Irradiation[5c] of **1a** and **1b** in methylcyclohexane:isopentane (4:1) glasses at *ca.* 5°K, in Supersil tubes in the cavity of an esr spectrometer,[6] generated strong, stable signals typical of triplet species[7] to which we assign structure **3a** and **3b**. Free radicals were also produced as evidenced by a strong signal at $g \sim 2$. Similar irradiation of **1c** produced the yellow color characteristic of **2c** and the signal due to the free radical(s); however, no signal due to a triplet (**3c**) could be detected. No signal due to **3a** was observed upon irradiation, direct or triplet-sensitized (benzophenone), of **4a** under these low temperature conditions.

The zero-field splitting parameters derived from the observed spectra are summarized in Table II along with

Table II. Zero-Field Splitting Parameters for Some Vinyl Methylenes and Model Compounds

Methylene	D/hc (cm^{-1})	E/hc (cm^{-1})	Ref
3a	0.3580	0.0206	a
3b	0.3643	0.0166	a
$(CH_3)_2C=CHC̈C_6H_5$	0.357	0.0194	b
$C_6H_5COC̈C_6H_5$	0.3815	0.0489	c
$C_6H_5C≡C̈CH$	0.541	0.0035	d

a This work. *b* J. L. Riemenschneider, Ph.D. Thesis, University of Chicago, 1969. *c* A. M. Trozzolo and S. R. Fahrenholtz, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., 1966, No. k23. *d* R. A. Bernheim, R. J. Kempf, J. V. Gramas, and P. S. Skell, *J. Chem. Phys.*, **43**, 196 (1965).

values reported for some model systems. The *D* value indicates a major contribution of the vinylmethylene valence bond structure (**3**) to the resonance hybrid. Assuming the electron–electron interaction is predominantly dipolar, the observed *D* values are equivalent to a mean separation of the electrons of *ca.* 2 Å, considerably smaller than in other trimethylenes.[8]

The stability of the triplet at 5°K indicates either that the triplet is the lowest energy state of the acyclic species (**3**) or is close enough in energy to the lowest singlet to be in thermal equilibrium with it at this low temperature. An analysis of the temperature dependence of the esr signals can distinguish between these possibilities.

For a constant concentration of triplets, the signal intensity due to the triplet will vary with temperature the same as the signal due to the free radical; thus, a plot of signal intensity *vs.* T^{-1} will be linear (Curie law)[9] and will extrapolate to zero intensity at infinite temperature. Plots of the observed intensities of the doublet signal and of the signals due to **3a** and **3b** exhibit Curie law dependence[10] over the range 5–45°K. For a triplet arising through thermal population from a singlet of lower energy, an estimate of the energy difference ΔE, of

(6) A Varian E-12 epr spectrometer was used. Variable temperatures were obtained using an Air Products and Chemicals LTD-3-110B Helitran, liquid helium transfer system.
(7) For a review of the esr spectrum of the triplet state see J. E. Wertz and J. R. Bolton, "Electron Spin Resonance," McGraw-Hill, New York, N. Y., 1972, Chapter 10.
(8) G. L. Closs, L. R. Kaplan, and V. I. Bendall, *J. Amer. Chem. Soc.*, **89**, 3376 (1967); D. R. Arnold, A. B. Evnin, and P. H. Kasai, *ibid.*, **91**, 784 (1969).
(9) C. P. Poole, Jr., "Electron Spin Resonance—A Comprehensive Treatise on Experimental Techniques," Interscience, New York, N. Y., 1967, p 545.
(10) Signals of maximum intensity unaffected by saturation above 15°K can be recorded at a microwave power of 1 mW. Below 15°K saturation becomes increasingly significant and the power must be reduced to 1 μW.

the two states is available from the relationship[11] between the signal intensity, I, and the temperature for a given energy difference

$$I = \frac{1}{T} \frac{3e^{-\Delta E/RT}}{1 + 3e^{-\Delta E/RT}}$$

These data indicate that either the triplets are the lowest energy states or are separated from singlets of lower energy by less than 4 cal mol^{-1}.

The lack of a triplet signal from the irradiation of **2c** may indicate that the singlet is the lowest energy state in this case and that the singlet–triplet separation is too large to maintain a significant concentration of triplets at these temperatures.

(11) R. Breslow, R. Hill, and E. Wasserman, *J. Amer. Chem. Soc.*, **86**, 5349 (1964).
(12) Visiting Professor (1973), on leave from the Department of Chemistry, University of Prince Edward Island, Charlottetown, Prince Edward Island, Canada.
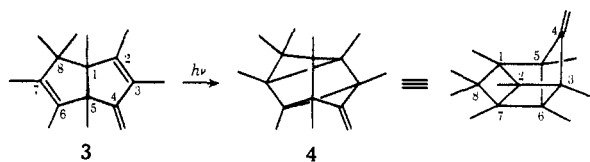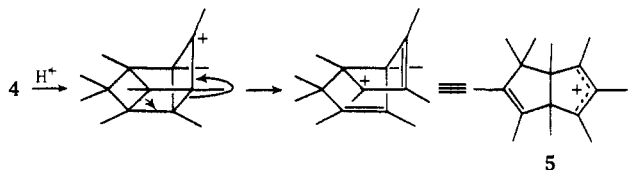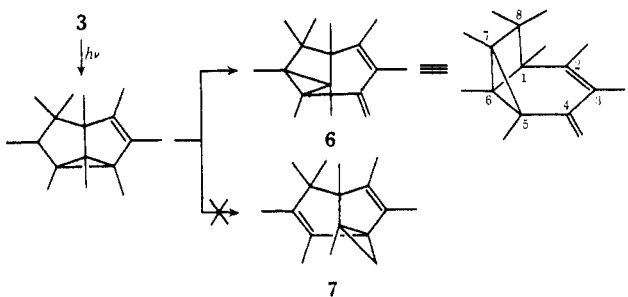(13) Alfred P. Sloan Fellow, 1972–1974.

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The Mechanism of Certain Intramolecular [$_\pi2 + _\pi2$] Cycloadditions

Sir:

We present here evidence, not yet conclusive but strongly suggestive, that certain intramolecular photochemical cycloadditions which on the surface appear to be of the [$_\pi2 + _\pi2$] type in fact occur in two steps; these are a di-π-methane rearrangement,[1] followed by a [$_\sigma2 + _\pi2$] cycloaddition. Examples are to be found in molecules which contain a di-π-methane moiety, but whose molecular geometry conspires, both with regard to bond distance and orbital dihedral angle, to make a direct [$_\pi2 + _\pi2$] process unfavorable.

It was recently reported[2] that neither **1** nor **2** under-

1

2
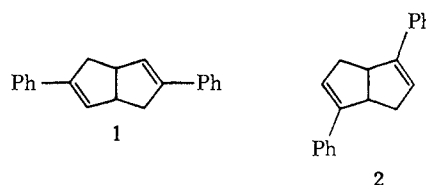
goes intramolecular photocycloaddition.[3] In contrast, we find that **3**[4] on irradiation (ether, Vycor) gave an essentially quantitative yield of the crystalline isomer **4**, whose structure corresponds to that of a cycloaddition of the two endocyclic π bonds. The structure of **4**

(1) For a recent review, see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).
(2) G. Kaupp and K. Krieger, *Angew. Chem., Int. Ed. Engl.*, **11**, 719 (1972).
(3) The double bonds in **1** and **2** are separated by about 3.5 Å.
(4) M. Kuzuya and H. Hart, *Tetrahedron Lett.*, 3891 (1973); see also erratum, *ibid.*, 4206 (1973).

3   **4**

follows from its spectral properties,[5] and its quantitative conversion in FSO_3H–SO_2ClF (*ca.* 1:4) at $-78°$ to the allylic ion **5** from which **3** had been prepared.[4,6]

5

The structural feature present in **3** but absent from **1** and **2** is the di-π-methane moiety. Of the two rearrangement modes, that which leads to **6** involves


6

7

breaking the cyclopropane bond in the direction of higher odd electron density (primary *vs.* tertiary) and is preferred.[1] Intermediate **6** was not detected; it would be expected to compete favorably with **3** for radiation and could rearrange to **4** by several paths (break 5–7, make 5–2, 7–3; break 5–6, make 5–2, 6–3; break 6–7, make 6–3, 7–2).[7] The preferred mechanism is shown.[7,8]

(5) Ir (CCl₄) $\nu_{C=C}$ 1678, 875 cm⁻¹ (methylenecyclobutane); pmr (CCl₄) methyl singlets at δ 0.63, 0.83, 0.97, and 1.07 (3 H each) and at δ 0.89, 0.91 (6 H each; accidental overlap) and vinyl protons at δ 4.15 and 4.22.

(6) The mechanism for the conversion of **4** to **5** may be more complex than shown; discussion is deferred for the full paper.

(7) In principle one could distinguish the last path from the first two by a labeling experiment. Efforts in this direction disclosed that **6** cannot only give **4** but return to **3**; further, return is fast compared with the formation of **4**, resulting in label scrambling in **3**. Detailed discussion is deferred for the full paper, but the essence of what may occur is shown in the scheme (* represents a CD₃ group). Cleavage of the 5–7 bond in **6** can lead to either diradical **8** or **9**, depending on whether

3

6   **8**

9   → **4**
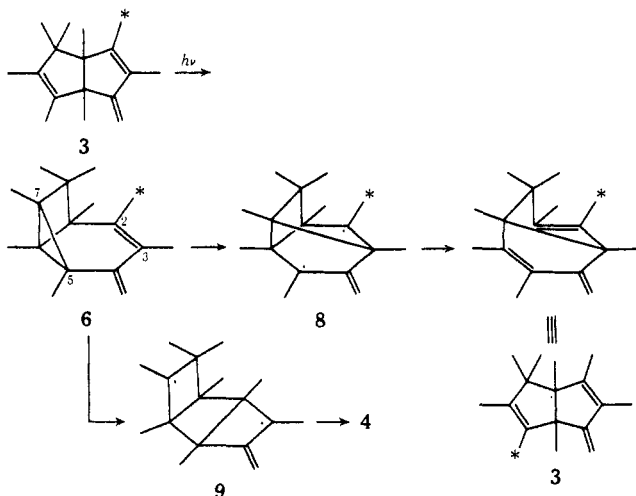
the 7–3 or 5–2 bond is formed first. 1,4-Diradical **8** can cleave to give label-scrambled **3**. This process is fast relative to the formation of **4**, since label in **3** gets scrambled among C2, C3, C5, and C6.

3   **8**

6   **9**
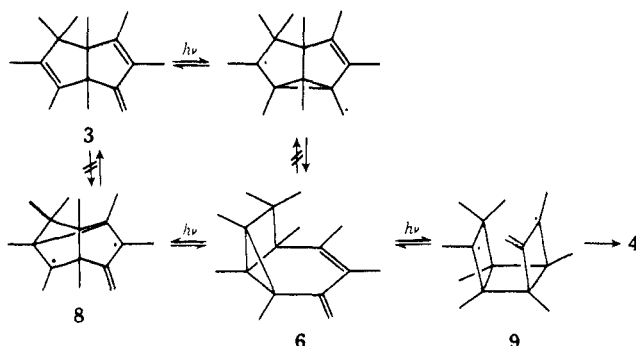
Another example of a reaction which appears to be a $[_\pi2 + _\pi2]$ cycloaddition but which probably involves two steps is the conversion of **10** to **11**.[9,10] Irradiation

10   **11**
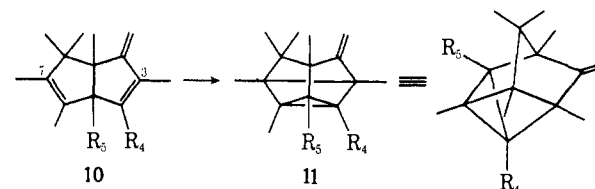
a, $R_4 = R_5 = CH_3$
b, $R_4 = H$; $R_5 = CH_3$
c, $R_4 = CH_3$; $R_5 = H$

of **10a** and **10b** (ether, Vycor) gave ($\sim$100%) **11a** and **11b**, respectively; the reaction could be sensitized by acetone, suggesting a triplet excited state. Irradiation of **10c** proceeded exceptionally slowly; under conditions where photoisomerization of **10a** and **10b** was complete only 30% of **10c** was converted to **11c**.

If the conversion of **10** to **11** were a direct $[_\pi2 + _\pi2]$ process, there is no obvious reason why substitution of H for CH_3 at C5 would affect the reaction efficiency; this observation can best be understood if a bond to C5 is broken during the reaction. Direct ring closure from diradical **12** (to give **11**) as has been suggested[2] seems highly unlikely in view of the large distance between C3 and C7 (*ca.* 3.8 Å in **10**, 3.1 Å in **12**) and the poor dihedral angle of the pertinent orbitals.

We suggest that the initial step is analogous to a di-π-methane rearrangement, with cleavage of the cyclopropane ring at the site of higher odd electron density (tertiary *vs.* allylic). The di-π-methane product **14** may be a discrete intermediate; if so, precedent exists for its photolability under the reaction conditions.[13] The

(8) **8** is not formed directly from **3** because the bond distance is too great and the orbital overlap is poor. Although **8** is readily formed from **6**,[7] bonding (to give **4**) does not occur for similar reasons. Bonding can occur in **9**, however, since the orbitals are directed toward one another; skewing makes this process slow and allows for label scrambling in **3**.[7]

(9) Similar reactions in compounds lacking the exocyclic methylene group have been described [ref 2; also P. J. Collin and W. H. F. Sasse, *Aust. J. Chem.*, **24**, 2325 (1971)].

(10) The preparations of **10a**,[4] **10b**,[11] and **10c**[12] have been described. Since the reaction has precedents,[9] structure proofs for **11a–c** are deferred to the full paper.

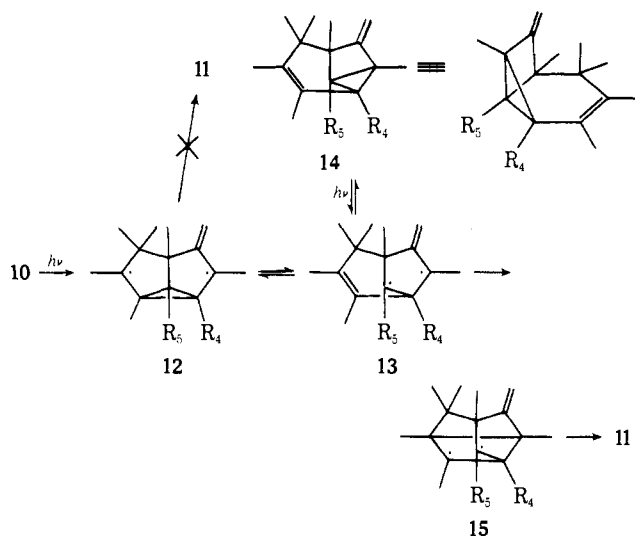(11) H. Hart and M. Kuzuya, *Tetrahedron Lett.*, 4123 (1973).

(12) H. Hart and M. Kuzuya, *J. Amer. Chem. Soc.*, in press.

(13) Compound **16** has an analogous chromophore and is photo-
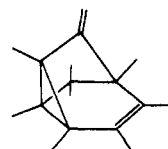
16

labile; H. Hart and M. Kuzuya, *Tetrahedron Lett.*, in press.

geometry of **13** is much more conducive to formation of the C3–C7 bond than is that of **12**; in **15**, the orbitals are close and properly oriented for the final bond-forming step to give **11**. If the reaction is stepwise as depicted, **10c** would be expected to react more slowly than **10a** or **10b** because in it C5 is secondary rather than tertiary.[14,15]

Our results suggest that it is important to consider multistep mechanisms for intramolecular $[_\pi 2 + _\pi 2]$ cycloadditions if the substrate also contains a di-π-methane moiety.[16]

(14) The scheme can also be analyzed as a sequence of concerted processes. If **14** is a discrete intermediate, inversion must occur at C5. Inversion is facilitated by electron-donating or delocalizing substituents (CH₃ > H). We believe this is a general phenomenon with broad implications for photochemistry but reserve discussion for the full paper.

(15) For papers dealing with the sensitivity of the di-π-methane reaction to substitution at the central carbon, see H. E. Zimmerman and J. A. Pincock, *J. Amer. Chem. Soc.*, **94**, 6208 (1972); **95**, 2957 (1973); H. E. Zimmerman, R. J. Boettcher, and W. Bray, *ibid.*, **95**, 2155 (1973). The example found by Zimmerman and Pincock (formation of a bicyclo[2.1.0]pentane from a 1,4-pentadiene) is easily recognized as a "false" $[_\pi 2 + _\pi 2]$ cycloaddition from the substitution pattern and should not be confused with the types of examples we discuss here.

(16) For other possible examples, see A. A. Gorman and J. B. Sheridan, *Tetrahedron Lett.*, 2569 (1969); G. Linstrumelle, *ibid.*, 85 (1970); A. R. Brember, A. A. Gorman, and J. B. Sheridan, *ibid.*, 481 (1973).

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## Cyclopropanes. XXXV. The Stereochemistry of the 1-Isocyano-2,2-diphenylcyclopropyl Anion[1]

Sir:

The reaction of $(-)$-(R)-1-cyano-2,2-diphenylcyclopropane with lithium diisopropylamide at $-60°$, in ether, resulted in the formation of 1-lithio-1-cyano-2,2-diphenylcyclopropane (**2**). Subsequent alkylation with methyl iodide yielded ($\pm$)-1-methyl-1-cyano-2,2-diphenylcyclopropane.[2] The inference from this datum

(1) The support of this work by a grant from Hoffmann-La Roche, Inc., and a Public Health Service grant (No. 04065) from the National Cancer Institute is gratefully acknowledged.

(2) H. M. Walborsky and F. M. Hornyak, *J. Amer. Chem. Soc.*, **77**, 6026 (1955).

was that in aprotic solvents the lithium cyclopropyl ion pair was incapable of maintaining its configuration. Since under comparable conditions optically active 1-lithio-1-methyl-2,2-diphenylcyclopropane (**1**) was shown to completely maintain its configuration,[3] the effect of the cyano group is to lower the barrier to inversion, presumably through delocalization. A similar result obtains when an acetylene, **3**, replaces the cyano group.[4] Both of these groups are attached to the cyclopropyl ring by an sp-hybridized carbon atom. We wish to report our results on the configurational stability of 1-lithio-1-isocyano-2,2-diphenylcyclopropane (**4**). Here,
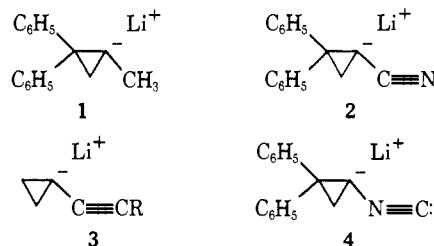
the isocyano function is directly attached to the ring by an sp-hybridized nitrogen atom.

The preparation of ($\pm$)- and (+)-2,2-diphenylcyclopropyl isocyanide from ($\pm$)- and (+)-2,2-diphenylcyclopropanecarboxylic acid was accomplished using a recently reported procedure.[5] The abolute configuration of (+)-2,2-diphenylcyclopropyl isocyanide was assigned as S based on its chemical correlation with (+)-(S)-2,2-diphenylcyclopropanecarboxylic acid.[6] The assignment of the S configuration to (+)-1-methyl-2,2-diphenylcyclopropyl isocyanide was made in a similar manner.[5]

In a typical experiment, a tetrahydrofuran solution of lithium diisopropylamide (6 mmol) kept under nitrogen atmosphere was cooled to $-72°$ and a 5 ml solution of 220 mg (1 mmol) of (+)-(S)-2,2-diphenylcyclopropyl isocyanide was added over a 10-min period. The reaction mixture was stirred for 30 minutes and then 1.5 g (10 mmol) of methyl iodide in 5 ml of tetrahydrofuran was added over a 10-min period. The reaction mixture was allowed to warm to ambient temperature and then poured onto ice water. The ether extract was dried and stripped and the crude product was purified by column chromatography (neutral alumina) to yield 224 mg (96%) of (+)-(S)-1-methyl-2,2-diphenylcyclopropyl isocyanide, mp 147–51°, optical purity 98%. Table I summarizes the results of a number of alkylations performed in an identical manner but varying the temperature.

The high degree of retention of configuration of the isocyanocarbanion **4** at temperatures between -52 to $-72°$ is surprising and contrasts dramatically with the results of the cyanocarbanion **2**. It suggests that the cyano group has a greater propensity for delocalizing an adjacent negative charge than does the isocyano group and that the isocyano group operates largely through an inductive effect. Resonance delocalization such as

(3) H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 2383 (1964).

(4) G. Kobrich, D. Merkel, and K. Imkampe, *Chem. Ber.*, **106**, 2017 (1973).

(5) H. M. Walborsky and G. E. Niznik, *J. Org. Chem.*, **37**, 187 (1972).

(6) H. M. Walborsky and C. G. Pitt, *J. Amer. Chem. Soc.*, **84**, 4831 (1962).