A New Substrate to Investigate Radical Cycloadditions. II.[1] Addition Reactions of Some Representative Carbenes to 1,1-Dicyclopropylethylene

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Abstract: While thermolysis of phenyl(tribromomethyl)mercury (2a) at 100° in a benzene solution of 1,1-dicyclopropylethylene (1) gave the expected cycloadduct 3a in 90% yield, thermolysis of 9-diazofluorene (2b) at 135–140° either in neat 1 or in decalin solution of 1 produced a mixture of cycloadduct 3b and noncyclized adduct 4b. In neat 1, the 3b/4b ratio was 9, but it was 0.1 in the presence of a large amount of decalin. The dependence of the 3b/4b ratio upon the reaction conditions can be attributed to the different spin states of the reacting carbene. Thermolysis of diphenyldiazomethane (2c) also gave a mixture of 3c and 4c, but the addition of decalin to the thermolysis mixture brought about only a small effect on the 3c/4c ratio. Photolysis experiments gave results similar to those of thermolysis, except that the adduct ratio 3/4 was larger than those observed in the thermolyses.

Addition of a diradical species to a vinylcyclopropane derivative will generate an intermediate diradical which has a cyclopropylcarbinyl site. Since the rearrangement of a cyclopropylcarbinyl radical to an allylcarbinyl radical is known to be a rapid process,[2] it is to be expected that the diradical may either cyclize to the expected cycloadduct or rearrange to a second diradical which, in turn, would give rise to a rearranged adduct. Thus, examination of cycloadditions to cyclopropylethylene can give information about the intermediates of the reaction. In the present paper, the additions of some representative carbenes to 1,1-dicyclopropylethylene (1) were investigated, and the results are discussed.

Results

Reaction of Phenyl(tribromomethyl)mercury (2a). In sealed tubes, a benzene solution of 2a[3] was thermolyzed at 100° in the presence of 1,1-dicyclopropylethylene (1). A 1:1 cycloadduct, 1,1-dibromo-2,2-dicyclopropylcyclopropane (3a), was isolated and characterized. The yield of 3a was high (90%) and no product other than 3a was detected by either glpc or nmr. Therefore, it is concluded that the addition proceeds cleanly to give 3a as a single adduct.

Thermolysis and Photolysis of 9-Diazofluorene (2b). Thermal decomposition of 9-diazofluorene (2b) in neat 1 at 135–140°[4] for 1 hr gave two 1:1 adducts, 3b and 4b, in 57 and 6% yield, respectively. The major adduct 3b was found to be an expected cycloadduct, 2,2-dicyclopropyldibenzo[b,d]spiro[2.4]hepta-4,6-diene, by analytical and spectral data. The uv spectrum indicates that it is a 9-alkylfluorene,[5] and the nmr spectrum exhibits

signals due to the aromatic protons and those on the cyclopropane rings. The two protons on the tetra-subtituted cyclopropane appeared at δ 1.70 as a singlet, which is compatible with the proposed structure. The minor product 4b was found to be a noncyclic adduct,

3a   3b

4b
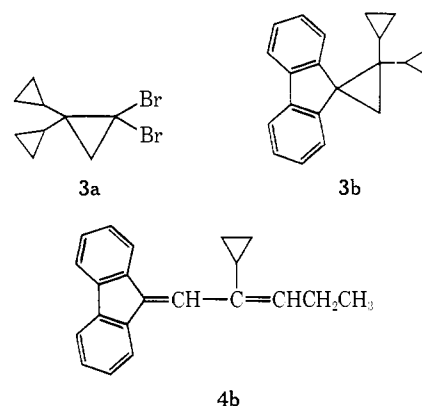
and the structure was deduced to be 9-(2'-cyclopropyl-pent-2'-enylidene)fluorene.[1,6]

The structure of 3b was further confirmed by the observation that 3b rearranged to 4b at higher temperatures.[7] This isomerization did not allow quantitative analyses of the product mixture by glpc, but it was proved to be negligibly slow at 135–140° or lower so that the ratios of the two products could safely be treated as those resulting under the given reaction conditions. The ratio of 3b to 4b was actually determined by uv spectroscopy at 257 and 272 nm after preliminary separation of the adduct fraction by alumina column chromatography.

(1) Part I: N. Shimizu and S. Nishida, Chem. Commun., 389 (1972).

(2) (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).

(3) D. Seyferth, J. M. Burlitch, R. J. Minaz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, J. Amer. Chem. Soc., 87, 4259 (1965).

(4) Thermolysis was conducted by placing the reaction flask in an oil bath adjusted at 140°. In the reaction in neat 1, the temperature of the reaction mixture did not reach 140° because of the slightly lower boiling point of 1, so that the thermolysis temperature in neat 1 is given as 135–140° throughout the paper.

(5) Characteristic uv spectra of 9-alkylfluorenes are reported by J. Dehler and K. Fritz, Tetrahedron Lett., 2157 (1969); see also H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1964.

(6) Stereochemistry of the side chain could not be fully established but the terminal methyl protons appeared as a clean triplet in the nmr spectrum, suggesting that the adduct is a single isomer. Mechanistic consideration suggests that it could be the E isomer; see text.

(7) Half-life at 160–170° was 4–5 hr and ca. 1 hr at 200°. Smooth thermal isomerizations of isomeric 1,2-dimethyldibenzo[b,d]spiro[2.4]-hepta-4,6-dienes have been reported, which suggest rather facile bond cleavage of the cyclopropane in the dibenzospiroheptadiene skeleton: W. von E. Doering and M. Jones, Jr., Tetrahedron Lett., 791 (1963).

When decalin was added to the thermolysis mixture, there was observed a dramatic change in the **3b/4b** ratio. As shown in Tables I and II, addition of 2 molar

Table I. Thermal and Photochemical Reactions of **2b** with **1**

| Olefin | Diluent[a] | Temp, °C | Product, %[c] | | | | | Residue[f] |
			3b	4b	5	6	7[d]	
		Thermal Reaction						
1	None	135–140[b]	57	6	21	5		27
1	Decalin (3)	140	11	17	18	6	21	56
		Photochemical Reaction[e]						
1	None	15	75	5	13	6		78
1	Benzene (5)	15	67	4	6	11		80

[a] The figure given in parentheses indicates its molar amount relative to **1**. [b] See ref 4. [c] Based on the consumed diazo compound. [d] A mixture of isomeric 9-decalylfluorenes; see text. [e] Photolysis was seriously interdicted by the formation of a polymeric film on the window surface of the photolysis cell. [f] Polymeric residue; figures given are weight per cent in the product mixture.

Table II. The **3b/4b** Ratio in the Reaction of **1** with **2b**

Olefin	Diluent	Extent of dilution[a]	Temp, °C	3b/4b[b]
		Thermal reaction		
1	None		135–140	9
1	Decalin	2.1	140	0.7
1	Decalin	3	140	0.7
1	Decalin	21	140	0.1
1	None		100	13
1	Benzene	3	80	2.3[c]
1	Benzene	21	80	1.2[c]
		Photochemical reaction		
1	None		15	16
1	Benzene	5	15	15
1	Benzene	51	15	7.5

[a] Molar ratio relative to **1**. [b] Determined by uv; see text. [c] Thermolysis proceeded very slowly at 80–100°, so that the reaction was interrupted at a certain extent and the ratio was determined.

equiv of decalin relative to the amount of **1** increased the yield of **4b** significantly, and the ratio dropped sharply from 9 to 0.7. In the presence of a large excess of decalin (20–30 times excess), **4b** was almost the exclusive adduct at 135–140°.[8] In these diluted reactions, considerable amounts of insertion products, probably a mixture of isomeric 9-decalylfluorenes (**7**) as deduced from analytical results and spectroscopic properties, were also isolated in addition to fluorenone azine (**5**) and bisfluorenylidene (**6**). Their amounts are also given in Table I.

The **3b/4b** ratio depends upon the temperature employed for the thermolysis: the higher the temperature, the larger the relative amount of **4b** to **3b**. Thus, the **3b/4b** ratio was 9 at 135–140°, but it was 13 at 100°. Therefore, it should be somewhat larger than 13 at 80°. From this consideration, it can be concluded that the effect of dilution of the thermolysis mixture with benzene

(8) In part I,[1] the ratio was determined by a tlc spot area technique. Later, however, it was found that the insertion products interfered with the determination to a considerable extent, so that the figure for the **3b/4b** ratio in the presence of a large excess of decalin was erroneously reported to be 1/3.0; the correct figure should be 1/10, as given in Table II. The same contamination of the insertion products should have happened in the less highly diluted experiments, but its contribution was so small that the figure reported was, in fact, the same as that determined in the present experiment. In any event, the conclusion drawn was not disturbed by this interference.

also brings about a marked lowering of the **3b/4b** ratio to 1.2, as seen in Table II.

From the photolysis of **2b** in **1**, the same set of adducts as that obtained in the thermolysis was isolated. Although the effect of dilution with benzene on the adduct ratio was small, it was appreciable under high dilution (Table II).

Reaction of Diphenyldiazomethane (2c). Similarly, **2c** was thermolyzed in **1** at 135–140° for 1 hr. Two adducts were isolated and characterized, in addition to benzophenone azine (**8**) and benzophenone (**9**). The major adduct was assigned as 1,1-dicyclopropyl-2,2-diphenylcyclopropane (**3c**) by analytical and spectroscopic examinations. The minor adduct was an olefinic compound, substituted by a cyclopropyl group, and it was assigned as 1,1-diphenyl-3-cyclopropylhexa-1,3-diene (**4c**).[6] Its ozonolysis gave benzophenone in 89%
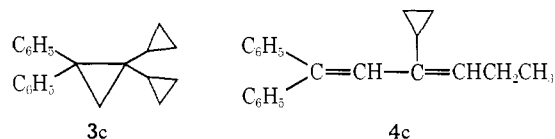
yield, and its hydrogenation over palladium black produced a 90% yield of a saturated hydrocarbon for which the structure of 4-(2',2'-diphenylethyl)heptane was deduced.

Contrary to **3b**, **3c** was found to be thermally stable at 200°, so that the quantitative analyses for the **3c/4c** ratio were made by glpc. When the thermolysis was carried out in a mixture of **1** and decalin, the yield of the adducts decreased considerably and 1,1,2,2-tetraphenylethane (**10**) was produced as a by-product, but the **3c/4c** ratio was influenced only slightly. Thus, it was 5.8 in neat **1** at 135–140°, but it was 4.2–4.5 under the diluted condition at 140°. This insensitivity to dilution is in marked contrast to the thermolysis of **2b**. The **3c/4c** ratio was also determined at various temperatures. The results are summarized in Tables III and IV.

Table III. Thermal and Photochemical Reactions of **2c** with **1**

| Olefin | Diluent[a] | Temp, °C | Product, %[c] | | | | | Residue[d] |
			3c	4c	8	9	10	
		Thermal reaction						
1	None	135–140[b]	52.9	9.1	7.5	7.1		24
1	Decalin (21)	140	16.4	3.6	2.0	5.4	25.5	50
		Photochemical reaction						
1	None	15	44.0	0.4	6.1	2.5		48
1	Benzene (51)	15	39.5	0.4	7.5	2.0		51

[a] The figure given in parentheses indicates its molar amount relative to **1**. [b] See ref 4. [c] Based on the consumed diazo compound. [d] Polymeric residue; figures given are weight per cent in the product mixture.

In the photochemical decomposition of **2c**, results similar to those of thermolysis were obtained, but mention should be made of the fact that the photolysis gave less rearranged adduct **4c** than that observed in the thermolysis at a given temperature.

Discussion

The formation of **3** and **4** in the reaction of both **2b** and **2c** with **1** can be best explained by the reaction

Table IV. The 3c/4c Ratio in the Reaction of 2c with 1

Olefin	Diluent	Extent of dilution[a]	Temp, °C	3c/4c[b]
		Thermal reaction		
1	None		135	5.8
1	None		125	7.5
1	None		100	10
1	None		90	12
1	None		80	16
1	None		72	19
1	None		63	24
1	None		40	50
1	Decalin	11	140	4.2
1	Decalin	21	140	4.6
		Photochemical reaction		
1	None		90	21[c]
1	None		70	35[c]
1	None		15	≥100
1	Benzene	16	15	≥100
1	Benzene	51	15	≥100

[a] Molar ratio relative to 1. [b] Determined by glpc. [c] Thermal reaction was negligible, because the photolysis was interrupted before the thermal reaction took place to any considerable extent.

scheme shown below. If one accepts the general assumption that the singlet carbene 11 adds to olefin in a concerted fashion,[9] then the triplet carbene 12 should
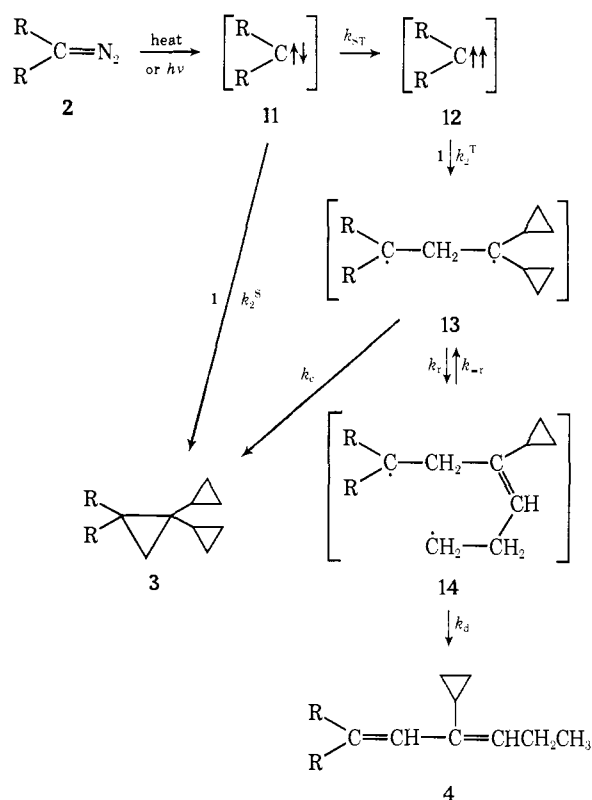
a, R = R = Br
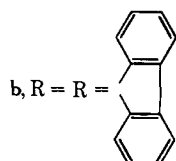
b, R = R =

c, R = R = C₆H₅

be solely responsible for the radical pathway.[9,10] The results in which the thermal decomposition of Seyferth's reagent 2a in a benzene solution of 1 at 100° gives no rearranged adduct seem to support this assumption, because a singlet configuration has been proposed for dibromocarbene generated by the thermolysis of this reagent.[11] Thus, triplet carbene 12 adds to 1 to give the diradical 13,[12] which either cyclizes to 3 or rearranges to diradical 14. The diradical 14 will then disproportionate to yield 4. The termination of 14 is most probably an intramolecular disproportionation of a 1,6-diradical. This is supported by the observation that the dilution did not bring about a decrease in the yield of 4, as large as would be expected, if the disproportionation were an intermolecular reaction. The intramolecular disproportionation is possible only in the E diradical, where the two radical carbons are in a cis relationship, and 1,5-hydrogen abstraction can take place. Although there are no available data to indicate the stereochemistry of the resultant allylcarbinyl radical 14, it is hard to believe that only the E diradical is produced. The Z diradical should also be produced, but it may have no way to terminate to the product, so that it would simply have gone back to 13, or it may have attacked another molecule of 1 to afford a polymeric residue.[13] In the following discussion, however, we should like to focus our attention on the 3/4 ratio; therefore, reaction routes other than those giving 3 and 4 may not interfere with the following discussions.

The most interesting observation in the present investigation is the dramatic change of the 3b/4b ratio upon the dilution of the reaction system with decalin or benzene. While 3b was produced in a much larger amount than 4b in neat 1, 4b became the major adduct when the reaction was carried out in decalin at 135–140°. A similar result was also noted in the reaction in benzene, although the lower reaction temperature (80°) seemed to slow down the rearranging process (k_r). These observations can be attributed to the enriched amount of the triplet carbene 12b in the addition reaction. The enrichment of 12b may arise primarily by the collisional deactivation of 11b, which has been shown to be the case in some carbenes,[14] but chemical scavenging of 11b by its insertion to the C–H bond of decalin may also play a part. The insertion reaction may be a reaction of singlet carbene.[15] Accordingly, the reacting species which gives 3b and 4b under 21-fold dilution with decalin is almost completely triplet 12b. The diradical 13b derived from it undergoes preferential rearrangement at 135–140°. On the other hand, the 9/1 ratio observed in the absence of diluent at the same temperature suggests that nascent 11b reacts preferentially with 1 before crossing into its triplet state.

The conclusions reached so far are in good accord with previous conclusions on the spin state and chemical

(10) P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, 78, 4496, 6427 (1956).

(11) D. Seyferth, *Accounts Chem. Res.*, 5, 65 (1972).

(12) The assumption that the addition of 12 to 1 will produce 13, but not a diradical of inverse orientation, might be reasonable because 13 would be much more stable than its alternative.

(13) In fact, the polymeric residue obtained in these reactions contains phenyl groups, which was proved spectrometrically.

(14) (a) M. Jones, Jr., and K. R. Rettig, *J. Amer. Chem. Soc.*, 87, 4013, 4015 (1965); (b) E. Ciganek, *ibid.*, 88, 1979 (1966); (c) W. H. Pirkle and G. F. Koser, *Tetrahedron Lett.*, 3959 (1968).

(15) W. Kirmse, L. Horner, and H. Hoffmann, *Justus Liebigs Ann. Chem.*, 614, 19 (1958).

(9) (a) P. P. Gasper and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1964, p 235; (b) G. L. Closs, *Top. Stereochem.*, 3, 193 (1968); (c) W. Kirmse, "Carbene Chemistry," 2nd ed., Academic Press, New York, N. Y., 1971.

behavior of fluorenylidene, based on stereochemical studies of its addition reaction.[9,10,14,16] Also, it may be worthwhile to note that the large dependence of the adduct ratio on dilution excludes the possibility that the reaction proceeds by way of a pyrazoline derivative. Such a reaction route would not bring about the significant dilution effect observed here.

Similarly, thermal decomposition of 2c in 1 produced 3c and 4c. It must be pointed out, however, that the 3c/4c ratio does not change significantly even with a 21-fold dilution at 140° and that this is a marked contrast to what is observed in the thermolysis of 2b at the same temperature. This seems to be in accord with the lack of dilution effect observed in stereochemical investigations of the same carbene.[17] It was reported that the ratio of cis adduct to trans adduct resulting in the photolysis of 2c in isomeric but-2-enes is not affected by dilution with a 200-fold excess of cyclohexane.[17] The lack of dilution effect observed in the present experiments may be explained by assuming that the singlet carbene 11c and the triplet carbene 12c are in rapid equilibrium, and that 11c has a much higher reactivity toward olefin than 12c, as postulated by Closs.[9b] In any event, the formation of 4c will provide a proof for the existence of the reaction path derived from the triplet 12c.

A plot of log (3c/4c) vs. $1/T$ gave a straight line of positive slope,[18] which indicates that the process leading to the rearranged 4c is the process of higher energy of activation than that leading to 3c. This implies that the radical coupling process (k_c) to give 3 is faster than the rearranging process (k_r). A recent calculation shows that the energy barrier for the cyclopropylcarbinyl radical to allylcarbinyl radical rearrangement is 8.7 kcal/mol,[19,20] which is low but appreciable. The preferential formation of the adduct 3b over 4b under highly diluted photolysis conditions should mostly be attributed to the lower temperature applied for the photolysis.

In conclusion, all of the experimental results described so far are in good compatibility with the hitherto proposed behavior of the related carbenes, which was based mostly on stereochemical studies. This strongly supports the potential validity of the present technique for investigating the spin multiplicity of carbene addition reactions. Cyclopropylethylene is a useful substrate to investigate such reactions.

Experimental Section

Ir spectra were recorded on a Hitachi 215 grating infrared spectrophotometer and uv spectra on a Hitachi EPS-2 recording spectrophotometer. Nmr spectra were recorded on a Hitachi R-20 high resolution nmr spectrometer; the abbreviations used in nmr data are: s = singlet, d = doublet, t = triplet, q = quintet, and m = multiplet. Both analytical and preparative glpc were carried

out on a Yanagimoto 550-T gas chromatograph using columns (1.5 m × 4 mm) packed with either 20% polyethylene glycol succinate on Chromsorb W (PEGS) or 20% Apiezon grease L on Cerite 545 (AGL). All boiling points and melting points are uncorrected. The yields given are all based on the consumed amount of the lesser reactant.

Materials. Phenyl(tribromomethyl)mercury (2a),[21] 9-diazofluorene (2b),[22] and diphenyldiazomethane (2c)[23] were prepared following the known routes and recrystallized before use: 2a, mp 119–120° (lit.[21] 119–120°); 2b, mp 93–94° (lit.[22] 94–95°); 2c, mp 26–28° (lit.[23] 30°). Preparation of 1,1-dicyclopropylethylene (1), bp 132–133° (lit.[24] 129–132°), is described elsewhere. Decalin[25] and benzene were purified by ordinary methods.

Reaction of 2a with 1. A mixture of 5.29 g (10 mmol) of 2a and 5.40 g (50 mmol) of 1 in 7.8 g of benzene was heated in a glass sealed tube at 100° for 1 hr. Filtration of precipitated phenylmercuric bromide [mp 282–284° (lit.[26] 283–285°), 3.5 g (98%)] left an organic mixture, which was fractionated. There were obtained recovered 1 (4.1 g) and a colorless fraction [bp 80–81° (2 mm), 2.52 g (90%)] which was characterized as 1,1-dibromo-2,2-dicyclopropylcyclopropane (3a): ir (liquid film) 3100, 3030, 1470, 1455, 1425, 1050 (s), 1030, 1020 (m), 955 (s), 895, 820 (s), and 680 (s) cm^{-1}; nmr (CCl₄) δ 1.05 (s, 2 H, C-3 methylene), 0.8–1.2 (m, 2 H), and 0.1–0.7 (m, 8 H). Anal. Calcd for C₉H₁₂Br₂: C, 38.6; H, 4.3; Br, 57.1. Found: C, 38.7; H, 4.3; Br, 57.3. The nmr spectrum of the crude product was superimposable on that of pure 3a. Moreover, glpc analysis (AGL, 140°) of the crude reaction mixture showed a clean single peak. Hence, the reaction of 2a with 1 in benzene gave 3a as a single adduct.

Thermolysis of 2b in the Presence of 1. (1) A mixture of 1.92 g (10 mmol) of 2b and 8.0 g (74 mmol) of 1 was heated at 135–140°[4] for 1 hr in a small flask equipped with a reflux condenser, to which a gas buret was connected through a drying tube. During the thermolysis, a total of 190 ml of nitrogen gas was evolved, which indicated that 90% of 2b was decomposed. Excess 1 (6.2 g) was recovered by rectification of the reaction mixture under reduced pressure. The residue was then dissolved in a mixture of benzene–petroleum ether[27] (20:80, 15 ml) and the solution was allowed to stand in a refrigerator for several hours. Red crystals of fluorenone azine (5) [mp 265–266° (lit.[28] 266°), 0.3 g] were collected by filtration. The mother liquor was concentrated, and the residue (2.75 g) was placed on the top of an alumina column (150 g). Elution with petroleum ether gave 1.74 g of a colorless solid (mp 75–80°), which was found to be a mixture of two components by tlc analysis. Elution of the column with benzene–petroleum ether (20:80) gave 82 mg of red bisfluorenylidene (6) [mp 188–189° (lit.[29] 188–189°)]. Further elution with benzene gave 0.81 g of red polymeric material: ir (film) 3100, 3030, 2950, 2875, 1610, 1585, 1450 (s), 1020, 770, and 730 (s) cm^{-1}. Finally, elution with methanol-benzene (5:95) gave 70 mg of additional azine 5.

The colorless solid obtained in the first elution was placed again on the top of a fresh alumina column (150 g). Careful elution with petroleum ether gave 140 mg of the first colorless adduct from the beginning fractions and 1.57 g of the second adduct from the later fractions. The first adduct, mp 68–69° after recrystallization from ethanol, showed the following spectral properties and was assigned as 9-(2'-cyclopropylpent-2'-enylidene)fluorene (4b): ir (Nujol) 3100, 3090, 1640, 1610, 1585, 1280, 1220, 1160, 1050, 1035 (m), 1020 (m), 950 770 (s), and 725 (s) cm^{-1}; uv (ethanol) λ_max (log ε) 230 nm (4.35), 248 (4.35), 257 (4.49), and 311 (3.83); nmr (CCl₄) δ 7.00–7.95 (m, 8 H, aromatic), 6.81 (s, 1 H, C-1' vinyl), 5.53 (t, J = 7 Hz, 1 H, C-3' vinyl), 2.00 (q, 2 H, C-4' methylene), 1.5–1.8 (m, 1 H, allylic cyclopropyl), 0.90 (t, J = 7 Hz, methyl), and 0.4–0.7 (m, 4 H, cyclopropyl). Anal. Calcd for C₂₁H₂₀: C,

(16) W. von E. Doering and M. Jones, Jr., Tetrahedron Lett., 791 (1963).

(17) (a) R. M. Etter, H. S. Skovronek, and P. S. Skell, J. Amer. Chem. Soc., 81, 1008 (1959); (b) G. L. Closs and L. E. Closs, Angew. Chem., Int. Ed. Engl., 1, 334 (1962).

(18) Since the 3c/4c ratio was practically insensitive to dilution, the plot was made by the figures obtained in the neat reactions. The temperature dependence of the 3b/4b ratio was not examined because of the experimental uncertainty caused by experimental inconveniences. Qualitatively, however, the same should be true for the thermolysis of 2b (Table II).

(19) W. J. Hehre, J. Amer. Chem. Soc., 95, 2643 (1973).

(20) From the data reported by Ingold,[2c] the energy barrier for the rearrangement in a steroidal compound can be estimated to be 6–8 kcal/mol.

(21) D. Seyferth and P. L. Lambert, Jr., J. Organometal. Chem., 16, 21 (1968).

(22) H. Staudinger and O. Kupfer, Chem. Ber., 44, 2197 (1911).

(23) L. Caglioti and M. Magi, Tetrahedron, 19, 1127 (1963).

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

(25) A mixture of cis and trans isomers (65:35) from Wako Jun-yaku Co., Ltd., Tokyo, Japan.

(26) D. Seyferth, J. Y.-P. Mui, M. E. Gordon, and J. M. Burlich, J. Amer. Chem. Soc., 87, 681 (1965).

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

(28) H. Wieland and A. R. Rosean, Justus Liebigs Ann. Chem., 381, 229 (1911).

(29) J. R. Sawpey and E. E. Reid, J. Amer. Chem. Soc., 69, 234 (1947).

92.6; H, 7.4. Found: C, 92.7; H 7.4. Nmr double resonance experiments support the proposed structure. Thus, irradiation at δ 2.00 resulted in the changes of the two triplets at δ 5.53 and 0.90 to two sharp singlets. This suggests also that the adduct **4b** is stereochemically pure and that it may have the E configuration.[6] The compound immediately decolorized bromine in carbon tetrachloride. Ozonolysis of **4b** (130 mg) in methanol at −70°, followed by the addition of dimethyl sulfide, gave fluorenone in a quantitative yield, 2,4-dinitrophenylhydrazone mp 289–290° (lit.[30] 289–290°). The second adduct was shown to be 2,2-dicyclopropyl-dibenzo[b,d]spiro[2.4]hepta-4,6-diene (**3b**), mp 91–92°; ir (Nujol) 3100, 1485, 1235, 1120, 1060, 1035, 1020 (m), 920 895, 830 (s), 755, and 730 (s) cm⁻¹; uv (ethanol) λ_max (log ε) 232 nm (4.47), 272 (4.28), 293 (4.00), and 304 (3.97); nmr (CCl₄) δ 6.9–7.8 (m, 8 H, aromatic), 1.70 (s, 2 H, C-3 methylene), and 0.1–1.1 (m, 10 H, two cyclopropyls). The uv spectrum is characteristic of 9-alkyl-fluorenes.[5] *Anal.* Calcd for C₂₁H₂₀: C, 92.6; H, 7.4. Found: C, 92.7; H, 7.4. The yields of **3b, 4b, 5**, and **6** were 57, 6, 21, and 5%, respectively.

(2) A solution was made with 1.8 g (9.4 mmol) of **2b**, 7.5 g (70 mmol) of **1**, and 19.2 g (139 mmol) of decalin,[25] and it was heated at 140° for 1 hr. Decalin and excess **1** were removed by fractionation, and the residual oil was placed on the top of an alumina column (150 g). Elution with petroleum ether gave fractions which were collected in 50-ml portions. The tlc analyses of each fraction indicated that fractions 4 and 5 contained practically one component, which was found to be **4b** (220 mg). Fractions 6–13 contained three components; the fractions were combined and rechromatographed on fresh alumina (150 g). Careful elution with petroleum ether gave 215 mg of additional **4b**, 603 mg of a colorless liquid, and 282 mg of **3b** in the order of elution. The liquid material was assigned as a mixture of five isomers of 9-decalylfluorenes (**7**): ir (neat) 3090, 3050, 2940, 2870, 1485, 1450, 740 (s), and 670 (s) cm⁻¹; uv (ethanol) λ_max (log ε) 229 nm (3.89), 258 (4.20), 267 (4.27), 292 (3.83), and 302 (3.96); nmr (CCl₄) δ 7.1–7.6 (m, 8 H, aromatic), 4.06, 3.96, 3.68 (broad s, total area of the three signals corresponded to 1 H, 9-fluorenyl), and 0.8–2.5 (m, 17 H, decalyl). *Anal.* Calcd for C₂₃H₂₆: C, 91.3; H, 8.7. Found: C, 91.5; H, 8.6. The assignment of **7** was further confirmed by the fact that a closely similar mixture was obtained by thermolysis of **2b** in decalin at 140° in the absence of **1**.

The yields of **3b, 4b, 5, 6**, and **7** were 11, 17, 18, 6, and 21%, respectively. The weight of polymeric material was 56% of the reaction products.

Photolysis of 2b in the Presence of 1. (1) A mixture of 1.5 g (7.8 mmol) of **2b** and 15.0 g (139 mmol) of **1** was irradiated at 15° for 4 hr in Pyrex tubes by a 450-W high-pressure mercury lamp.[31] The inner surfaces of the tubes were coated with a polymeric film after irradiation. Following work-up procedures described above, **3b, 4b, 5**, and **6** were isolated from the photolyzed mixture in 75, 5, 13, and 6% yields, respectively. The major photoproduct was in fact polymer (78 wt %).

(2) A benzene (54 g, 700 mmol) solution of 1.5 g (7.8 mmol) of **2b** and 15.0 g (139 mmol) of **1** was irradiated similarly in a cylindrical vessel, and **3b, 4b, 5**, and **6** were isolated in 67, 4, 6, and 11% yields, respectively. A substantial amount of polymer was also produced in this photolysis (80 wt %).

Thermal Isomerization of 3b to 4b. A decalin (5 ml) solution of **3b** (320 mg) was heated in a glass tube at 200° for 5 hr. Decalin was removed by fractionation under reduced pressure, and the residue was chromatographed on alumina (50 g). Elution by petroleum ether gave 240 mg of **4b** (75%). The remainder was yellow polymeric material. The half-life of **3b** was *ca.* 5 hr at 170° and 1 hr at 200°. Thus, glpc analyses (AGL, 240°) of **3b** and **4b** caused their decomposition. Both **3b** and **4b**, however, proved to be stable, either on heating at 140° for 1 hr or on irradiation at 15° for 4 hr in benzene through a Pyrex filter.

Determination of the Adduct Ratio, 3b/4b. The reactions to determine the **3b/4b** ratio were generally carried out by using 300 mg of **2b** and 1.5 g of **1**. The reaction mixture was made free of **1** and solvent, and it was chromatographed on alumina (50 g). Elution was done with petroleum ether, until no more **3b** could be detected by tlc.[32] After the eluent was evaporated, each fraction

was analyzed by uv as a solution in ethanol. The adduct ratio was determined by solving eq 1–3. A^n is the absorbance at n nm of

$$A^{257} = 14100[\mathbf{3b}] + 30700[\mathbf{4b}] + 16600[\mathbf{7}] \quad (1)$$

$$A^{267} = 17800[\mathbf{3b}] + 8380[\mathbf{4b}] + 18800[\mathbf{7}] \quad (2)$$

$$A^{272} = 18600[\mathbf{3b}] + 8130[\mathbf{4b}] + 15500[\mathbf{7}] \quad (3)$$

the mixture. In the absence of decalin, the reaction mixture contains no **7**, so that the ratio can be determined more simply; the **3b/4b** ratio thus determined coincided within experimental error (±10%) with the previous ratio[1] determined by the tlc spot area technique.[33] The experimental results are summarized in Table II.

Thermolysis of 2c in the Presence of 1. (1) A mixture of 1.94 g (10 mmol) of **2c** and 8.0 g (74 mmol) of **1** was heated at 135–140°[4] for 1 hr; 195 cc of nitrogen evolved. The reaction mixture was allowed to stand overnight at room temperature. Separated benzophenone azine (**8**) [mp 163–164° (lit.[34] 163–164°), 105 mg] was collected by filtration. Rectification of the filtrate under reduced pressure gave 6.3 g of recovered **1**. The residual oil (2.85 g) was chromatographed on alumina (150 g). Elution with petroleum ether gave 1.69 g of a colorless liquid, which was found to be a mixture of two components by glpc analysis (PEGS, 220°). Further elution with ether–petroleum ether mixture (5:95) gave benzophenone (9, 129 mg) and yellow polymeric material (690 mg) in order of elution. The latter showed the following spectral properties: ir (neat) 3100, 3020, 2950 (s), 2875, 1605, 1500, 1450, 1020, 820, 740, and 700 (s) cm⁻¹; nmr (CCl₄) showed broad signals at δ 7.2, 5.1, and 0.4–2.0. Final elution with a methanol–ether mixture (5:95) gave 30 mg of additional **8**.

The oily product obtained in the first elution was placed on the top of fresh alumina (150 g). Careful elution with petroleum ether gave 0.80 g of a liquid and 0.85 g of a colorless solid in order of elution. Recrystallization of the solid gave colorless crystals (mp 64–65°), assigned as 1,1-dicyclopropyl-2,2-diphenylcyclopropane (**3c**): ir (Nujol) 3100, 3050, 1605, 1500, 1030, 1020 (m), 910, 890, 775 (s), 705 (s), and 695 (s) cm⁻¹; uv (ethanol) λ_max (log ε) 227 nm (4.14) and 261 (2.91); nmr (CCl₄) δ 6.9–7.5 (m, 10 H), 0.88 (s, 2 H), and −0.3–0.7 (m, 10 H). *Anal.* Calcd for C₂₁H₂₂: C, 91.9; H, 8.1. Found: C, 92.0; H, 8.1. The uv spectrum is similar to that of diphenylmethane.[35]

The liquid product was purified by collecting it by glpc (PEGS, 220°). It is assigned as 1,1-diphenyl-3-cyclopropylhexa-1,3-diene (**4c**): ir (liquid film) 3100, 3090, 3050, 3030 (m), 2980, 2955, 1660, 1605, 1585, 1500, 1450, 1280, 1080, 1035, 1020, 915, 825, 770 (s), 760 (s), and 690 (s) cm⁻¹; uv (ethanol) showed broad absorptions weakly shouldered at 235 nm (log ε 4.11), 255 (3.95), and 261 (2.91) between two λ_max at 220 nm (4.20) and 340 (2.87); nmr (CCl₄) δ 7.16 (s, 10 H, aromatic), 6.30 (s, C-2 vinyl), 5.04 (t, J = 7 Hz, 1 H, C-4 vinyl), 1.80 (q, J = 7 Hz, 2 H, C-5 methylene), 1.1–1.3 (m, 1 H, allylic cyclopropyl), 0.70 (t, J = 7 Hz, 3 H, methyl), and 0.40 (d, 4 H, cyclopropyl). Double resonance by irradiation at δ 1.80 left two sharp singlets at δ 0.70 and at 5.04, which suggests that **4c** is a single isomer, probably the E isomer. *Anal.* Calcd for C₂₁H₂₂: C, 91.9; H, 8.1. Found: C, 92.0; H, 8.0. Ozonolysis of **4c** (105 mg) in methanol at −70° followed by addition of dimethyl sulfide gave benzophenone in 85% yield, 2,4-dinitrophenylhydrazone mp 231–232° (lit.[36] 232°).

Hydrogenation of **4c** (300 mg) over palladium black in methanol at room temperature gave a colorless liquid (302 mg), after 3 molar equiv of hydrogen had been absorbed.[37] The liquid was found to be a mixture of two products (1:8.9) by glpc (AGL, 220°). The major product was isolated by preparative glpc and was assigned as 4-(2′,2′-diphenylethyl)heptane: ir (liquid film) 3080, 3050, 2975, 2935 (s), 2890 (s), 1605, 1500 (s), 1475, 1460, 770, 760, and 700 (s)

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used as an ascending developer. R_f values for **4b, 7**, and **3b** were 0.87, 0.74–0.79, and 0.73, respectively.

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(37) Two double bonds and a cyclopropane were hydrogenated; see M. Charton in "The Chemistry of Alkenes," Vol. 2, J. Zabicky, Ed., Interscience, New York, N. Y., 1970, Chapter 10, for hydrogenation of a cyclopropane ring.

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(31) Model PIH-500S, made by Eikosha Co., Ltd., Minami-dori, 2–11, Nakatsu, Oyodo-ku, Osaka, Japan.

(32) The tlc analyses were carried out by using a 20 cm × 4 cm glass plate coated with a 0.15-mm thickness of Wako Gel B-5. *n*-Hexane was

cm^{-1}; nmr (CCl₄) 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 C₂₁H₂₈: 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.

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 reactions[2] 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-diradical[4] 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-

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