

cm^{-1} ; nmr (CCl_4) δ 7.10 (s, 10 H), 3.92 (t, $J = 7$ Hz, 1 H), 1.88 (broad d, $J = 7$ Hz, 2 H), 1.24 (broad s, 9 H), and 0.90 (t, $J = 7$ Hz, 6 H). *Anal.* Calcd for $\text{C}_{21}\text{H}_{28}$: C, 89.9; H, 10.1. Found: C, 89.7; H, 10.2. The yields of **3c**, **4c**, **8**, and **9** were 53, 9, 8, and 7%, respectively.

(2) Diazo compound **2c** (1.5 g, 7.7 mmol) was thermolyzed in a mixture of **1** (6.5 g, 60 mmol) and decalin²⁵ (166 g, 1.2 mol) at 140° for 1 hr. Decalin and excess **1** were removed by fractionation, and the residue was dissolved in 15 ml of petroleum ether. After the solution stood overnight in a refrigerator, 1,1,2,2-tetraphenylethane (**10**) [mp 210–211° (lit. 209°), 320 mg (25.5%)] separated and was collected by filtration. From the mother liquor, by following work-up procedures described above, **3c**, **4c**, **8**, and **9** were isolated in 16.4, 3.6, 2.0, and 5.4% yields, respectively. The polymeric material was a major product (50 wt %).

Photolysis of 2c in the Presence of 1. (1) A mixture of 1.94 g (10 mmol) of **2c** and 15.0 g (139 mmol) of **1** was irradiated in Pyrex glass tubes as in the photolysis of **2b**. After irradiation for 4 hr at 15°, excess **1** was removed by fractionation under reduced pressure. Chromatography of the residue on alumina (150 g) gave **3c** (1.20 g, 44.4%), contaminated by a small amount of **4c** (**3c/4c**

was 110 by glpc), in addition to **8** (108 mg, 6.1%), **9** (45 mg, 2.5%), and polymer (1.26 g, 48 wt %).

(2) A benzene (200 g) solution of 1.0 g (5.2 mmol) of **2c** and 5.6 g (52 mmol) of **1** was irradiated in a cylindrical vessel at 15° for 4 hr. Workup as before gave a mixture of **3c** and **4c** (99:1) (554 mg, 39.9%), in addition to **8** (70 mg, 7.5%) and **9** (19 mg, 2.0%).

Determination of the Adduct Ratio, 3c/4c. The reactions to determine the **3c/4c** ratio were carried out by using 100 mg of **2c** and 1.0 g of **1**. After removal of **1** and solvent, the adducts were separated by column chromatography from **8** and **9**. The combined fraction (ca. 500 ml) containing **3c** and **4c** was concentrated, and the residual liquid was analyzed by glpc (PEGS, 220°) using *n*-hexadecane as an internal standard. In contrast to **3b** and **4b**, **3c** and **4c** were stable under glpc analysis conditions. The results are summarized in Table IV.

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A New Substrate to Investigate Radical Cycloadditions. III.¹ Photocycloaddition of Aromatic Carbonyl Compounds to Vinylcyclopropane and Its Derivatives

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Abstract: Irradiation of a benzene solution of cyclopropylethylene (**1**) and aromatic carbonyl compound (**2**) by uv light produced an expected oxetane (**3**) and a rearranged tetrahydrooxepin (**4**) as the principal photocycloadducts. In some photoreactions, olefin **6** was obtained in addition to **3** and **4**. The olefin was, however, found to have resulted by cleavage of **3**, so that **3** was the primary photoadduct. The (**3** + **6**)/**4** ratio depends upon the temperature applied for the photoreactions; an increasing amount of **4** was produced at higher temperatures. These results can be best explained by a mechanism in which diradical **10** is derived by an addition of photoexcited triplet 2_T^* to **1**, and **10** undertakes two competing processes, one giving **3** by simple cyclization and the other giving **4** by cyclization after cyclopropylcarbinyl-allylcarbinyl radical rearrangement. The effect of the substituents on the (**3** + **6**)/**4** ratio was in accord with the mechanism. Oxetanes of inverse orientation (**7**) were isolated in certain photoreactions, but the process remained minor in all photoreactions.

In the preceding paper, it was demonstrated that cyclopropylethylene (**1**) is a useful substrate to investigate the spin multiplicity of carbene addition reactions.¹ The adduct produced after cyclopropylcarbinyl-allylcarbinyl radical rearrangement is shown to be observed only when the triplet carbene attacks **1**. In the present paper, Paterno-Büchi reactions² utilizing **1** as a substrate olefin are examined. Photoexcited aromatic carbonyl compounds such as benzophenone (**2a**) and benzaldehyde (**2b**) undergo intersystem crossing extremely rapidly and they react principally from the triplet state.³ Thus, the reaction will involve intermediate 1,4-diradical⁴ possessed of a cyclopropyl-

carbinyl radical site which may live long enough to undergo the rearrangement.

Results

Paterno-Büchi Reactions. Photoreactions at room temperature were carried out by irradiating a deoxygenated benzene solution of an equimolar mixture of **1** and **2** (ca. 0.4 *M*) in an ordinary photoapparatus (see Experimental Section). Photoreactions at higher than room temperature were carried out in the following manner. The solution was sealed in Pyrex glass am-

(1) Part II: N. Shimizu and S. Nishida, *J. Amer. Chem. Soc.*, **96**, 6451 (1974).

(2) (a) E. Paterno and G. Chieffe, *Gazz. Chim. Ital.*, **39**, 341 (1909); (b) G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Amer. Chem. Soc.*, **76**, 4327 (1954).

(3) For example, see N. J. Turro in "Technique of Organic Chemistry," Vol. 14, L. A. Leermakers and A. Weissberger, Ed., Interscience, New York, N. Y., 1969, Chapter III.

(4) (a) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962); (b) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964); (c) N. C. Yang, M. Nissim, M. J. Jorgenson, and S. Murov, *ibid.*, 3657 (1964); (d) J. S. Bradshaw, *J. Org. Chem.*, **31**, 237 (1966); (e) N. C. Yang, R. Loesch, and D. Mitchell, *J. Amer. Chem. Soc.*, **89**, 5465 (1967); (f) L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions," Interscience, New York, N. Y., 1967, p 111; (g) R. Srinivasan and K. A. Hill, *J. Amer. Chem. Soc.*, **90**, 3765 (1968); (h) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968), and references cited therein; (i) N. J. Turro, D. A. Wriede, and J. C. Dalton, *J. Amer. Chem. Soc.*, **90**, 3274 (1968); (j) L. A. Singer, G. A. Davis, and V. P. Muralidharan, *ibid.*, **91**, 897 (1969).

poules, which were affixed in close proximity around a 450-W immersion-type high-pressure mercury lamp (see Experimental Section). The whole photoapparatus was then placed in a bath, previously adjusted at a given temperature, and photoreaction was carried out. In the reaction of **2a** with **1a**, consumption of **2a** after 7 hr of irradiation at 160° was 14%. It was 16.5% for the reaction of **2a** with **1b** under similar conditions. In all runs, the combined yield of photoadducts was 10–90% based on the consumed amount of **2**. The results are summarized in Table I.

Table I. Photoreactions between Arylcarbonyl Compound (**2**) and Cyclopropylethylene (**1**)

Reactant	Temp, °C	Product ^b (%)		
		Oxetane	Tetrahydrooxepin	Others ^c
1a 2a	160	3a (29.4)	4a (64.5)	
	130	3a (36.0)	4a (55.0)	
	100	3a (61.0)	4a (34.0)	
	70	3a (62.5)	4a (16.7)	
	rt ^a	3a (86)	<i>h</i>	
1b 2a	160	3b (21.0)	4b (45.0)	
	130	3b (43.1)	4b (31.2)	
	100	3b (57.5)	4b (29.0)	
	70	3b (55.0)	4b (13.0)	
	rt ^a	3b (86.5)	4b (3.0)	
1c 2a	100	<i>d</i>	4c (29.6)	
	75	<i>d</i>	4c (10.0)	6c (9.0) ⁱ
	50	<i>d</i>	4c (6.0)	6c (19.0) ⁱ
	25	<i>d</i>	4c (5.0)	6c (35.0) ⁱ
1d 2a	100	3d (18.5) ^e	4d (31.8)	6c (3.3) ⁱ
1a 2b	rt ^a	3e (65)	<i>h</i>	
1b 2b	130	3f (32.2) ^f	4f (10.1)	
	100	3f (39.8) ^f	4f (5.2)	
	70	3f (49.6) ^f	4f (2.3)	
1c 2b	100	3g (5.9) ^g	4g (2.9)	6f (0.5) [*]
	75	3g (14.8) ^g	4g (4.2)	6f (4.3) [*]
	50	3g (8.2) ^g	4g (0.6)	6f (0.6) [*]
	25	3g (17.3) ^g	<i>h</i>	6f (0.7) [*]

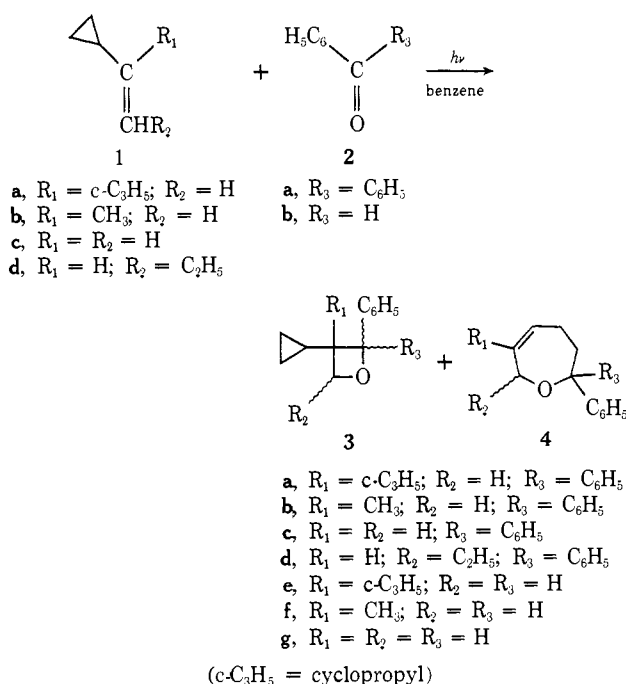
^a Photoreaction at room temperature (20–25°). ^b Analyzed by glpc. ^c Olefin resulted from **3**; products other than **6** are given in footnotes. ^d See text. ^e Oxetane **7a** was also obtained in 15.9% yield. ^f The *E/Z* ratio was found to be 2.3–2.4. ^g The *trans/cis* ratio was found to be 2.2–2.8. ^h Could not be detected. ⁱ 1,1-Diphenylethylene (0.4–0.9%) and spirooxetane (**8**) (1.0–3.0%) were also obtained. ^j 1,1-Diphenylbut-1-ene was also obtained in 3.0% yield. ^{*} *Trans* isomer.

In general, two 1:1 photocycloadducts were isolated. Elemental and spectroscopic analyses indicated that one of them was oxetane derivative (**3**), while the other was a cyclopropane-cleaved cycloadduct, *i.e.*, 2,3,4,7-tetrahydrooxepin derivative (**4**). The structure of **3** was confirmed by its cleavage to olefin. For example, a treatment of **3a** with dilute methanolic perchloric acid⁵ at reflux for 8 hr gave olefin **6a** in an almost quantitative yield; the ir spectrum of **6a** thus obtained was superimposable on that of the authentic specimen.⁶ Less substituted oxetanes (**3c**, **3d**, **3e**, **3f**, and **3g**) were found to be cleaved thermally to olefin⁷ (**6c**, **6c**, **6d**, **6e**, and **6f**, respectively). These cleavage experiments established the structure, and hence the orientation of the

(5) J. A. Barltrop and H. A. J. Carless, *J. Amer. Chem. Soc.*, **93**, 4794 (1971).

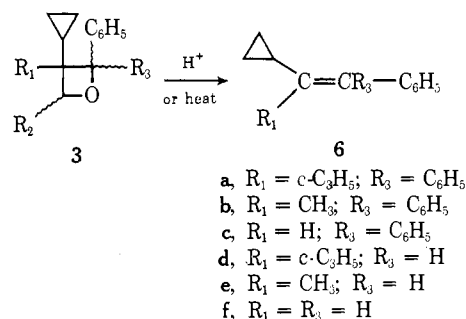
(6) T. Teraji, I. Moritani, E. Tsuda, and S. Nishida, *J. Chem. Soc.*, 3252 (1971).

(7) (a) M. Bartok, *Acta Chim. Acad. Sci. Hung.*, **51**, 403 (1967); (b) M. Bartok and B. Kozma, *ibid.*, **52**, 83 (1967); (c) G. Jones, II, S. B. Schwartz, and M. T. Marton, *Chem. Commun.*, 374 (1973).



addition, of the photoadducts **3** as shown in the scheme.

It should be pointed out that **3c** was so labile that it could be characterized only by ir and nmr examinations of the crude mixture; attempted purification either by column chromatography or by glpc inevitably resulted in the formation of **6c**. Therefore, in the

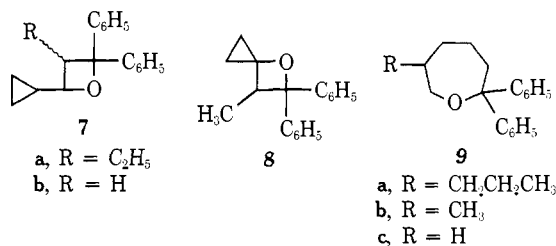


following discussion, the yield of **3c** is based on the amount of **6c** present, after complete conversion of **3c** to **6c**. It is also of considerable interest to note the different thermal behavior of the isomeric **3g**. The oxetane fraction obtained in the photoreaction of **1c** with **2c** was a mixture of geometrical isomers. The oxetane produced in a larger amount was assigned to be the *trans*-**3g** which exhibited a smaller vicinal coupling constant in its nmr than that of the minor component.³ Interestingly, *trans*-**3g** thermolyzed smoothly at 200° to give *trans*-**6f**, with retention of configuration, whereas *cis*-**3g** remained practically unchanged under the same conditions. 2-Cyclopropylstyrene (**6f**) isolated from the photoreaction mixture was also found to be a *trans* olefin (Table I).

In the photoreactions of **1c** with **2a** and **1d** with **2a**, oxetane of inverse orientation (**7**) and/or olefin were produced, but they remained minor products in all cases. In the photoreaction of **1c** with **2a**, the third oxygen-containing adduct, to which the spiro structure **8** was tentatively given, was obtained (1–3% yield).

(8) J. A. Barltrop and H. A. J. Carless, *J. Amer. Chem. Soc.*, **94**, 1951 (1972).

The structural confirmation of **4** was made by its derivation to a saturated seven-membered cyclic ether **9** by catalytic hydrogenation.



The (3 + 6)/4 Ratio. It is to be noted that the formation of **3** is dominant over that of **4** at room temperature, but the reverse is true for photoreactions at, or higher than, 130°. As mentioned above, **6** was produced from **3** at certain stages of the experiments; the combined (**3** + **6**) should be the amount of **3** produced initially. The (**3** + **6**)/**4** ratios at various temperature are summarized in Table II. Now, in five reactions examined,

Table II. The (**6** + **3**)/**4** Ratio at Various Temperatures

T, °C	The 3/4 ratio in the reaction of						
	1a-2a	1b-2a	1c-2a	1d-2a	1a-2b	1b-2b	1c-2b
25	(3a) ^{a,b}	28.0 ^b	7.0 ^d		(3e) ^a		(3g + 6f) ^a
50			3.3 ^d				14.6 ^e
75	4.0 ^c	4.3 ^c	0.91 ^d			21.0 ^c	3.5 ^e
100	1.8	1.5	0.1 ^d	0.69		7.6	2.2 ^e
130	0.67	0.71				3.4	
160	0.44	0.56					

^a Tetrahydrooxepin derivative (**4**) was not detected. ^b At room temperature (20–25°). ^c At 70° ^d The figure given is **6c**/**4c**. ^e The figure given is (**3g** + **6f**)/**4g**.

a plot of log (**3** + **6**)/**4** vs. 1/T gave a straight line. Apparent differences in the activation parameters between the two processes are estimated from the slope and intercept of the plot (Table III). Control experiments

Table III. Activation Parameter Difference between the Two Processes

Olefin	Carbonyl compd	ΔE _a , ^a kcal/mol	Δ log A ^b
1a	2a	-7.4 ± 0.5	-4
1b	2a	-7.0 ± 0.5	-4
1c	2a	-6.9 ± 1.5	-4
1b	2b	-8.3 ± 0.5	-4
1c	2b	-8.2 ± 1.5	-5

^a (E_a for **3**) - (E_a for **4**). ^b Log (A for **3**)/(A for **4**).

indicated that the cyclopropane incorporated in the starting olefins and photoproducts, **3** and **6**, did not undergo the rearrangement under the experimental conditions.

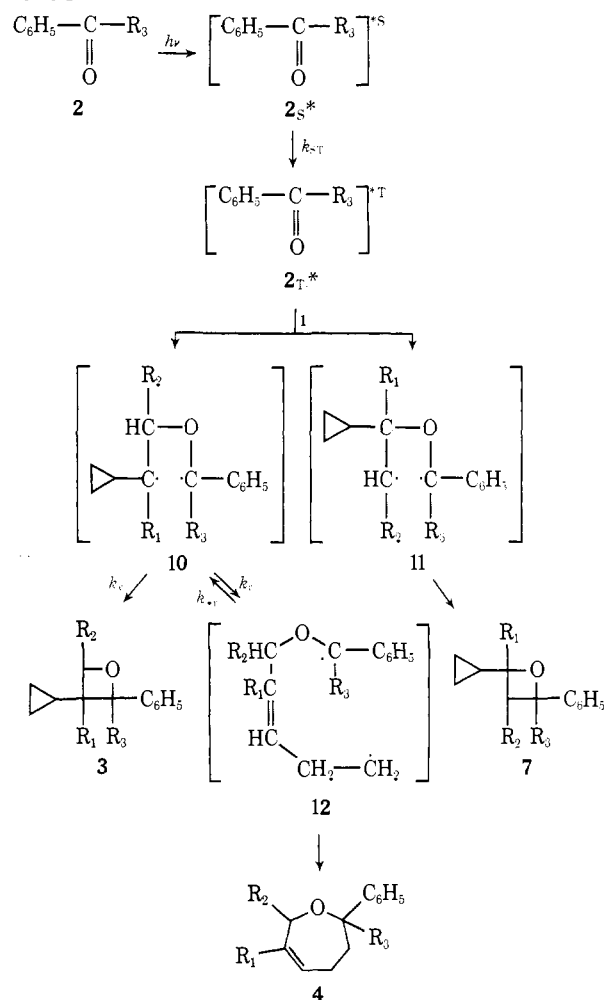
At 100°, the photoreaction of **1b** with **2a** gave **3b** and **4b** in a ratio of 1:1.5. The consumption of **2a** after 8 hr of irradiation (5.0 mmol of each reactants in 20 ml of benzene) was found to be 20%, while the addition of an equimolar amount of naphthalene to the solution depressed the consumption of **2a** markedly; it was only 1%. It should be pointed out here, however, that the **3**/**4** ratio observed in this incomplete quenching was the

same as that observed in the absence of the quencher. Addition of excess (5×) naphthalene quenched the photoreaction completely. Since the end absorption of naphthalene at 340 nm was low enough to assume that sufficient light was absorbed by **2a** under the experimental conditions, it can be concluded that the photoreaction was quenched by the triplet quencher. Similar observations were made in the photoreaction of **1b** with **2b** at 100°.

Discussion

Reaction Scheme. The formation of the two photoadducts **3** and **4** in the present experiments can be best explained by a mechanism in which a long-lived diradical held on a cyclopropylcarbiny radical site is involved (Scheme I). It has been established that

Scheme I



photoexcited aromatic carbonyl compounds undergo intersystem crossing extremely rapidly ($k_{\text{ST}} \geq 10^{10} \text{ sec}^{-1}$)³ and hence they react principally from the triplet state. In the Paterno-Büchi reactions, however, complex formation between 2_{T}^* and olefin prior to the formation of the 1,4-diradical is indicated to occur,⁹ but the present results do not allow us to discuss such primary interactions. In any event, the 1,4-diradical may

(9) (a) I. Kochevar and P. J. Wagner, *J. Amer. Chem. Soc.*, **92**, 5742 (1970); (b) *ibid.*, **94**, 3859 (1972); (c) R. A. Caldwell, G. W. Sovocool, and R. P. Gajewski, *ibid.*, **95**, 2549 (1973).

most safely be assumed to be a discrete intermediate in such reactions.^{2b, 3-5, 8-10} Thus, diradicals **10** and **11** are considered to be intermediates in the present reactions. The diradical **10** should be produced in a larger amount than **11**, either because it is more stable than **11**,¹⁰ or because it is produced from the prior complex of preferred orientation.⁹ In fact, the oxetane derived from **11** remained minor in the photoadducts.

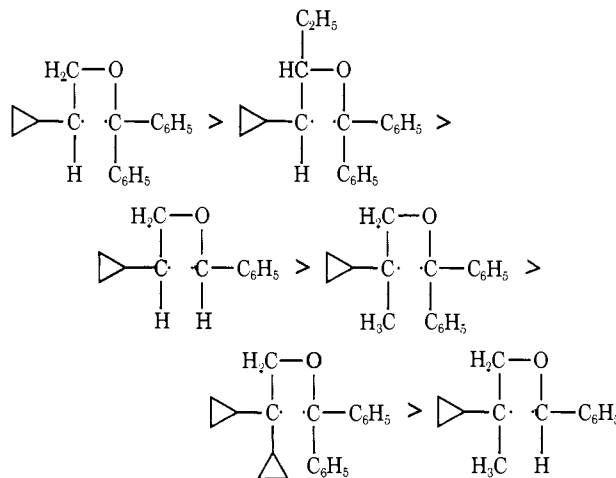
Now, **10** might be relatively long lived because it was derived from triplet precursor 2_T^* . Consequently, processes of low-energy barrier other than k_c will participate in the reaction. Rotation around a single bond has long been known for such a process.^{3, 4f, 4h} However, recent results suggest that the cyclopropylcarbinyl-allylcarbinyl rearrangement may also be one of such processes.¹¹ Thus, **10** will take two competing reaction paths, one giving **3** by simple cyclization and the other giving **4** by cyclization after rearrangement to **12**. A possibility that **4** is produced from a vibrationally hot **3**¹² is unlikely. Upon heating, certain oxetanes (**3c-g**) have given olefin **6** in high yield but no **4**, and hence the hot oxetane should give olefin similarly.

In order to cyclize to a seven-membered **4**, **12** should have a *cis* configuration with respect to the two side chains which carry the radical carbon. It is unlikely that *cis*-**12** was produced exclusively, but *trans*-**12** must also have been produced. However, *trans*-**12** should have a relatively high-energy barrier to cyclize, so that it will go back to **10** (k_{-}) or it may undertake routes to give products other than **3** or **4**.

Temperature Dependence of the (3 + 6)/4 Ratio. A plot of $\log (3 + 6)/4$ vs. $1/T$ gave a straight line. The plots suggest that the rearranging process is of a higher energy barrier than the cyclization process by *ca.* 7–8 kcal/mol. On the other hand, the entropy term is in favor of the rearrangement (Table III). The results do not contradict the proposed mechanism, in which the products are derived from a common intermediate **10**. In the present case, the substituent R_1 will increase the energy barrier of the rearrangement substantially, while the formation of a strained oxetane ring will make k_c no longer the coupling process of a nearly zero energy barrier. It is hence conceivable that the net effect of these factors has given the aforementioned difference, which is rather close to the calculated energy barrier of parent cyclopropylcarbinyl radical.^{11a} A favorable entropy term for the rearrangement is also consistent with the proposed mechanism. The formation of a four-membered ring will result in the decrease of the activation entropy, while the rearrangement to **12** will increase it.

Substituent Effect on the (3 + 6)/4 Ratio. From the data, we can reach a conclusion that a more stabilized

cyclopropylcarbinyl radical gives the higher (3 + 6)/4 ratio, whereas a more stabilized benzyl radical gives a lower ratio. The overall ease of giving **4** is thus as follows. The sequence can be rationalized by considering that a stabilizing substituent at the cyclopropylcarbinyl radical reduces k_r ,¹³ and hence increases the amount of **3**, while the more stabilized benzyl radical



slows down the cyclization (k_c), which will increase the amount of **4**. Accordingly, the effects of the substituents on the ratio are strong support for the justification of the product-determining partition mechanism given above.

Conclusion

From these discussions, it can be concluded that the formation of **4** provides unequivocal evidence that the photochemical oxetane formation proceeds through a discrete diradical intermediate. It turns out that cyclopropylethylene is indeed a unique substrate to investigate radical cycloadditions. Should an intermediate diradical held on a cyclopropylcarbinyl radical site be involved, it would give the rearranged product at a sufficiently high temperature. Among the choices to be made based on the ease of giving the rearranged adduct, a pair of reactants which produces a diradical possessed of a less stabilized cyclopropylcarbinyl site and a more stabilized opposite site will certainly be the best.

Experimental Section

Ir and uv spectra were recorded on the same instruments as before.¹ Nmr spectra were recorded either on a Hitachi R-20 or on a JEOL PS-100 high resolution nmr spectrometer. The chemical shifts were determined in carbon tetrachloride. The abbreviations given in the nmr data are s = singlet, d = doublet, t = triplet, and m = multiplet. Gpc was carried out either on a Yanagimoto 550-T or on a Yanagimoto G-8 gas chromatograph using columns packed with either 20% polyethylene glycol succinate on Chromosorb W (PEGS) or 20% polyethylene glycol 20M on Cerite (PEG). All boiling points and melting points are uncorrected. Yields given are based on the consumed amount of the carbonyl compound.

Material. Preparations of 1,1-dicyclopropylethylene (**1a**),¹⁴ bp 132–133° (lit.¹⁴ 129–130°), 2-cyclopropylpropene (**1b**),^{14, 15} bp

(10) (a) J. F. Harris, Jr., and D. D. Coffman, *J. Amer. Chem. Soc.*, **84**, 1553 (1962); (b) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965; (c) J. Saltiel, R. M. Coates, and W. G. Dauben, *J. Amer. Chem. Soc.*, **88**, 2745 (1966); (d) N. J. Turro, P. Wriede, J. C. Palton, D. R. Arnold, and A. H. Glick, *ibid.*, **89**, 3950 (1967); (e) N. J. Turro and P. Wriede, *ibid.*, **92**, 320 (1970); (f) J. A. Barltrop and H. A. J. Carless, *ibid.*, **93**, 1794 (1971); (g) T. Kubota, K. Shima, and H. Sakurai, *Chem. Lett.*, 343 (1972); (h) J. A. Barltrop and H. A. J. Carless, *J. Amer. Chem. Soc.*, **94**, 8761 (1972).

(11) (a) L. K. Montgomery and J. W. Matt, *J. Amer. Chem. Soc.*, **89**, 6556 (1967); (b) S. J. Cristol and R. V. Barbour, *ibid.*, **90**, 2832 (1968); (c) D. J. Carlson and K. U. Ingold, *ibid.*, **90**, 7047 (1968); (d) R. A. Sheldon and J. K. Kochi, *ibid.*, **92**, 4395, 5175 (1970); (e) W. J. Hehre, *ibid.*, **95**, 2643 (1973).

(12) S. M. Jasper, M. Pomerantz, and E. W. Abrahamson, *Chem. Phys. Lett.*, **3**, 137 (1968).

(13) D. C. Neckers, A. D. Schaap, and J. Hardy, *J. Amer. Chem. Soc.*, **88**, 1265 (1966).

(14) T. Teraji, I. Moritani, E. Tsuda, and S. Nishida, *J. Chem. Soc. C*, 3252 (1971).

(15) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

72–73° (lit.¹⁴ 72–73°), vinylcyclopropane (**1c**),^{16,17} bp 40–41° (lit.¹⁶ 40.2°), and 1-cyclopropylbut-1-ene (**1d**),¹⁸ bp 104–105°, are described elsewhere. Benzophenone (**2a**) was purified by vacuum distillation followed by recrystallization from ethanol. Benzaldehyde (**2b**) was distilled just before use. Benzene was purified by an ordinary method.

General Procedures of Irradiation. All photoreactions were carried out in a deoxygenated (argon bubbled) benzene solution of an equimolar mixture of **1** and **2**. Photoreactions at room temperature were performed in a cylindrical Pyrex cell (55-mm i.d., 75-mm o.d., 150-mm height, 100-ml capacity) with two necks, to which a gas inlet tube and an outlet tube were connected. Irradiation was made with a Halo 450-W high-pressure mercury lamp, Model PIH-500S (150-mm length of illuminating tube, 37-mm o.d.),¹⁹ which was inserted into the central room of the cell. The cell and the lamp were set in a large water bath, and the photoreaction was carried out.

For photoreactions at higher temperatures, the solution was sealed in Pyrex glass ampoules (16-mm diameter, 15-ml capacity). The Pyrex ampoules were then affixed in close proximity around the same immersion-type uv lamp as above. The whole photoapparatus was immersed in a bath, previously adjusted at a given temperature, and the photoreaction was carried out. For irradiations below 100°, water was used for the bath; freshly distilled decalin was substituted for water in the photoreactions at/or above 100°.

Photoreaction of 2a with 1a. (1) A benzene (40 g) solution of 3.64 g (20 mmol) of **2a** and 2.16 g (20 mmol) of **1a** was irradiated in the Pyrex cylindrical cell at room temperature for 50 hr. Glpc analysis indicated that 20% of **2a** was consumed. Solvent and recovered reactants were removed by fractionation under reduced pressure. The residue, mp 98–103° (1.2 g), was recrystallized from *n*-hexane to give colorless crystals (1.0 g), mp 113.5–114.5°, which was found as 3,3-dicyclopropyl-2,2-diphenyloxetane (**3a**) by spectroscopic properties and chemical conversion to **6a**: ir (Nujol) 3100, 3075, 1600, 1500, 1050 (m), 1025, 1020 (m), 1000 (s), 995 (s), 760 (s), 745, 710 (s), 695 (s) cm⁻¹; nmr δ 7.02–7.57 (m, 10 H), 3.80 (s, 2 H), 0.0–1.0 (m, 10 H). *Anal.* Calcd for C₂₁H₂₂O: C, 86.9; H, 7.6. Found: C, 86.9; H, 7.8. The yield based on consumed **2a** was 86%.

(2) A benzene (50 ml) solution of 3.64 g (20 mmol) of **2a** and 2.16 g (20 mmol) of **1a** was irradiated in Pyrex sealed tubes at 160° for 7 hr. Glpc showed that 14% of **2a** was consumed. The solvent and recovered reactants were removed by fractionation under reduced pressure and the resulted residue (3.6 g) was placed on the top of an alumina column (150 g). Elution with ether–petroleum ether²⁰ (10:90) gave fractions which were collected in 50-ml portions. Fractions 3–6 gave colorless crystals, mp 67.5–68° (0.6 g), which were characterized as 6-cyclopropyl-2,2-diphenyl-2,3,4,7-tetrahydrooxepin (**4a**) by spectral data and hydrogenation to **9a**: ir (Nujol) 3100, 3075, 1650, 1500, 1260, 1240, 1125, 1115, 1095, 1080 (s), 1060 (s), 1040, 1030, 1020, 920, 910, 815, 765 (s), 755 (s), 700 (s) cm⁻¹; nmr δ 7.0–7.4 (m, 10 H, aromatic), 5.36 (t, *J* = 5 Hz, split further into doublet, *J* = 1 Hz, 1 H, C-5 vinyl), 3.98 (s, 2 H, C-7 methylene), 2.50–2.60 (m, 2 H, C-3 methylene), 2.04 (broad s, 2 H, C-4 methylene), 1.10 (quintet, *J* = 6 Hz, 1 H, allylic cyclopropyl), 0.24–0.60 (m, 4 H, cyclopropyl). Double resonance by irradiation at δ 2.04 left sharp singlets at δ 5.36 and at 2.55. *Anal.* Calcd for C₂₁H₂₂O: C, 86.9; H, 7.6. Found: C, 86.8; H, 7.6.

Fractions 7 and 8 contained both **3a** and **4a** (150 mg). The **3a/4a** ratio was estimated by analysis of the relative peak intensity in ir at 1030 and 995 cm⁻¹. Fractions 9–12 gave recovered **2a** (1.80 g). Final elution of the column with methanol–ether mixture (5:95) gave 0.8 g of yellow polymeric material: ir (neat) 3500, 3080, 3040, 2945 (s), 2875, 1710 (broad, s), 1670 (broad, s), 1600, 1500, 1445 (s), 1330 (broad), 1170 (broad), 1020, 750 (s), 695 (s) cm⁻¹. The combined yields of **3a** and **4a** were calculated to be 29 and 65%, respectively.

(3) In Pyrex tubes, the photoreaction of **2a** with **1a** was carried out at 130, 100, and 70° for 7 hr. The yields of **3a** and **4a** were 36

and 55% at 130°, 61 and 34% at 100°, and 63 and 17% at 70°, respectively.

Photoreaction of 2a with 1b. (1) A benzene (60 g) solution of **2a** (5.46 g, 30 mmol) and **1b** (2.46 g, 30 mmol) was irradiated in Pyrex sealed tubes at 160° for 7 hr. Consumption of **2a** was found to be 16.5% by glpc. Similar work-up including chromatographic separation as before gave 580 mg of **4b**, mp 83.5–84° from *n*-hexane [ir (Nujol) 3100, 3080, 1605, 1500, 1265 (m), 1235, 1205, 1170, 1100 (s), 1085 (s), 1070 (s), 1035, 1005, 985, 905, 855, 830, 760 (s), 750 (s), 700 (s) cm⁻¹; nmr δ 6.90–7.40 (m, 10 H, aromatic), 5.36 (t, *J* = 4.5 Hz, split further into quartet, *J* = 1 Hz, 1 H, C-5 vinyl), 3.91 (s, 2 H, C-7 methylene), 2.50–2.62 (m, 2 H, C-3 methylene), 2.00 (broad s, 2 H, C-4 methylene), 1.53 (d, *J* = 1 Hz, 3 H, methyl) (*Anal.* Calcd for C₁₃H₂₀O: C, 86.3; H, 7.6. Found: C, 86.1; H, 7.6.), and 380 mg of **3b**, mp 61.0–62.0° from ethanol [ir (Nujol) 3100, 3080, 1605, 1500, 1120, 1040, 1020 (m), 995 (s), 940, 915, 825, 760 (s), 745 (s), 710 (s), 700 (s) cm⁻¹; nmr δ 6.96–7.56 (m, 10 H), 4.10 (d, *J* = 5.6 Hz, 1 H), 3.98 (d, *J* = 5.6 Hz, 1 H), 0.88 (s, 3 H, methyl), 0.7–0.9 (m, 1 H), 0.00–0.48 (m, 4 H) (*Anal.* Calcd for C₁₃H₂₀O: C, 86.3; H, 7.6. Found: C, 86.3; H, 7.6.)]. Yellow polymeric material (0.6 g) was also obtained: ir (neat) 3500, 3080, 3040, 2950, 1670 (broad), 1600, 1495, 1445 (s), 1330 (broad), 1020 (broad), 750 (broad), 695 (s) cm⁻¹. The yields of **3b** and **4b** were 21 and 45%, respectively.

(2) Similar photolyses at different temperatures gave the following results. The yields of adducts and the **3b/4b** ratio determined by glpc (PEGs, 200°), using *n*-decane as an internal standard, were 75% (**3b/4b** = 0.71) at 130°, 86.5% (1.5) at 100°, 68.0% (4.3) at 70°, and 89.5% (28.0) at room temperature, respectively.

Photoreaction of 2a with 1c. (1) A mixture of 5.0 g (74 mmol) of **1c** and 13.5 g (74 mmol) of **2a** in benzene (50 ml) was irradiated in Pyrex sealed tubes at 50° for 50 hr. The reaction mixture was fractionated to remove benzene and recovered **1c**, leaving a yellow residue. The residue was chromatographed on alumina (150 g). Elution with ether–petroleum ether mixture (5:95) gave a colorless liquid (0.9 g) and **2a** (10.7 g), in the order of elution. Yellow polymeric material (4.35 g) was also obtained by elution with ether: ir (neat) 3100, 3080, 3040, 2945 (s), 2875, 1710 (s), 1660 (broad), 1600, 1495, 1450 (s), 1310, 1280 (broad), 1180 (broad), 1050 (broad), 1025 (broad), 970 (broad), 910, 750 (s), 695 (s) cm⁻¹. The liquid product obtained in the first elution was placed on the top of a fresh alumina column, and elution was carefully done by petroleum ether. There was obtained a colorless liquid, which was found to be a mixture of two components, which were separated by preparative glpc (PEG, 140°) and were identified as 1-cyclopropyl-2,2-diphenylethylene (**6c**) and 1,1-diphenylethylene by comparison of their ir with those of authentic specimens. Further elution of the column with ether–petroleum ether (5:95) gave 206 mg of a colorless solid, 400 mg of a colorless liquid, and 39 mg of the second colorless solid in the order of elution. Recrystallization of the first solid from *n*-hexane gave colorless crystals, mp 82–83°, which were characterized as 2,2-diphenyl-2,3,4,7-tetrahydrooxepin (**4c**): ir (Nujol) 3070, 3040, 1260, 1190, 1125 (s), 1085 (s), 1060 (s), 1025, 775, 760 (s), 750 (s), 705 (s), 700 (s) cm⁻¹; nmr δ 6.90–7.44 (m, 10 H, aromatic), 5.66 (d, *J* = 10 Hz, split further into t, *J* = 4 Hz, 1 H, C-5 vinyl), 5.50 (d, *J* = 10 Hz, split further into t, *J* = 4 Hz, 1 H, C-6 vinyl), 4.00 (broad d, *J* = 4 Hz, 2 H, C-7 methylene), 2.60 (m, 2 H, C-3 methylene), 2.04 (broad s, 2 H, C-4 methylene). *Anal.* Calcd for C₁₈H₁₈O: C, 86.4; H, 7.3. Found: C, 86.2; H, 7.3.

The liquid product eluted secondly was assigned as 3-cyclopropyl-2,2-diphenyloxetane (**3c**) by the spectroscopic data: ir (neat) 3100, 3080, 3040, 3020, 2970, 2950, 2890, 1600, 1500 (s), 1450 (s), 1080, 1030 (m), 1020 (m), 990 (s), 910, 760 (s), 745 (s), 700 (s) cm⁻¹; nmr δ 7.0–7.5 (m, 10 H), 4.60 (double d, *J* = 8.4 and 6 Hz, 1 H), 4.35 (double d, *J* = 6.5 and 6 Hz, 1 H), 2.75 (quartet, *J* = 7 Hz, 1 H), 0.0–0.7 (m, 5 H). However, all attempts to purify **3c** failed and olefin **6c** resulted. Column chromatography on silica gel eluted by ether–petroleum ether (5:95) gave only **6c** in quantitative yield. Preparative glpc (PEG, 150°) gave a mixture of **3c** and **6c**. The amount of **6c** finally collected was 607 mg.

The second solid obtained in the chromatography was assigned as 4-methyl-5,5-diphenyl-6-oxaspiro[2.3]hexane (**8**), mp 98–99° from *n*-hexane: ir (Nujol) 3080, 3040, 1320, 1215 (s), 1200, 1010 (s), 985 (s), 970 (s), 950 (s), 930 (s), 770 (s), 750 (s), 700 (s) cm⁻¹; nmr δ 7.0–7.4 (m, 10 H), 3.88 (quartet, *J* = 7 Hz, 1 H), 0.76 (d, *J* = 7 Hz, 3 H), 0.6–1.0 (m, 2 H), 0.4–0.6 (m, 2 H); mass spectrum *m/e* 250 (M⁺). *Anal.* Calcd for C₁₈H₁₈O: C, 86.4; H, 7.3. Found: C, 86.6; H, 7.5.

The yields of **6c**, **4c**, **8**, and 1,1-diphenylethylene isolated were 19, 6, 1, and 0.6%, respectively.

(16) V. A. Slabey, *J. Amer. Chem. Soc.*, **74**, 4930 (1952).

(17) S. Nishida, I. Moritani, K. Ito, and K. Sakai, *J. Org. Chem.*, **32**, 939 (1967).

(18) S. Nishida, N. Shimizu, and T. Tsuji, to be published. The olefin used in the present experiments was a mixture of *cis* and *trans* isomers in a ratio of 24:76.

(19) Eiko-sha Co. Ltd., Nakatsu-minami-dori 2-11, Oyodo-ku, Osaka, Japan.

(20) Fractionated petroleum ether, bp 40–60°, was used in all experiments described hereafter.

(2) Similar photoreactions at different temperatures gave **6c**, **4c**, **8**, and 1,1-diphenylethylene in 9, 10, 1, and 0.4% yields at 75°, and in 35, 5, 3, and 0.9% yields at 25°, respectively. The major product was intractable polymer (60–80 wt %) in all cases.

Photoreaction of 2a with 1d. A benzene (30 g) solution of 3.64 g (20 mmol) of **2a** and 1.96 g (20 mmol) of **1d**¹⁸ was irradiated in Pyrex tubes at 100° for 8 hr. Glpc analysis of the reaction mixture indicated the presence of at least five products. Fractionation of the reaction mixture gave 0.8 g of recovered **1d**, which was found to be a mixture of 13% *cis* and 87% *trans* isomer by nmr analysis. The yellow oily residue (4.4 g) was chromatographed on alumina (150 g). Elution with ether–petroleum ether (5:95) gave fractions which were collected in 50-ml portions. Each fraction was analyzed by glpc (PEGS, 180°). Fractions 3–7 contained two components (90 mg). They were purified by glpc and identified as **6c** and 1,1-diphenylbut-1-ene by comparison of their ir spectra with those of authentic specimens. Fractions 8 and 9 contained one component, 250 mg of a colorless solid, which was characterized as 7-ethyl-2,2-diphenyl-2,3,4,7-tetrahydrooxepin (**4d**), mp 89.5–90.5° from *n*-hexane; ir (Nujol) 3100, 3050, 1650, 1605, 1500, 1270, 1200, 1120 (s), 1065 (s), 1060 (s), 1030 (s), 940, 840, 780, 775, 750 (s), 700 (s) cm⁻¹; nmr δ 6.90–7.44 (m, 10 H, aromatic), 5.64 (broad m, 1 H, C-5 vinyl), 5.38 (double d, *J* = 10 and 2 Hz, 1 H, C-6 vinyl), 4.02 (broad s, 1 H, C-7 methyne), 2.76 (m, 1 H) and 2.40 (m, 1 H, C-3 methylene), 2.04 (m, 2 H, C-4 methylene), 1.52 (quintet, 2 H), 0.84 (t, *J* = 8 Hz, 3 H). *Anal.* Calcd for C₂₀H₂₂O: C, 86.3; H, 8.0. Found: C, 86.2; H, 8.1.

Fractions 10–15 contained seven components, three of which were characterized as **6c**, **4d**, and 1,1-diphenylbut-1-ene by glpc. The fractions were combined and the solvent was evaporated. The residue was chromatographed once again on fresh alumina (150 g). There were obtained 60 mg of a mixture of **6c** and 1,1-diphenylbut-1-ene, 390 mg of **4d**, and 690 mg of a colorless liquid in the order of elution by ether–petroleum ether (5:95). The last liquid portion was found to be a mixture of two components, which were isolated by glpc (SE-30, 180°; the ratio of the two components was 1:1.2). The major component was characterized as a mixture of isomeric 3-cyclopropyl-4-ethyl-2,2-diphenyloxetane (**3d**) (the ratio of the two isomers was 95:5); ir (neat) 3100, 3080, 3040, 3020, 2970, 2945, 2890, 1605, 1500, 1455 (s), 1030, 1020, 990 (s), 940, 920, 820, 765, 750 (s), 700 (s) cm⁻¹; nmr δ 7.0–7.5 (m, 10 H), 4.36 (quartet, *J* = 6.8 Hz, 1 H), 2.24 (broad t, 1 H), 1.60 (m, 2 H), 0.84 (t, *J* = 8 Hz, 3 H), 0.0–0.6 (m, 5 H). *Anal.* Calcd for C₂₀H₂₂O: C, 86.3; H, 8.0. Found: C, 86.5; H, 8.2. Acid-catalyzed decomposition of **3d** in methanol gave only **6c**.

The minor component was found to be a mixture (30:70) of isomeric 4-cyclopropyl-3-ethyl-2,2-diphenyloxetane (**7a**): ir (neat) 3100, 3040, 2975, 2940, 2890, 1605, 1500, 1450, 1020, 990 (s), 765, 750 (s), 700 (s) cm⁻¹; nmr (the peaks due to the more abundant isomer, where resolvable, are given in italics) δ 7.0–7.5 (m, 10 H), 3.80 (t, *J* = 6.5 Hz) and 3.76 (double d, *J* = 9 and 7 Hz, total 1 H), 3.30 (t, *J* = 6.5 Hz) and 3.05 (double t, *J* = 9 and 6 Hz, total 1 H), 1.0–1.5 (m, 2 H), 0.84 (t, *J* = 7 Hz) and 0.80 (t, *J* = 7 Hz, total 3 H), 0.1–0.5 (m, 5 H). *Anal.* Calcd for C₂₀H₂₂O: C, 86.3; H, 8.0. Found: C, 86.0; H, 8.1. Acid-catalyzed decomposition of **7a** in methanol gave only 1,1-diphenylbut-1-ene.

From fractions 16–18, 2.3 g of **2a** was recovered. Final elution with methanol–ether (5:95) gave 1.4 g of yellow polymeric material: ir (neat) 3450 (broad), 3080, 3040, 2980 (s), 1660 (broad), 1600, 1500 (s), 1450 (s), 1330 (broad), 1170 (broad), 1030 (broad), 750 (broad), 700 (s) cm⁻¹.

The yields, determined by glpc, of **3d**, **7a**, **4d**, **6c**, and 1,1-diphenylbut-1-ene were 18.5, 15.9, 31.8, 3.3, and 3.0%, respectively.

Photoreaction of 2b with 1a. A solution of 5.3 g (50 mmol) of **2b** and 5.4 g (50 mmol) of **1a** in benzene (50 ml) was irradiated in a Pyrex cylindrical cell at room temperature for 16.5 hr. After removal of the solvent and the recovered reactants by fractionation under reduced pressure, the residue was dissolved in ether and washed with a saturated sodium bisulfite solution. The concentrated organic material (4.0 g) was then chromatographed on alumina (150 g). Elution of the column with benzene gave a colorless liquid, which was assigned as 3,3-dicyclopropyl-2-phenyloxetane (**3e**), 1.5 g (65%); ir (neat) 3100, 3020, 2900, 1600, 1500, 1450, 1020, 990 (s), 900, 820, 740, 700 (s) cm⁻¹; nmr δ 7.25 (m, 5 H), 5.40 (s, 1 H), 4.15 (d, *J* = 6 Hz, 1 H), 3.83 (d, *J* = 6 Hz, 1 H), 1.00 (m, 2 H), 0.0–0.7 (m, 8 H). *Anal.* Calcd for C₁₅H₁₈O: C, 84.1; H, 8.5. Found: C, 83.7; H, 8.2.

Elution with methanol–benzene (5:95) gave 2.5 g of yellow polymeric material: ir (neat) 3450 (broad), 3100, 3030, 2950 (s), 1685

(broad, s), 1600, 1500, 1450 (s), 1270 (broad), 1220, 1020 (broad, s), 985 (broad, s), 820, 745, 695 (s) cm⁻¹.

Photoreaction of 2b with 1b. (1) A solution of 3.18 g (30 mmol) of **2b** and 3.24 g (30 mmol) of **1b** in benzene (50 ml) was irradiated in Pyrex sealed tubes at 130° for 7 hr. Recovery of **2b** was 1.3 g. Column chromatograph, similar to that used before, gave 6-methyl-2-phenyl-2,3,4,7-tetrahydrooxepin (**4f**), 310 mg, as a colorless liquid [ir (neat) 3100, 3045, 2980, 2940 (s), 2850, 1640, 1500, 1450, 1265, 1205, 1165, 1105 (s), 1075, 1060, 1030, 825, 740 (s), 730 (s), 700 (s) cm⁻¹; nmr δ 7.20 (m, 5 H), 5.46 (t, *J* = 4 Hz, 1 H), 4.60 (double d, *J* = 7 and 4 Hz, 1 H), 4.07 (s, 2 H), 2.22 (broad s, 2 H), 1.7–2.2 (m, 2 H), 1.60 (s, 3 H) (*Anal.* Calcd for C₁₃H₁₆O: C, 82.9; H, 8.6. Found: C, 82.7; H, 8.4)], a mixture of (*E*)- and (*Z*)-3-cyclopropyl-2-methyl-2-phenyloxetanes (1:2.3), 1.64 g [the major isomer: ir (neat) 3100, 3040, 2970, 2940, 2890, 1500, 1455, 1040, 1020, 995 (s), 875, 820, 740 (s), 700 (s) cm⁻¹; nmr δ 7.2 (s, 5 H), 5.36 (s, 1 H), 4.22 (d, *J* = 6 Hz, 1 H), 3.94 (d, *J* = 6 Hz, 1 H), 0.96 (m, 1 H), 0.70 (s, 3 H), 0.1–0.6 (m, 4 H) (*Anal.* Calcd for C₁₃H₁₆O: C, 82.9; H, 8.6. Found: C, 82.6; H, 8.6); the minor isomer: ir (neat) 3100, 3040, 3020, 2970, 2890, 1040, 1020, 990 (s), 740 (s), 700 (s) cm⁻¹; nmr δ 7.2 (m, 5 H), 5.38 (s, 1 H), 4.18 (d, *J* = 6 Hz, 1 H), 3.92 (d, *J* = 6 Hz, 1 H), 1.24 (s, 3 H), 0.1–0.6 (m, 5 H) (*Anal.* Calcd for C₁₃H₁₆O: C, 82.9; H, 8.6. Found: C, 82.8; H, 8.7)], and 2.8 g of yellow polymeric material [ir (neat) 3450, 3100, 2950 (s), 2895 (s), 1685 (broad), 1610 (s), 1500, 1450 (s), 1340 (broad), 1020, 990 (broad), 750 (s), 700 (s) cm⁻¹].

(2) Under similar conditions as above, but at different temperatures, **1b** and **2b** gave **3f** and **4f** in the following yields: 39.8 and 5.2% for **3f** (in a ratio of 1:2.4) and **4f** at 100°, and 49.6 and 2.3% for **3f** (in a ratio of 1:2.4) and **4f** at 70°, respectively.

Photoreaction of 2b with 1c. (1) A benzene (40 ml) solution of 2.34 g (22 mmol) of **2b** and 1.50 g (22 mmol) of **1c** was irradiated in Pyrex sealed tubes at 75° for 8 hr. After removal of the solvent and recovery of the reactants by fractionation under reduced pressure, the residue (2.7 g) was chromatographed on alumina (150 g). Elution by ether–petroleum ether (5:95) gave fractions which were collected in 50-ml portions. Since glpc analysis indicated that fractions 1–5 contained two components, the fractions were combined and evaporated. Rechromatography of the residue (0.3 g) on fresh alumina (100 g) eluted by ether–petroleum ether (5:95) gave 54 mg of a colorless liquid and 148 mg of a second colorless liquid. The first liquid was characterized as *trans*-2-cyclopropylstyrene (**6f**): ir (neat) 3100, 3075, 3045, 3030, 1650, 1500, 1455, 1050, 1020, 960 (s), 810, 745 (s), 690 (s) cm⁻¹; nmr δ 7.1–7.3 (m, 5 H), 6.34 (d, *J* = 16 Hz, 1 H), 5.58 (double d, *J* = 16 and 7 Hz, 1 H), 1.5 (m, 1 H), 0.5–0.8 (m, 4 H). *Anal.* Calcd for C₁₁H₁₂: C, 91.6; H, 8.4. Found: C, 91.4; H, 8.3. The second liquid was assigned as 2-phenyl-2,3,4,7-tetrahydrooxepin (**4g**): ir (neat) 3100, 3080, 3045, 2950, 2850, 1660, 1500, 1455, 1270, 1135 (s), 1080, 1065, 1035, 890, 750 (s), 745 (s), 700 (s) cm⁻¹; nmr δ 7.20 (s, 5 H), 5.70 (m, 2 H, olefinic), 4.60 (double d, *J* = 8 and 4 Hz, 1 H, C-2 methyne), 4.24 (d, *J* = 3 Hz, 1 H) and 4.15 (double d, *J* = 3 and 1 Hz, 1 H, both C-7 methylene), 2.30 (broad s, 2 H, C-4 methylene), 1.7–2.2 (m, 2 H, C-3 methylene). *Anal.* Calcd for C₁₂H₁₄O: C, 82.7; H, 8.1. Found: C, 82.6; H, 8.1.

Fractions 6–13 of the first column chromatography contained three components (570 mg), one of which was characterized as **6f**. The remaining two were shown to be *cis*-3-cyclopropyl-2-phenyloxetane and its *trans* isomer (**3g**), *cis/trans* = 1/2.6. The isomers could not be obtained in a pure form by preparative glpc because of their poor separation as well as instability under glpc condition (PEGS, 160°). However, quick glpc allowed us to obtain a sample enriched with one of the isomers, and characterization of each isomer was done by spectroscopic examinations of the mixtures. The major isomer gave following spectral characteristics: ir (neat) 3100, 3050, 3025, 2960, 2895, 1600, 1500, 1455 (s), 1025, 990 (s), 900, 820, 745 (s), 700 (s) cm⁻¹; nmr δ 7.18 (m, 5 H), 5.38 (d, *J* = 6 Hz, 1 H), 4.48 (double d, *J* = 9 and 6 Hz, 1 H), 4.30 (t, *J* = 6 Hz, 1 H), 2.2 (m, 1 H), 0.0–0.7 (m, 5 H). The minor isomer showed the following: ir (neat) 3100, 3050, 3030, 2960, 2895, 1600, 1500, 1460, 1020, 990 (s), 900, 820, 745 (s), 700 (s) cm⁻¹; nmr δ 7.18 (m, 5 H), 5.77 (d, *J* = 9 Hz, 1 H), 4.77 (double d, *J* = 9 and 6 Hz, 1 H), 4.31 (t, *J* = 6 Hz, 1 H), 2.5 (m, 1 H), 0.0–0.7 (m, 5 H). Elemental analysis was made for a mixture of the isomers (*trans/cis* = 2.6). *Anal.* Calcd for C₁₂H₁₄O: C, 82.7; H, 8.1. Found: C, 82.9; H, 8.0.

Finally, elution of the column with methanol–ether (5:95) gave 1.78 g of yellow polymeric material: ir (neat) 3450 (broad), 3100, 3050, 3020, 2955 (s), 2900 (s), 1690 (broad), 1670, 1615 (broad),

1500, 1460, 1340 (broad), 1310, 1220, 1020, 990, 900, 750 (s), 700 (s) cm^{-1} .

The yields of **3g**, **4g**, and **6f** by glpc were 14.8, 4.2, and 4.3%, respectively.

(2) Under similar conditions, an equimolar mixture of **1c** and **2b** was irradiated at 100, 50, and 25° for 8 hr. The products **3g** (a mixture of trans and cis isomer), **4g**, and **6f** were obtained in 5.9 (trans/cis = 2.6), 2.9, and 0.5% yields at 100°; 8.2 (trans/cis = 2.2), 0.6, and 0.6% yields at 50°; and 17.7 (trans/cis = 2.8), none, and 0.7% yields at 25°, respectively. A substantial amount (5–7 g) of polymer was also produced in all runs.

Photoreactions in the Presence of Naphthalene. (1) **Photoreaction of 2a and 1b.** Three benzene (20 ml) solutions of an equimolar mixture (5.0 mmol) of **2a** and **1b** were placed in Pyrex tubes. The first tube was sealed without the addition of naphthalene, while 5.0 mmol of naphthalene was added to the second tube and 25 mmol to the third. The tubes were sealed and irradiated at 100° for 8 hr in a merry-go-round manner. The reaction mixtures were then analyzed by glpc (PEGS, 180°). In the absence of naphthalene, **2a** was consumed by 20% to give the adducts, **3b** and **4b**, in a ratio of 1:1.5. In the presence of equimolar amount of naphthalene, **2a** was consumed only by 1.0%, but the same adducts (**3b/4b** = 1/1.5) were detected. However, no appreciable change could be detected in the photoreaction of the third tube.

(2) **Photoreaction of 2b with 1b.** Two benzene (20 ml) solutions, one containing equimolar amounts (5.0 mmol) of **1b** and **2b** and the other containing equimolar amounts (5.0 mmol) of **1b**, **2b**, and naphthalene, were irradiated in Pyrex tubes at 100° for 8 hr. Glpc (PEGS, 140°) analyses indicated that the photoreaction proceeded in both cases, but the extent of the reaction in the presence of naphthalene was found to be only 7% of that in the absence of naphthalene. Relative amounts of the adducts were, however, found to be closely similar: (*E*)-**3f**:(*Z*)-**3f**:**4f** = 5.5:2.0:1.0 in the absence of the quencher and 5.6:2.0:1.0 in its presence.

Hydrogenation of 2,3,4,7-Tetrahydrooxepins (4a–c). A methanol solution of **4b** (500 mg) was hydrogenated at room temperature for 30 min in the presence of palladium black. A white solid obtained from the reaction mixture was recrystallized from *n*-hexane to give colorless crystals, mp 88.5–89.0°, 420 mg (83.5%), which were characterized as 6-methyl-2,2-diphenyloxepane (**9b**); ir (Nujol) 1270, 1080 (s), 1070 (s), 1040 (m), 760, 750 (s), 705 (s), 700 (s) cm^{-1} ; nmr δ 7.1–7.5 (m, 10 H), 3.60 (d, J = 12 Hz, split further into multiplet, 1 H), 3.24 (m, 1 H), 2.50 (m, 2 H), 1.0–2.2 (m, 5 H), 0.85 (d, J = 6.8 Hz, 3 H). *Anal.* Calcd for $\text{C}_{15}\text{H}_{22}\text{O}$: C, 85.7; H, 8.3. Found: C, 85.7; H, 8.4.

Similar hydrogenation of **4c** (500 mg) gave 452 mg (89.7%) of 2,2-diphenyloxepane (**9c**), mp 79–80° from *n*-hexane: ir (Nujol) 1280, 1120, 1100 (s), 1080 (s), 1035, 755, 745 (s), 705 (s) cm^{-1} ; nmr δ 7.0–7.4 (m, 10 H), 3.50–3.60 (m, 2 H), 2.44 (m, 2 H), 1.4–1.8 (m, 6 H). *Anal.* Calcd for $\text{C}_{15}\text{H}_{20}\text{O}$: C, 85.7; H, 8.0. Found: C, 85.7; H, 8.1.

Catalytic hydrogenation of **4a** (500 mg) was completed after 2 molar equiv of hydrogen had been absorbed. Chromatographic purification (alumina 50 g, eluent petroleum ether) gave 402 mg (80%) of 2,2-diphenyl-6-propyloxepane (**9a**) as a colorless liquid: ir (neat) 3100, 3080, 2970, 2950, 2890 (s), 1605, 1500, 1455 (s), 1125, 1090 (s), 1080 (s), 1040, 760, 750 (s), 700 (s) cm^{-1} ; nmr δ 7.0–7.4 (m, 10 H), 3.56 (d, J = 12 Hz, split further into multiplet, 1 H), 3.20 (double d, J = 12 and 8 Hz, 1 H), 2.40 (m, 2 H), 1.0–1.8 (m, 9 H) and 0.88 (t J = 7 Hz, 3 H). *Anal.* Calcd for $\text{C}_{21}\text{H}_{26}\text{O}$: C, 85.7; H, 8.9. Found: C, 86.0; H, 9.0.

Preparation of Reference Olefins. Some olefins were prepared by Wittig reaction¹⁴ for comparison purposes: 2-cyclopropyl-1,1-diphenylethylene (**6c**), bp 119–120° (1 mm) (lit.²¹ 95° (0.01 mm)),

(21) A. Maercher, *Angew. Chem., Int. Ed. Engl.*, **6**, 557 (1967).

63% yield; 2,2-dicyclopropylstyrene (**6d**), bp 96–98° (3 mm) (lit.¹⁴ 94–95° (2.5 mm)); 2-cyclopropyl-2-methylstyrene (**6e**), a mixture of *E* and *Z* isomers, bp 103–105° (11 mm) [ir (neat) 3100, 3020, 2950, 1640, 1020, 920, 730 (s), and 700 (s) cm^{-1} ; nmr (the peak due to the more abundant isomer (4:1) is given in italics, where it is resolvable) δ 7.12 (m, 5 H), 6.22 (broad s, 1 H), *I*.72 and 1.61 (d, J = 1 Hz, 3 H), 1.50 (m, 1 H), and 0.5–0.7 (m, 4 H) (*Anal.* Calcd for $\text{C}_{12}\text{H}_{14}$: C, 91.1; H, 8.9. Found: C, 91.1; H, 8.7)]; and 1,1-diphenylbut-1-ene, bp 110–111° (3 mm), 72% [ir 3100, 3040, 2970, 1635, 1080, 865, 765 (s), 700 (s) cm^{-1} ; nmr δ 7.10 (m, 10 H), 5.80 (t, J = 7 Hz, 2 H), 0.98 (t, J = 7 Hz, 3 H) (*Anal.* Calcd for $\text{C}_{16}\text{H}_{16}$: C, 92.3; H, 7.7. Found: C, 92.3; H, 7.6)]. 1,1-Diphenylethylene was prepared by an ordinary method,²² bp 136–137° (11 mm) (lit.²² 139° (11 mm)).

Acid-Catalyzed Cleavage of Oxetane (3). In a general procedure, the oxetane (**3a**, **3b**, **3c**, **3d**, or **7a**) was dissolved in methanol containing a trace amount (1 μl in 10 ml of methanol) of 60% perchloric acid, and the solution was heated under reflux for 3–8 hr. After removal of the solvent under reduced pressure, the residue was dissolved in ether; the ether solution was washed with a potassium carbonate solution and dried over an appropriate drying agent. Ether was then evaporated and the residue was dissolved in petroleum ether. The petroleum ether solution was passed through an alumina column. Evaporation of the solvent gave the olefin **6**, which was found to be practically pure. The resulted olefins **6a**,⁶ **6c**, and 1,1-diphenylbut-1-ene were characterized by comparison with a respective authentic specimen. The olefin **6b** was characterized by the following data: ir (neat) 3100, 3080, 3050, 1635 (w), 1600, 1500, 1450, 1075, 1030, 1020, 940, 910, 810, 765, 750, 700 cm^{-1} ; nmr δ 6.9–7.2 (m, 10 H), 1.68 (m, 1 H), 1.40 (s, 3 H), 0.45–0.60 (m, 4 H). *Anal.* Calcd for $\text{C}_{15}\text{H}_{18}$: C, 92.3; H, 7.7. Found: C, 92.1; H, 7.7.

On the other hand, a similar treatment of **3f** and **3g** gave no olefin but yielded unidentified products, which were not examined further.

Thermal Decomposition of 3c, 3f, and 3g. The oxetane **3f** (a single isomer, probably *E* configuration), 562 mg, was heated in a sealed tube at 250° for 5 hr. The product was chromatographed on alumina with petroleum ether as an eluent. The first fraction gave **6e**, 262 mg (94%): ir (neat) 3100, 3065, 3030, 2970, 2930, 2860, 1640, 1600, 1500, 1445, 1060, 1030, 1020, 925, 915, 810, 750, 700 cm^{-1} ; nmr δ 7.0–7.2 (m, 5 H), 6.21 (s, 1 H), 1.68 (s, 3 H), 1.55 (m, 1 H), 0.50–0.65 (m, 4 H). The nmr suggests that the olefin obtained is a single isomer, probably with an *E* configuration. *Anal.* Calcd for $\text{C}_{12}\text{H}_{14}$: C, 91.1; H, 8.9. Found: C, 90.9; H, 8.8. Similar thermolysis of **3c** gave a quantitative yield of **6c**, which was characterized by the comparison with an authentic sample.

When a mixture of *cis*- and *trans*-**3g** (30:70) was heated at 200° for 3 hr, only the *trans* isomer decomposed to the extent of 75%, while the *cis* isomer remained unchanged. Chromatographic separation of the thermolysis mixture on alumina gave 80 mg of *trans*-**6f** (92% based on the amount of reacted **3g**) in addition to the recovered **3g**. In contrast to above-mentioned oxetanes, tetra-substituted oxetanes, **3a** and **3b**, were found to be thermally stable on heating at 250° for 8 hr.

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(22) C. F. Allen and S. Converse, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1956, p 226.