. (two protons). The infrared spectrum of **22** shows a C=C absorption at 1585 cm.$^{-1}$ (norbornene 1575 cm.$^{-1}$). These spectra define the structures given to the two adducts.

The n.m.r. spectrum of the major adduct **23** shows complex bands from 6.2 to 5.5 (two protons), 3.8 to 2.6 (two protons), and 2.5 to 1.8 p.p.m. (four protons). The infrared spectrum of **23** shows a C=C absorption at 1630 cm.$^{-1}$.

The n.m.r. spectrum of the minor adduct **24** shows broad complex absorption from 6.2 to 5.3 p.p.m. (two protons) and a complex series of bands from 3.7 to 1.2 p.p.m. (six protons). The infrared spectrum of **24** shows C=C absorption at 1650 and 1630 cm.$^{-1}$. These data do not suffice to distinguish rigorously between the two possible cycloadducts. The tentative structural assignments are thus based on analogy to the other cycloadditions studied.

---

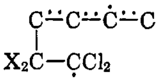
(12) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964).

Discussion

The photosensitized cycloaddition of halo olefins and 1,3-dienes appear to be a general reaction. Although diene dimerization is competitive with cross addition, by employing an excess of halo olefins satisfactory yields of cross adducts may be achieved.

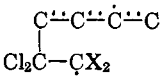
Several points of interest in connection with these studies are (a) a comparison of the results of thermal and photosensitized cycloadditions; (b) a comparison of the direct and sensitized photoreactions; (c) determination of the excited partner involved in these photosensitized cycloadditions; and (d) the scope of these reactions.

A biradical intermediate (or a transition state whose stability is governed by factors similar to those which would be expected to stabilize biradical intermediates) accounts for the products obtained in these 1,2 cycloadditions. If it is assumed that the first step in 1,2 cycloaddition is the formation of an intermediate which possesses a carbon–carbon single bond and that the two ends of the intermediate possess free-radical character, then the formation of the structures **25** should be favored over **26** if X is fluorine or hydrogen, because a free radical should be stabilized more by chlorine substitution than by either fluorine or hydrogen.[6]



$$\mathrm{C{\cdots}C{\cdots}\dot{C}{\cdots}C(-CX_2-\underset{\cdot}{C}Cl_2)}$$

25

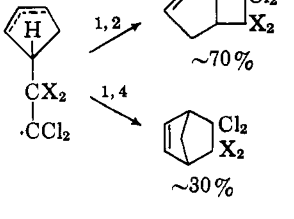


$$\mathrm{C{\cdots}C{\cdots}\dot{C}{\cdots}C(-CCl_2-\underset{\cdot}{C}X_2)}$$

26

Consideration of the factors which contribute to stabilizing the allylic moiety leads to rationalization of the structures of products formed from substituted butadienes.[6]

There is clearly a parallelism between the number and structure of products formed in the thermal and photosensitized cycloadditions of 1122 and 1,3-dienes. The main difference (with the exception of the case of 1,3-pentadiene) is the *ratio* of cross adducts formed under the two conditions. Thus, the ratio of **6**:**7** is 1:5 in thermal cycloaddition and 2:1 in photosensitized cycloaddition. It should be noted that these results were obtained at different temperatures (80 and 0°, respectively). It is interesting that the ratio of 1,2 to 1,4 cycloaddition of haloethylenes and cyclopentadiene is quite similar for the three ethylenes studied.



Direct excitation of a mixture of haloethylene and 1,3-diene invariably led to very low yields of adducts. A greater number of adducts are formed (according to v.p.c. analysis). The direct excitation of the 1,3-diene (the main absorbing species) must therefore produce an excited singlet state which does not cross efficiently to the triplet. The excited singlet of the diene apparently possesses too short a lifetime to undergo efficient cycloaddition and too high an energy to react selectively.

It may be concluded that diene triplets are the attacking species in the photosensitized cycloaddition reaction. This follows from the observations that (a) no dimers of the halo olefins were detected in the photosensitized experiments (even in the absence of diene); (b) the triplet energy of halo olefins should be higher than that of the sensitizers employed; and (c) the quantum yield for cross addition drops off only *slightly* as the ratio of halo olefin to diene is increased (see Table III), whereas the quantum yield for dimerization drops off sharply. The intermediate formed immediately after formation of one bond must be a "triplet" biradical. However, the rate of spin inversion of such an intermediate may be so fast that such an intermediate may be experimentally indistinguishable from a comparable "singlet" biradical.[13]

In addition to the experiments reported above, preliminary work has shown that both *cis*- and *trans*-1,2-dichloroethylene efficiently add to cyclic dienes under photosensitized conditions. Perchlorobutadiene, however, does not appear to react with either halo olefins or 1,3 hydrocarbon dienes under photosensitized conditions.

Experimental

Materials.—**Butadiene** [Matheson Coleman and Bell (MCB)] was purified by bulb-to-bulb distillation and then kept at −25°. **Isoprene** (Monomer-Polymer Laboratory) was distilled, b.p. 33–34°. **2,3-Dimethylbutadiene** (Aldrich Chemical Co. reagent grade) was distilled, b.p. 70–72°. **Piperylene** (MCB technical grade) was distilled, b.p. 40–42°. Pure *trans*-piperylene was obtained by preparative v.p.c. employing a 6 ft. × 0.625 in. column packed with $AgNO_3$ on benzyl cyanide at 25° (Megachrom). **Cyclopentadiene** (MCB, 95%) was cracked by distillation, b.p. 40–42°. **Cyclohexadiene** (Columbia Chemicals) was distilled, b.p. 80°. **Cyclopentene** (Columbia Chemical Co.) was used without further purification. **Sensitizers** (reagent quality) were used without further purification. **Cyclohexane** (Fischer reagent) was used without further purification. **1,1-Dichloroethylene** (Borden Co.) was used as received. **Tetrachloroethylene** (Eastman White Label) was used without further purification.

Irradiation Procedure.—A typical procedure for the sensitized irradiations was as follows. A test tube (either 13 × 100 mm. or 7 × 50 mm.) provided with a constriction was cooled and appropriate amounts of dichlorodifluoroethylene and diene or olefin were added (usually a 5–10-fold excess of the 1122 was employed), and finally 10–50 mg. of sensitizer was added. The resulting solution was then frozen in liquid nitrogen, evacuated, and sealed under vacuum. The samples were then strapped to the outer jacket of a Hanovia 450-w. immersion apparatus, immersed in a pail of water equipped with cooling coil, and irradiated for 2.4 hr. Analyses of the irradiated samples were made by v.p.c. on a 6 ft. × 0.25 in. vapor chromatography column packed with 1,2,3-tris(cyanoethoxy)propane, which was found to be satisfactory for all analyses. The ratio of areas under peak was determined by counts on a disk integrator. An F and M Model 609 flame ionization detector was used for the preliminary studies. The sensitivity of the flame toward the various peaks was not determined for these preliminary runs, but conditions for parallel runs were kept constant so that the comparison of results for one sensitizer with those for another sensitizer was valid. The retention times of known adducts were employed as means of identification of the peaks appearing in the chromatograms. In addition, adducts of the following dienes were prepared on a large scale, purified by preparative v.p.c., and identified by comparison of their n.m.r. spectra with those of authentic materials: cyclopentadiene, cyclohexadiene, butadiene, 2,3-dimethylbutadiene, piperylenes, and *trans*-2,4-hexadiene.

---

(13) Identical reactivity in the cage effect has been demonstrated for "singlet" and "triplet" radical pairs from azo compounds: P. D. Bartlett and S. F. Nelsen, paper presented at 10th National Conference on Reaction Mechanisms, Corvallis, Ore., June 1964; J. R. Fox and G. S. Hammond. *J. Am. Chem. Soc.*, **86**, 4031 (1964).

Preparative Photosensitized Addition of Cyclopentadiene to 1122 at 0°.—Freshly cracked cyclopentadiene (6 mmoles) and distilled 1122 (60 mmoles) were added to a constricted 13 × 100 mm. test tube which was then corked and cooled to −78°. After 40–50 mg. of sensitizers was added the tubes were frozen at −198°, evacuated, and sealed under vacuum. The samples were strapped to a 450-w. quartz immersion apparatus and irradiated for 2 hr. Analyses were then made on an F and M Model 609 vapor chromatograph equipped with flame ionization detector on a 5 ft. × 0.25 in. column packed with 20% 1,2,3-tris(cyanoethoxy)propane (TCEP) on 60–80-mesh Chromosorb P at 135°. Adducts and dimers were identified by retention time comparison with authentic materials. The adducts were also isolated by preparative vapor chromatography on TCEP and were shown to have n.m.r. spectra which were superposable upon those of authentic materials.

Preparative Cycloadditions of 1122 and Cyclohexadiene, Butadiene, Isoprene, 2,3-Dimethylbutadiene, Piperylene, and *trans*-2,4-Hexadiene.—A procedure similar to that described for cyclopentadiene was employed for the photosensitized cycloaddition of the above dienes. 1,2,3-Tris(cyanoethoxy)propane was found to be a suitable partition liquid for all gas chromatographic analyses. Adducts were identified by retention time comparison with authentic materials, by isolation by preparative v.p.c., and by comparison of their n.m.r. spectra with those of authentic materials.

Only in the case of the piperylenes did new adducts which were not produced thermally appear in the vapor chromatograms. Both of these were isolated but only one could be obtained in sufficient quantity for a satisfactory n.m.r. spectrum. This material shows a vinyl-like pattern in the unsaturation region and a broad band (δ 2.6) followed by a shallow set of absorptions up to about 1.2 (two protons) and a broad doublet centered at 1.0. This suggests the structure of one stereoisomer of 1,1-difluoro-2,2-dichloro-3-vinyl-4-methylcyclobutane. The n.m.r. spectrum of the second isomer in dilute solution was not inconsistent with that of the other stereoisomer of this cyclobutane.

Initial runs with *trans*-2,4-hexadiene gave evidence of a smooth photosensitized addition to form all four stereoisomeric adducts corresponding to the more stable biradical intermediate.[5,6] However, *cis–trans* isomerization also occurred simultaneously and it was decided not to pursue this system further.

Preparative Photosensitized Cycloadditions of Cyclopentadiene and Cyclohexadiene with Tetrachloroethylene.—A solution of 240 g. (1.45 moles) of tetrachloroethylene, 12.8 g. (0.188 mole) of cyclopentadiene, and 7.0 g. of 2-acetonaphthone was prepared and added at −10° to eight 13 × 300 mm. Pyrex test tubes. The samples were strapped to the 450-w. quartz immersion apparatus, cooled to 0° by means of an ice bath, and irradiated for 15 hr. The sample was then stripped of tetrachloroethylene and cyclopentadiene dimers (227 g. was collected) and a fraction, b.p. 85–90° (1–2 mm.), was collected. This fraction (12 g.) consisted of about 90% adducts and 10% dimers. The adducts amounted to 10.8 g. (0.0465 mole), a 40% yield based on cyclopentadiene.

Alternatively the adducts were prepared by use of a jacket on the immersion apparatus and a 39% yield of adducts was obtained.

The cyclohexadiene adducts were prepared in a similar manner in comparable yields.

Photosensitized Cycloadditions of 1,1-Dichloroethylene and 1,3-Dienes. Cyclopentadiene.—A solution of 470 g. (4.85 moles) of 1,1-dichloroethylene, 27 g. (0.41 mole) of cyclopentadiene, and 11 g. of benzophenone was added to the outer jacket of a 450-w. Pyrex immersion apparatus which was precooled to 0°. The sample was maintained at 0° by means of an external ice bath and irradiated for 5 hr. Vapor chromatographic analysis showed that 90% of the diene had reacted at this point. The materials were concentrated on a rotary evaporator at 25° and then vacuum distilled to yield a fraction, b.p. 45–90° (40–43 mm.), 10.6 g., which contained 31% dimers and 69% adducts; a second fraction, b.p. 90–92° (40–43 mm.), 6.0 g., which contained 10% dimers and 90% adducts; and a final fraction, b.p. 74–76° (25 mm.), 2.5 g., containing only adducts. The crude reaction mixture contained 80% adducts and 20% dimers, and the collected yield of adducts was 15.3 g. (0.092 moles, 26%) and of dimers 3.8 g. (0.020 moles, 34%).

Cyclohexadiene.—A solution of 154 g. (1.6 moles) of 1,1-dichloroethylene, 88 g. (0.11 mole) of cyclohexadiene, and 32 g. of 2-acetonaphthone was added to seven 18 × 200 mm. Pyrex test tubes which then were corked, strapped to a 450-w. immersion apparatus, and irradiated for 5 hr. at 0°. Analysis by v.p.c. showed a 67% yield of adducts and 24% yield of dimers based on cyclohexadiene consumed. The solution was concentrated on a rotary evaporator at 25° and then vacuum distilled to yield a fraction boiling at 80–82° (67–68 mm.), 12.0 g., containing 25% dimers and 75% adducts, and a fraction, b.p. 103–105° (25 mm.), 3.7 g., of nearly pure adduct. The over-all yield of adducts was 11.7 g. (0.067 mole, 60%), of dimers 4 g. (0.025 mole, 40%). The n.m.r. spectrum of the adduct showed a multiplet centered at δ 6.0 (two protons), a broad band from 3.7 to 3.2 (one proton), a multiplet from 3.2 to 2.5 (three protons), and broad absorptions from 2.5 to 2.0 (two protons) and 1.9 to 1.5 (two protons).

Butadiene.—To each of five 15 × 200 mm. constricted Pyrex test tubes 15–20 ml. of 1,1-dichloroethylene, 5.7 ml. of butadiene, and 1 g. of 1-acetonaphthone were added. The tubes were cooled to −78°, evacuated, and sealed under vacuum, then irradiated at 25° for 30 hr. on a 450-w. quartz immersion apparatus. The work-up procedure was similar to that described above for other dienes, but was not done quantitatively. Vapor chromatographic analysis on the described 1,2,3 column at 150° showed the presence of two adducts (20%) in addition to the butadiene dimers (80%). These were shown to be 1,1-dichloro-2-vinylcyclobutane (91%) and 4,4-dichlorocyclohexene (9%) by their n.m.r. spectra.

Quantum Yield Determinations.—The apparatus employed for quantum yield measurements has been described earlier[14] and consists of a device in which the reaction cells may be placed in holders in the rotating portion of the apparatus and kept at a constant distance from the lamp which is placed in the center of the system. The lamp housing was a quartz immersion well blackened out with electrical tape everywhere except for a 2-in. cylindrical space at the level of the samples. Four Corning glass filters (7-37), 2 in. × 0.4 mm., were placed about this spacing and the edges were blackened so that only light passing through the filters reached the samples. The entire apparatus was immersed in a water bath. A 450-w. Hanovia immersion lamp was employed for these studies. Quantum yields were determined by running a benzophenone–benzhydrol actinometer simultaneously with the samples.[15]

Acknowledgment.—Support of this work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. N. J. T. also thanks the National Science Foundation for a postdoctoral fellowship.

---

[14] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

[15] W. M. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, **83**, 2789 (1961); W. M. Moore and M. Ketchum, *ibid.*, **84**, 1368 (1962).