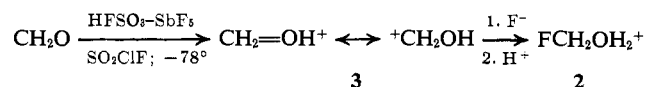Figure 1. Nuclear magnetic resonance spectra of protonated fluoromethyl alcohol: (a) proton spectrum at 60 MHz; (b) fluorine spectrum at 56.4 MHz.

fluoride or hydrogen fluoride) at $-78°$ protonated fluoromethyl alcohol, 2, is obtained.

$$CH_2O \xrightarrow[SO_2ClF; \ -78°]{HFSO_3-SbF_5} CH_2=OH^+ \longleftrightarrow \ ^+CH_2OH \xrightarrow[2. \ H^+]{1. \ F^-} FCH_2OH_2^+$$
$$\qquad\qquad\qquad\qquad\qquad 3 \qquad\qquad\qquad\qquad 2$$

Ion 3 reacts through its hydroxycarbonium ion nature with fluoride ion giving fluoromethyl alcohol which then is protonated in the superacid medium.

$$^+CH_2OH + F^- \longrightarrow FCH_2OH \rightleftharpoons FCH_2OH_2^+$$
$$\qquad\qquad\qquad\qquad 1 \qquad\qquad 2$$
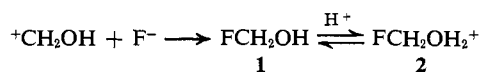
When formaldehyde is dissolved in a 1:1 HF–SO₂ClF solution at $-78°$, the ^{19}F nmr spectrum shows the nearly exclusive presence of bis(fluoromethyl) ether, 4, formed through the acid-catalyzed self-condensation of the initially produced fluoromethyl alcohol, 1.

$$2CH_2O + 2HF \longrightarrow 2FCH_2OH \longrightarrow FCH_2OCH_2F + H_2O$$
$$\qquad\qquad\qquad\qquad\qquad 1 \qquad\qquad\qquad 4$$
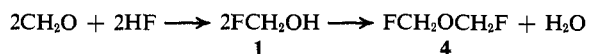
The self-condensation could involve the alkylation of fluoromethyl alcohol by the hydroxycarbonium ion and subsequent fluorination of the fluoromethyl hydroxymethyl ether by HF.[10]

$$FCH_2OH + \ ^+CH_2OH \longrightarrow FCH_2OCH_2OH \xrightarrow{HF} FCH_2OCH_2F$$

The preparation of protonated fluoromethyl alcohol from protonated formaldehyde with fluoride ion seems to be the first direct experimental evidence of a stable protonated carbonyl intermediate reacting through its hydroxycarbonium ion nature and thus is in agreement with conclusions reached by ¹H and particularly ¹³C nmr studies of the contribution of the hydroxycarbonium ion form in protonated formaldehyde. Fluoro-

(10) The zinc chloride catalyzed condensation reaction of fluoromethyl alcohol with aromatic hydrocarbons was previously observed to produce diphenylmethane derivatives.² The reaction is also considered to involve hydroxymethylation of the aromatic followed by acid-catalyzed condensation of the benzyl alcohol.

methyl alcohol also represents a molecule of substantial interest as the parent compound of α-halo alcohols.

Whereas in its protonated form fluoromethyl alcohol is stable, the free alcohol readily loses HF to form formaldehyde and could not be isolated so far for direct studies. We are continuing our studies at lower temperatures, and are also investigating other halomethyl alcohols.

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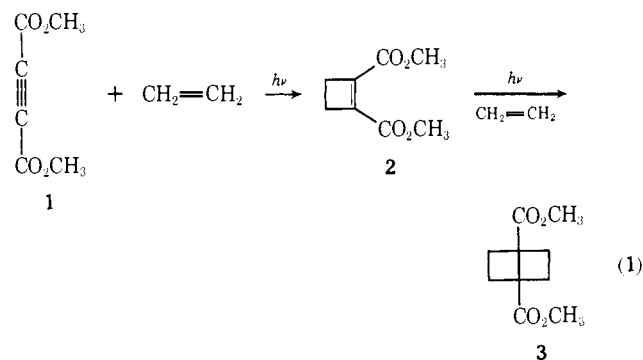Cleveland, Ohio 44106*
Received November 10, 1970

Photochemistry of Acetylenes. I. The Photoaddition of Ethylene to Dimethyl Acetylenedicarboxylate

Sir:

Dimethyl acetylenedicarboxylate (1) has played an important role in organic synthesis because it undergoes a wide variety of thermal cycloaddition and conjugate addition reactions.[1] Very little is known, however, about its photochemistry. Dimethyl cyclooctatetraene-1,2-dicarboxylate is formed when 1 is irradiated in benzene solution.[2,3] Furthermore, when 1 is irradiated in cyclic ether solvents, products are formed which are the result of its alkylation by solvent *via* a free-radical mechanism.[4] We wish now to report the first example of the photochemical reaction of dimethyl acetylenedicarboxylate with two molecules of a simple olefin.[5]

It was expected that the photolysis of 1 in the presence of ethylene would lead to dimethyl bicyclo[2.2.0]-hexane-1,4-dicarboxylate (3) *via* two consecutive [2 + 2] cycloadditions to 1 and the intermediate dimethyl cyclobutene-1,2-dicarboxylate (2, eq 1). Direct irradi-

ation of a 0.5% solution[6] of 1 in ethylene-saturated di-

(1) R. Fuks and H. G. Viehe in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N.Y., 1969, Chapter 8, pp 435, 460–520, 550–567, and 574–575.

(2) E. Grovenstein, Jr., and D. V. Rao, *Tetrahedron Lett.*, 148 (1961).

(3) D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 695 (1963).

(4) P. Singh, *Tetrahedron Lett.*, 2155 (1970).

(5) A 1:1 photoadduct of norbornene and dimethyl acetylenedicarboxylate has been reported (4% yield): M. Hara, Y. Odaira, and S. Tsutsumi, *Tetrahedron*, 22, 95 (1966).

(6) The solutions were irradiated by a 450-W Hanovia medium-pressure mercury arc in the variable-temperature preparative photochemical apparatus previously described (14.2 g of acetylenic ester in 2800 ml of dichloromethane); *cf.* D. C. Owsley and J. J. Bloomfield, *Org. Prep. Proc.*, in press.

chloromethane at $-80°$ for 18 hr resulted in a clear oil which was distilled at 75–80° (0.2 mm). A 63% yield of a 9:1 mixture of dimethyl α,α'-dimethyleneadipate[7] (4) and a new compound 5 was obtained (eq 2). The adipic ester 4 was identified by its nmr spectrum and melt-

$$1 + 2CH_2{=}CH_2 \xrightarrow{h\nu} 3 + 5 \xrightarrow{\text{distill}}$$
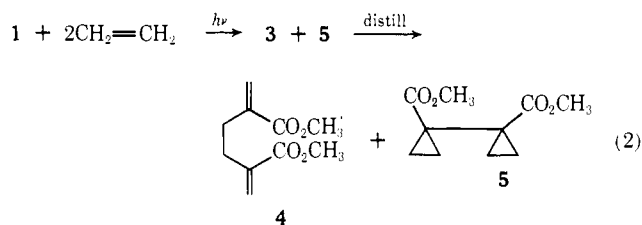
ing point.[7] The unknown 5 was collected by preparative glc and was shown to be dimethyl bicyclopropyl-1,1'-dicarboxylate on the basis of ir, nmr,[8a] and mass spectral data, and the melting point[8b] of the parent acid. It should be noted that the intermediate cyclobutene 2 was never observed when the photolysis was monitored by glc, indicating that the quantum efficiency of its reaction with ethylene is greater than that of 1 with ethylene. The solvent and temperature are quite important in this reaction. When 1 is photolyzed in ether at 0 or $-80°$ a variety of compounds are formed with 3 and 5 as the minor products. Nmr spectra of crude photolysis mixtures of 1 before distillation show that 3 is present as the major product.

Dimethyl bicyclo[2.2.0]hexane-1,4-dicarboxylate (3) was also synthesized from dimethyl cyclobutene-1,2-dicarboxylate[9] (2) quantitatively in analytical purity as a low melting solid, liquid at room temperature: $n^{25}D$ 1.4645, nmr (downfield from internal TMS)[10] 3.65 (s, 6 H) and 3.00–2.00 ppm (complex multiplet, 8 H); mass spectrum,[10] m/e (rel intensity) 198 (0.12), 107 (48), 79 (100), 77 (48), 59 (71), 39 (90).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.66; H, 7.22.[10]

The first-order rate constant for isomerization of the bicyclic ester 3 to the hexadiene 4 was found to be $0.99 \pm 0.09 \times 10^{-4}$ sec^{-1} at 75° in chloroform solution[11] (eq 3). This rate constant is contrasted with
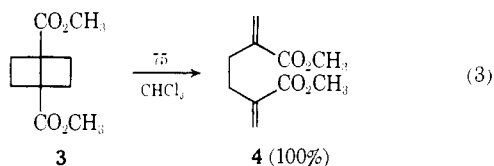
that calculated from the activation parameters for the rearrangement of bicyclo[2.2.0]hexane to 1,5-hexadiene ($k_{75°} = 4 \times 10^{-12}$ sec^{-1}).[12,13]

(7) C. S. Marvel and S. D. Vest, *J. Amer. Chem. Soc.*, 81, 984 (1959).

(8) (a) *Cf.* J. M. Conia and J. M. Denis (*Tetrahedron Lett.*, 3454 (1969)) for ir and nmr spectra of the diethyl ester; (b) mp 268–275° (sealed tube); L. Eberson, *Acta Chem. Scand.*, 13, 46 (1959) (mp 256–275°).

(9) (a) E. Vogel, D. Roos, and K. H. Disch, *Justus Liebigs Ann. Chem.*, 653, 55 (1962); (b) W. H. Perkin, Jr., *J. Chem. Soc.*, 65, 950 (1894); (c) D. Seebach, *Chem. Ber.*, 97, 2953 (1964); (d) F. B. Kipping and J. J. Wren, *J. Chem. Soc.*, 1733 (1957).

(10) Analysis by Alfred Bernhardt, Mikroanalytisches Laboratorium, 5251 Elbach über Engelskirchen; nmr spectra were obtained on a Varian T-60 and mass spectra were obtained on a Varian MAT CH-7.

(11) A full treatment of the kinetics of the thermal rearrangement of 3 to 4 will appear at a later date.

(12) For a review of bicyclo[2.2.0]hexane chemistry, *cf.* K. B. Wiberg, *Advan. Alicyclic Chem.*, 2, 230–241 (1968).

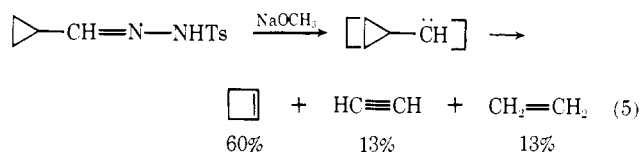(13) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Amer. Chem. Soc.*, 86, 679 (1964).

Bicyclopropyl compounds similar to 5 have been found in photochemical additions of excited olefins to acetylenes 6 and 7.[14–16] The fact that bicyclopropyl

6, R = H, CH$_3$ 7
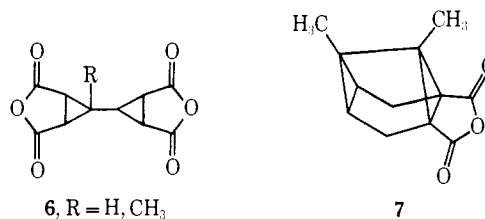
compounds are formed in photoadditions in which acetylenes are both the excited and nonexcited partners indicates that a common set of intermediates is involved in each case. Hartmann[14] has proposed either diradical or carbene intermediates to account for his results. However, the result of Askani[16] in which 7 is the major product in the photosensitized addition of 2-butyne to 3,6-dihydrophthalic anhydride strongly suggests that a triplet diradical 8 undergoes ring closure to a cyclopropyl carbene 9 at a much higher rate than it undergoes spin relaxation to a singlet diradical 10 and subsequent ring closure to the cyclobutene derivative 11 (eq 4).
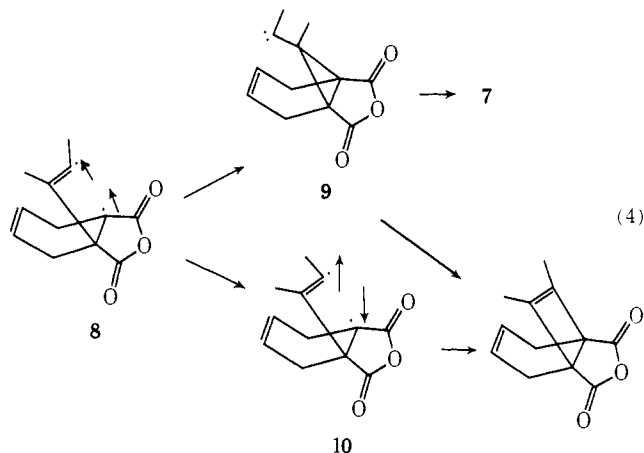
That cyclopropyl-conjugated carbenes rearrange to cyclobutenes and olefins and acetylenes has been established previously (eq 5).[17] The principle of micro-

scopic reversibility suggests that cyclopropyl-conjugated carbenes can be produced from olefins and acetylenes under the proper conditions. The involvement of ether solvent in the photoaddition of 1 to ethylene implicates the triplet state of 1 in the formation of products 3 and 5. Scheme I is offered to account for the formation of all the products. We are presently in-
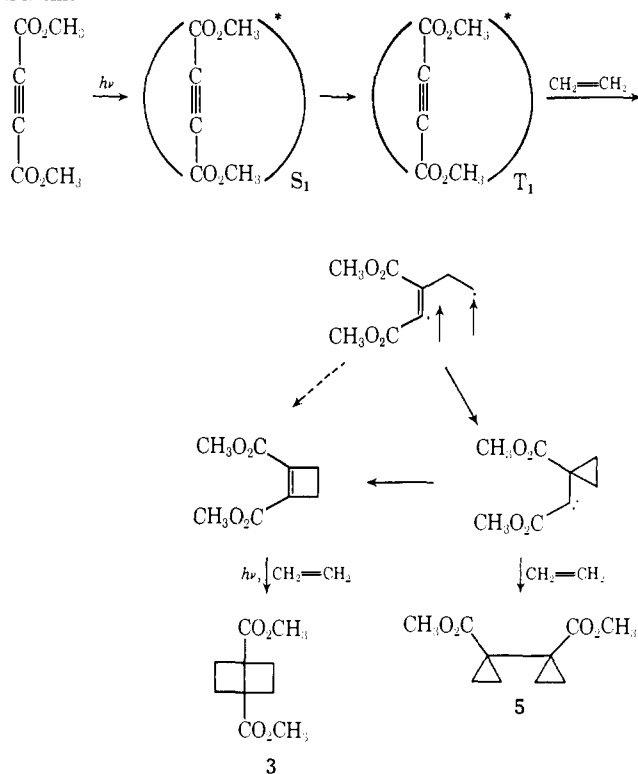
(14) W. Hartmann, *Chem. Ber.*, 102, 3974 (1969).

(15) G. Klotzenberg, P. G. Fuss, and J. Leitch, *Tetrahedron Lett.*, 3409 (1966).

(16) R. Askani, *Chem. Ber.*, 98, 3618 (1965).

(17) (a) L. Friedmann and H. Schechter, *J. Amer. Chem. Soc.*, 82, 1002 (1960); (b) W. Kirmse and K. H. Pook, *Chem. Ber.*, 98, 4022 (1965); (c) S. J. Cristol and J. K. Harrington, *J. Org. Chem.*, 28, 1413 (1963).

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Scheme I

vestigating the photoaddition of other unsaturated substrates to dimethyl acetylenedicarboxylate.

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Walsh's Rules as the Rule of the Closed Shell[1,2]

Sir:

Consider a molecule M, of formula AH_mB_n, comprising m hydrogen atoms H and n other first-row atoms B, bound to a central heavy atom A, in a linear or nonlinear configuration if $m + n = 2$, in a planar or nonplanar configuration if $m + n = 3$, and so on. Cases for which ligands are bound to one another are excluded. Then it has been well known since the work of Walsh in 1953[3] that the stable configuration of M can be predicted from the number of valence electrons of M. Namely, molecules HAH are linear if they have 4 or fewer valence electrons, molecules HAB are linear if they have 10 or fewer valence electrons, molecules CAB are linear if they have 16 or fewer valence electrons, molecules AH_3 are planar with 6 or fewer valence electrons, molecules BAH_2 are planar with 12 or fewer valence electrons, molecules BACH are planar with 18 or fewer valence electrons, and molecules BACD are planar with 24 or fewer valence electrons. A lower symmetry occurs when the number of valence electrons exceeds the number indicated. For

HAB and CAB, linearity results again for 16 or more and 22 or more valence electrons, respectively.

The Walsh rules as just stated refer to most ground states of stable species; Walsh's own discussion included excited states. The rules were viewed by Walsh, and they have been viewed by most subsequent authors, as being a consequence of molecular orbital theory, although their elucidation from molecular orbital theory is not yet complete.[4] We here initiate a discussion more reminiscent of valence bond theory.

Noting that Walsh's magic numbers can all be recovered from the formula

$$W = 2m + 8n \tag{1}$$

we see that Walsh's rules are equivalent to the following prescription. Assign valence electrons to the ligand hydrogen atoms until each possesses a closed shell of two electrons, and assign valence electrons to the ligand heavy atoms until each possesses a closed octet. If there are no (or a negative number of) valence electrons left over, the molecule takes its most symmetric configuration; if there are valence electrons left over, the molecule assumes a lower symmetry.[5]

The closed-shell configurations here invoked may be viewed as ionic valence bond structures; for example, $H^-Be^{2+}H^-$ for BeH_2 (linear), $H^-O^{2+}H^-$ for H_2O (nonlinear), $H^-C^{4+}N^{3-}$ for HCN (linear), $H^-C^{3+}O^{2-}$ for HCO (nonlinear), $N^{3-}N^{5+}O^{2-}$ for N_2O (linear), $O^{2-}N^{4+}O^{2-}$ for NO_2 (nonlinear), and $N^{3+}H_3^{3-}$ for NH_3 (nonplanar). This very ionicity provides a mechanism for holding the molecule in its most symmetric configuration or causing its distortion, depending on the absence or presence of excess valence electrons on the central atom. Coulomb repulsion between ligand ions preserves the high symmetry unless a counter force of comparable magnitude arises. That can happen through 2s–2p hybridization at the central atom when excess electrons are there, producing finite atomic dipoles in the field of which the ligand atoms are displaced toward positions of lower symmetry. Degeneracy between 2s and 2p orbitals on the central cation would make this effect formally a second-order Jahn–Teller effect.[6] The atomic dipoles could then be created with no loss in energy and the distortion would occur with a gain in stability. In the foregoing examples, the electronic configurations of the central ions are Be^{2+} $(1s)^2$, O^{2+} $(1s)^2(2s$ or $2p)^4$, C^{4+} $(1s)^2$, C^{3+} $(1s)^2(2s$ or $2p)$, N^{5+} $(1s)^2$, N^{4+} $(1s)^2(2s$ or $2p)$, and N^{3+} $(1s)^2(2s$ or $2p)^2$; the possibility for such distortions being favorable is clear in the second, fourth, sixth, and seventh cases.

The reference closed-shell ionic structure must have the same symmetry as the molecular state of interest, and the appropriate reference ionic structures may not always permit the formation of an asymmetric hybrid. Symmetries of actual low-lying molecular states require that the p_σ orbitals on the central ion be the last to be

(4) Among the key more recent discussions are the following: W. A. Bingel, *J. Chem. Phys.*, 30, 1250, 1254 (1959); 32, 1522 (1960); Z. *Naturforsch. A*, 16, 668 (1961); C. E. Wulfman, *J. Chem. Phys.*, 31, 381 (1959); 33, 1567 (1960); C. A. Coulson and A. H. Nielson, *Discuss. Faraday Soc.*, 35, 71 (1963); S. E. Peyerimhoff, R. J. Buenker, and L. C. Allen, *J. Chem. Phys.*, 45, 734 (1966).
(5) This prescription may also be found in R. D. Gillard, *Rev. Port. Quim.*, 11, 70 (1969).
(6) Compare R. G. Pearson, *J. Chem. Phys.*, 52, 2167 (1970); *J. Amer. Chem. Soc.*, 91, 4947 (1969); R. F. W. Bader, *Can. J. Chem.*, 40, 1164 (1962).