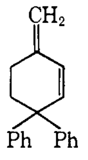
Mechanistic and Exploratory Organic Photochemistry. LV. Geometric Control of Multiplicity in the Di-π-methane Rearrangement[1]

Sir:

In an earlier report on the di-π-methane rearrangement we suggested[2] that acyclic di-π-methane reactants utilize singlet pathways and have unreactive triplets while bicyclic systems tend to prefer triplet mechanisms. This suggestion has had recent confirmation.[1,3] In the preceding communication,[1b] evidence was described which indicates that the lack of di-π-methane rearrangement of acyclic triplets is due to a free rotor effect dissipating excitation energy. A critical test of this concept was suggested by the photochemistry of the monocyclic diene 1-methylene-4,4-diphenyl-2-cyclohexene (**1**).[4] This di-π-methane was found to rearrange only *via* the singlet and to have an unreactive triplet. In the excited state of this molecule (**1**), the exocyclic methylene group was available for free rotation; consequently, the free rotor rationale was applicable.

Hence, to the extent that our reasoning was valid, the photochemistry of the endocyclic analog **2** of **1** should react *via* the triplet since this molecule lacks a potential free rotor. The present communication describes such a test.



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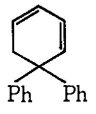

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5,5-Diphenyl-1,3-cyclohexadiene (**2**), mp 58.5–59.5°, was synthesized[5,6] by the method of Dauben[6] starting with 4,4-diphenylcyclohexenone.[7] Benzophenone-sensitized photolysis of 5,5-diphenyl-1,3-cyclohexadiene (**2**) afforded mainly two primary products, **3a**, mp 59.0–59.5°, and **3b**, mp 72–73°, plus a third product, **4**, mp 188–190°.

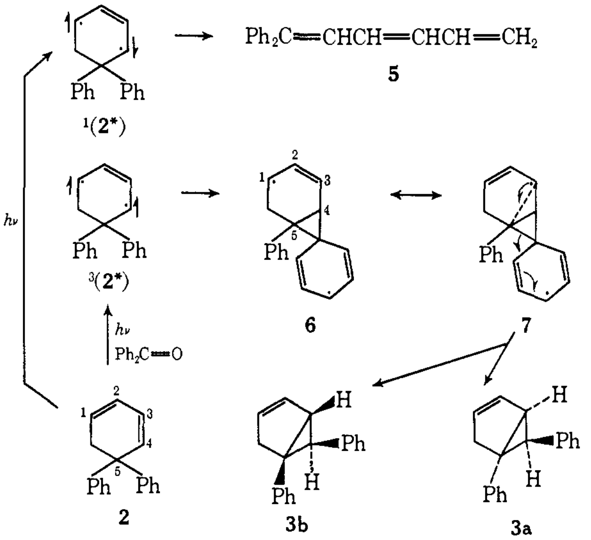
The structures of **3a** and **3b** were suggested by their nmr[5] spectra and were firmly established by synthesis as *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene (**3a**) and *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene (**3b**). Thus the Dauben reaction[6] of *trans*-5,6-diphenylbicyclo[3.1.0]-hexan-2-one[8] afforded **3a** and similar treatment of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one gave **3b**.

A study of product distribution *vs.* extent of irradiation established that the ratio of *trans* and *cis* bicyclic products **3a** and **3b** was essentially constant at 13.5 ± 2.4:1 while the relative amount of **4** decreased with lower conversion. Hence only **3a** and **3b** appear to be primary products. The mass balance based on identified products was 85% and the residual material appeared not to contain detectable amounts of any single monomeric product.[9] Compound **4** was found by elemental analysis and spectral data[5] to be an oxetane in which benzophenone had been incorporated and was a secondary photoproduct.

Direct irradiation of 5,5-diphenyl-1,3-cyclohexadiene (**2**) afforded one primary photoproduct **5** in a clean and facile reaction. Elemental analysis, the ultraviolet spectrum (in EtOH λ 316 mμ (ϵ 8200)), and the nmr spectrum which revealed ten aromatic hydrogens and six vinyl protons suggested 1,1-diphenyl-1,3,5-hexatriene as the structure of **5**.

One striking result is the contrasting behavior of the triplet excited state, as generated in the benzophenone sensitization, compared with the singlet reaction in direct photolysis. Thus the triplet gave rise to a di-π-methane rearrangement while the singlet excited state led to ring opening (see Chart I).

Chart I. The Photochemistry of 5,5-Diphenyl-1,3-cyclohexadiene



Most interesting is the pattern of reactivity as a function of multiplicity which is inverted from that found[4] for the analogous exocyclic diene **1**. The difference in reactivity, resulting in the ability of the triplet of diene **2** to undergo the di-π-methane rearrangement, clearly derives from the absence of an exocyclic methylene group which, acting as a free rotor, can dissipate energy. This interpretation is consistent with that derived independently from other evidence (*vide supra*).[1]

Two further points are noteworthy. First, the stereochemical preference for formation of the *trans* isomer parallels the photochemistry[4] of the exocyclic diene **1**, and the controlling factors seem likely to be the same. Second, consideration of resonance structure **6** reveals the potentiality for bonding between atoms 1 and 5 rather than 3 and 5 as observed. Di-π-methane rearrangements such as **2** → **3** can be considered[4] to proceed *via* species consisting of a cyclic array of six orbitals and an odd number of sign inversions. Inclusion of two extra orbitals, as would be required for bonding between atoms 1 and 5, without introduction of additional sign inversions leads to a

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(1) Paper LIII: H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **92**, 1407 (1970); (b) paper LIV: *ibid.*, **92**, 1409 (1970).

(2) H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969).

(3) H. E. Zimmerman and C. O. Bender, *ibid.*, **91**, 7516 (1969).

(4) H. E. Zimmerman and G. L. Samuelson, *ibid.*, **91**, 5307 (1969).

(5) Full experimental details will be given in our full paper; all compounds analyzed acceptably.

(6) Using the reaction of butyllithium with the *p*-toluenesulfonylhydrazone of 4,4-diphenylcyclohexenone as patterned after the method of W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *J. Amer. Chem. Soc.*, **90**, 4762 (1968).

(7) H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962).

(8) H. E. Zimmerman and J. W. Wilson, *ibid.*, **86**, 4036 (1964).

(9) We acknowledge with pleasure exchange of information with Professor John Swenton. While our residual material did contain one further minor secondary product, it did not appear to contain any other bicyclohexane derivatives as obtained by Professor Swenton. The difference seems most likely due to use of different sensitizers.

4*N*-orbital, 4*N*-electron system which will be excited state forbidden.[10]

Acknowledgment. Appreciation is expressed for support of this research by the National Science Foundation and by a National Institutes of Health Predoctoral Fellowship to G. A. E.

(10) (a) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564 (1966); (b) *Angew. Chem.*, **81**, 45 (1969); *Angew. Chem. Int. Ed. Engl.*, **8**, 1 (1969).

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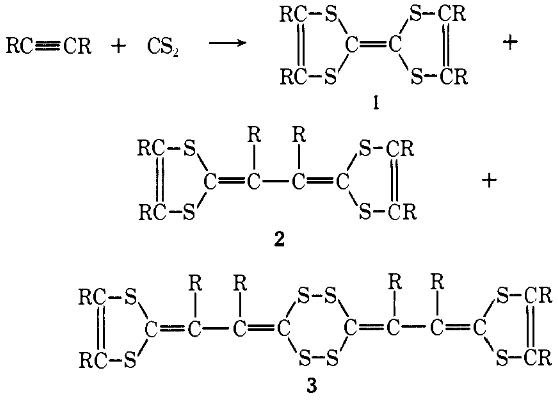
Nucleophilic 1,3-Dithiolium Carbenes

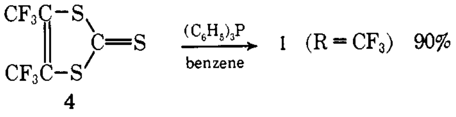
Sir:

At 100° carbon disulfide was added to acetylenes having at least one electron-attracting substituent to give products **1**, **2**, and **3**, any one of which can be made the predominant product by variation of reaction conditions. Compound **3** (R = CF$_3$) was obtained in 60% yield when a sevenfold excess of carbon disulfide was employed. With a 3.5-fold excess of carbon disulfide a 40% yield of **2** (R = CF$_3$) and a 20% yield of **3** were obtained. Compound **1** (R = CF$_3$) was normally formed in yields of the order of 2%, but could be produced quantitatively in the presence of trifluoroacetic acid. Compounds **1**, **2**, and **3** are stable under the reaction conditions. A mixture of **1**, **2**, and **3** (R = COOCH$_3$) was heated with hexafluoro-2-butyne and carbon disulfide and no cross products were formed.



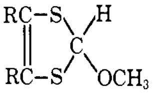
R = CF$_3$, COOCH$_3$

The bidithiole **1** (R = CF$_3$) was prepared in 90% yield by desulfurization of the known trithiocarbonate **4** with triphenylphosphine. Compound **2** was identical with material previously prepared.[1] The structures of **3** are consistent with all analytical and spectral data and are assigned for reasons given below.



4

The reaction of hexafluoro-2-butyne, carbon disulfide, and methanol gave no **1**, **2**, or **3**, but only the methoxydithiole **5** (R = CF$_3$). A similar reaction with dimethyl acetylenedicarboxylate gave principally **5** (R = COOCH$_3$) along with small amounts of **1** (R = COOCH$_3$). Completely analogous reactions occurred with esters of propiolic acid.



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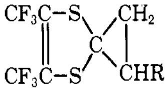

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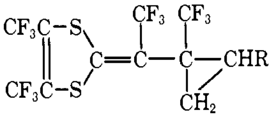
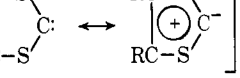


7

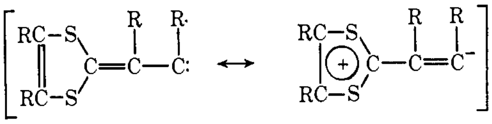
The reaction of hexafluoro-2-butyne, carbon disulfide, and olefins gave cyclopropanes **7**. Yields of **7** as high as 77% (R = OCH$_3$) have been obtained.

These data suggest that acetylenes and carbon disulfide generate 1,3-ditholium carbenes (A) and that the carbenes react as nucleophiles. Such a species has a 6-π-electron system and would be expected to be greatly stabilized by electron delocalization. Stable, aromatic, 1,3-dithiolium cations are well known[2–4] and 1,3-dithiolium carbenes have been suggested as intermediates in reactions of the ions with bases.[5,6] The formation of alkoxydithioles **5** indicates that alcohols can very effectively capture A, presumably by protonation.



A

In the presence of olefins, A preferentially reacts with the electron-deficient triple bond of the acetylene to generate a new carbene B which is trapped with the olefin to form cyclopropanes **7**. These reactions of A are again those of a nucleophile. Interaction of A with electron-deficient olefins can occur. The reaction of hexafluoro-2-butyne, carbon disulfide, and dimethyl maleate gave **1**, **2**, and **3** (R = CF$_3$) and dimethyl fumarate. Control experiments demonstrated that neither the acetylene nor carbon disulfide caused isomerization of dimethyl maleate under reaction conditions. It seems most reasonable that A underwent reversible Michael-type addition to the ester to give zwitterion C which lived long enough to allow bond rotation.



B

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(1) C. G. Krespan and D. C. England, *J. Org. Chem.*, **33**, 1850 (1968).

(2) D. Leaver, W. A. H. Robertson, and D. M. McKinnon, *J. Chem. Soc.*, 5104 (1962).

(3) E. Klingsberg, *J. Amer. Chem. Soc.*, **84**, 3410 (1962).

(4) The parent 1,3-dithiolium perchlorate[2] undergoes rapid deuterium exchange at C-2 and reacts with triethylamine to give a high yield of $\Delta^{2,2'}$-bi-1,3-dithiole.

(5) H. Prinzbach, H. Berger, and A. Lüttringhaus, *Angew. Chem.*, **77**, 453 (1965).

(6) H. Prinzbach and E. Futterer, *Advan. Heterocycl. Chem.*, **7**, 121–124 (1966).