Reactions of Carbene with 1,1-Dicyclopropylethylene. A New Tool to investigate Radical Cycloadditions

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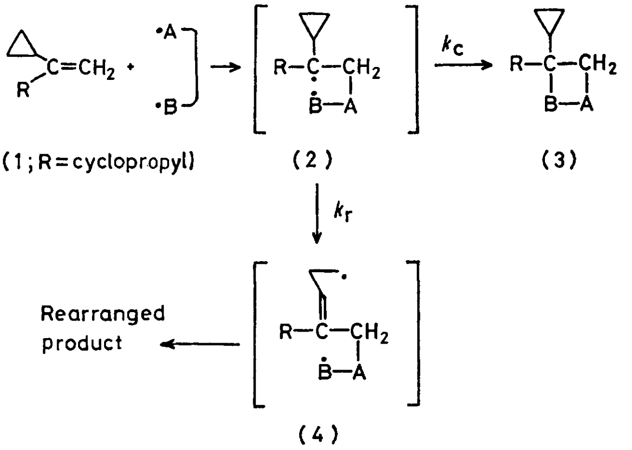
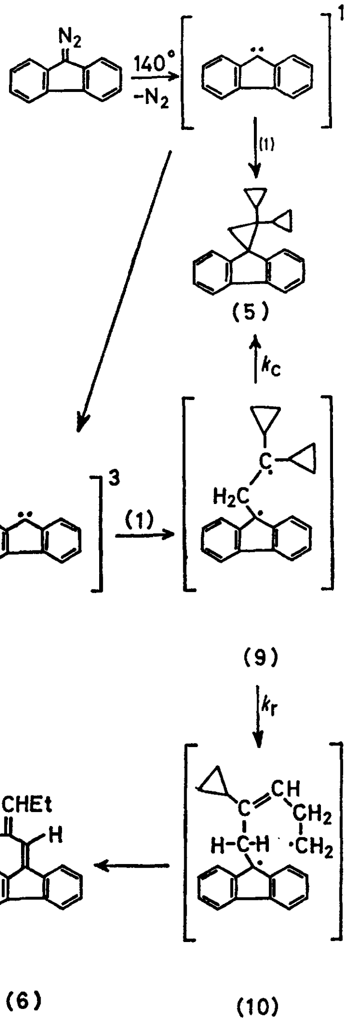
Summary Fluorenylidene reacts with 1,1-dicyclopropylethylene to give a cycloadduct (**5**) and the rearranged adduct (**6**) in a ratio of 10:1; dilution with decalin inverses the ratio to 1:3, which may be due to the increased amount of triplet fluorenylidene.

When a vinylcyclopropane derivative is used as a substrate for radical cycloaddition reactions, it can be expected to generate an intermediate biradical (**2**) which has a cyclopropylmethyl radical site. Since the rearrangement of the cyclopropylmethyl radical to the allylmethyl radical has been recently shown to be a very fast process (*ca.* 10^8 s^{-1} at 30°, and it can compete with molecular diffusion or radical recombination processes),[1] it is to be expected that the biradical (**2**) may either cyclize to (**3**) with k_c or rearrange to (**4**) with k_r.† The ratio of the two routes will depend upon relative magnitude of k_c and k_r at a given temperature, and hence the nature and reactivity of the intermediate biradical. Thus, examination of cycloaddition reactions with cyclopropylethylene could give information about the intermediate other than that obtained by stereochemical studies.[2] In the present work the addition of fluorenylidene and dibromocarbene[3] to 1,1-dicyclopropylethylene (**1**)[4] was examined.



Thermal decomposition of 9-diazofluorene (140°, 1 h) in (**1**) gave two 1:1 adducts of fluorenylidene and (**1**), (**5**; m.p. 91—92°, 57%), and (**6**; m.p. 68—69°, 6%)‡ in addition to azine (**7**; m.p. 264—265°, 21%) and 9,9′-bifluorenylidene (**8**; m.p. 186—187°, 5%). The major adduct (**5**) was the expected cycloadduct as shown by spectral properties. The minor product (**6**) was olefinic; u.v. λ_{max} (EtOH) 230 nm (log ϵ 4·35), 248 (4·35), 256 (4·49), and 312 (3·83);§ n.m.r. (CCl_4) τ 2·1—3·0 (m, 8H, aromatic), 3·20 (s, 1H, vinylic), 4·47 (t, J 6·0 Hz, vinylic), 8·00 (broad quintet, 2H), 8·2—8·5 (m, 1H, allylic cyclopropyl), 9·10 (t, J 6·2 Hz, 3H), and 9·3—9·6 (m, 4H, cyclopropyl); (**6**) retains one cyclopropane ring, and the structure is deduced to be 9-(2′-cyclopropyl-



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† There will be a reverse process (M. E. H. Howden, A. Maercker, J. Burdon, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1966, **88**, 1732), but radical additions to (**1**) seem to result in the predominant formation of rearranged product. Thus, benzoyl peroxide catalysed addition of bromotrichloromethane to (**1**) gives a single product, 4-cyclopropyl-6,6,6-trichlorohex-3-enyl bromide, in 70% yield (S. Nishida, I. Moritani, and T. Teraji, unpublished observation), and radical polymerization of (**1**) produces a polymer composed of a cyclopropane cleaved chain unit (J. P. Kennedy, J. J. Elliott, and P. E. Butler, *J. Macromol. Sci.*, 1968, **2**, 1415).

‡ All new compounds gave satisfactory elemental analysis.

§ The geometrical structure of (**6**) has not been established yet.

pent-2′-enylidene)fluorene.§ Ozonolysis of (**6**) gave fluorenone in quantitative yield.

Table

Thermal decomposition of 9-diazofluorene in the presence of 1,1-dicyclopropylethylene (140°, 1 *h*)

Reaction conditions	Yield (%) (**5**) + (**6**)	(**7**)	(**8**)	Residue[a]	Ratio[b] (**6**) : (**5**)
Neat	63	21	5	(27)	0·1
Diluted with decalin, 2 times	28	18	6	(56)	1·5
Diluted with decalin, 30 times	21	18	4	(67)	3·0

[a] Intractable polymeric product; figures given are weight percent in the product mixture. [b] Obtained from a calibration curve and are average of three measurements,[7] ±10%.

The best established way to enrich the triplet carbene in the solution is by a dilution technique.[3,6] The reactants were therefore diluted with decalin and the ratios (**5**):(**6**) were examined by the t.l.c. spot area technique.[7] Addition of decalin in the same volume as (**1**) in the thermolysis reaction increased the amount of rearranged product (**6**) significantly; (**6**) became the major adduct in an experiment carried out at 30 times the dilution.¶ On the other hand, thermal decomposition of phenyl(tribromomethyl)mercury (100°, 1 h) in a benzene solution of (**1**) gave 1,1-dibromo-2,2-dicyclopropylcyclopropane (b.p. 80—81°/2 mm, 90%) as the only product. No rearranged product has been detected.

The present results can best be explained by the assumption that the singlet carbene reacts with (**1**) to give the cycloadduct (**5**), while triplet carbene produces a biradical (**9**), which rearranges to (**10**), at least in major part at 140°, because of its triplet derived nature.[8] (**6**) is derived from (**10**) by hydrogen abstraction. The initially produced fluorenylidene remains in its singlet state and the major part of the products is derived from it in neat olefin. Dilution increased the amount of triplet species and the rearranged product becomes predominant. These results are consistent with previous observations on the stereochemical studies of similar carbene additions.[3]

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¶ Product (**5**) rearranged to (**6**) at high temperature (half-life at 160—170° was *ca.* 4—5 h), which did not allow analyses of the product compositions by g.l.c., but the rearrangement was proved to be negligible under the thermolysis conditions.

[1] D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, 1968, **90**, 7047; R. A. Sheldon and J. K. Kochi, *ibid.*, 1970, **92**, 4395, 5175.
[2] P. D. Bartlett, *Quart. Rev.*, 1970, **24**, 473, and references cited therein.
[3] W. Kirmse, "Carbene Chemistry," Academic Press, New York, 1964; G. L. Closs, *Topics Stereochem.*, 1968, **3**, 193.
[4] T. Teraji, I. Moritani, E. Tsuda, and S. Nishida, *J. Chem. Soc.* (*C*), 1971, 3252.
[5] U.v. spectrum of 9-isopropylidenefluorene: J. Dehler and K. Fritz, *Tetrahedron Letters*, 1969, 2157.
[6] M. Jones, jun., and K. R. Rettig, *J. Amer. Chem. Soc.*, 1965, **87**, 4013.
[7] J. C. Morrison and L. G. Chatten, *J. Pharm. Sci.*, 1964, **53**, 1205.
[8] P. J. Wagner, *Accounts Chem. Res.*, 1971, **4**, 168.