It is probable that the "$(C_{10}H_8)_2Fe_5(CO)_{13}$"[13] of Burton, *et al.*,[14] will provide a further example of this ligand-to-cluster bonding. A single-crystal structural analysis of this iron complex is currently in progress and will be reported in due course.

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(13) Preliminary mass spectral studies show the parent ion peak to be at *m/e* 760. The accidental mass relationship $^{56}Fe = 2(^{12}C^{16}O)$ leaves us unable to distinguish, at present, between $(C_{10}H_8)_2Fe_5(CO)_8$ or $(C_{10}H_8)_2Fe_4(CO)_{10}$ as the correct formulation.

(14) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4290 (1960).

Melvyn R. Churchill, Peter H. Bird
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

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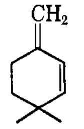
The Photochemistry of 4,4-Dimethyl-1-methylene-2-cyclohexene, a Methylene Analog of a Cyclohexenone[1]

Sir:

Earlier studies of the photochemical transformation of the transoid dienes of the 1-methylene-2-cycloalkene series have shown that the compounds under singlet conditions (direct irradiation) are readily transformed to their valence isomeric bicyclo[1.1.0]butanes or compounds derivable from such intermediates.[2] These studies have now been extended to **1**, the methylene analog of 4,4-dimethyl-2-cyclohexenone (**2**), a compound known to undergo the so-called "lumirearrangement" to 6,6-dimethylbicyclo[3.1.0]hexan-2-one (**3**) upon photoexcitation.[3] Such a study will permit evaluation of the behavior of a similar compound lacking the n → π* excited state.



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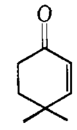

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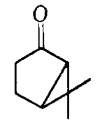

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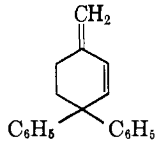
Reaction of the ketone **2** with methylenetriphenylphosphorane gave 4,4-dimethyl-1-methylene-2-cyclohexene as a colorless liquid:[4] bp 131–133°; λ_{EtOH}^{max} 232 mμ (ε 13,400); $\gamma_{max}^{CCl_4}$ 3030, 2990, 1640, 1600, 1470, 1460, 1360, 880 cm^{-1}; nmr (τ, CCl_4) AB quartet centered at 4.34 (2 H, –CH═CH–, $\delta_A - \delta_B = 0.33$ ppm, $J_{AB} = 9$ cps), 5.32 br singlet (2H, ═CH_2), triplet centered at 7.67 (2 H, ring CH_2, $J_{AB} = 7$ cps), triplet centered at 8.52 (2 H, ring CH_2, $J_{AB} = 7$ cps), singlet 9.01 (6 H, geminal CH_3).

Since the enones are known to undergo the lumirearrangement *via* a triplet,[5] the triplet of the diene analog **1** was generated. When the irradiation was carried out using triphenylene ($E_T = 68$ kcal) as a sensitizer (Pyrex filter, λ >280 mμ) in pentane, starting material was observed to disappear slowly but no monomeric photoproducts were obtained. When the sensitized irradiation was repeated using methanol as the solvent, again no monomeric photoproducts and no ethers were formed.[6] Thus, unlike the enone **2** which is transformed to the lumiproduct **3** *via* the triplet, the triplet of the diene analog **1** behaves as triplets of other exocyclic olefins and slowly polymerizes.[7] Furthermore, in contrast to the *transoid* dienes such as 3,5-hexalin[8] and 3,5-cholestadiene[9] whose internal rotations are constrained and which readily add methanol under sensitized conditions, the unconstrained diene **1**, which is capable of forming an orthogonal triplet, fails to react with methanol.

Recently, Zimmerman and co-workers[10] have investigated the photochemistry of the methylene analog **4** of 4,4-diphenylcyclohexenone (**5**), and it was found that



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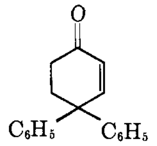

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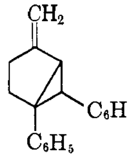

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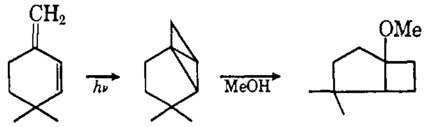
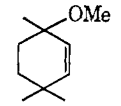
the diene upon reaction under triplet conditions did not yield any monomeric photoproducts. However, under singlet conditions the *cis* and *trans* isomers of 5,6-diphenyl-2-methylenebicyclo[3.1.0]hexane (**6**) were formed, products which are similar in structure to the photoproducts derived from the triplet of the related enone **5**. Similar studies in this laboratory confirm these results with **4**. When the diene **1** was irradiated directly in pentane, no monomeric rearrangement products were observed. When methanol was used as a solvent, the only monomeric products obtained were the ethers **7** and **8**. Such ethers are typical reaction products formed from a transoid diene upon direct irradiation,[2] **7** coming *via* the bicyclobutane.



1 **7**



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Thus, unlike the diphenyl-substituted methylene analog **4**, the dimethyl diene **1** behaves in a manner typical of a normal transoid diene in both direct and sensitized irradiation. The formation of a bicyclo[3.1.0]hexane resulting from the rearrangement of a peripheral grouping at position 4 is limited to the 4-phenyl substituent. The inability to form a methylene analog of the typical "lumi" product **3** may be attributed either to the necessity of a n → π* triplet in the reaction manifold or to a difference in the charge distribution in a π → π* triplet of an enone and a diene.

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(1) This work was supported in part by PHS Grant 00709, National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

(2) W. G. Dauben and C. D. Poulter, *Tetrahedron Letters*, 3021 (1967).

(3) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *ibid.*, 2049 (1963).

(4) All compounds described gave satisfactory analyses.

(5) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Am. Chem. Soc.*, **88**, 159, 1965 (1966); O. L. Chapman, J. B. Sieja, and W. J. Welstead, Jr., *ibid.*, **88**, 161 (1966).

(6) Under conditions where the diene absorbed no light (Pyrex filter), the rate of its disappearance was 20 times that of the sensitizer. Thus, energy transfer from sensitizer to diene occurred.

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(8) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964).

(9) J. Pusset and R. Beugelmans, *Tetrahedron Letters*, 3259 (1967).

(10) H. E. Zimmerman and G. E. Samuelson, *J. Am. Chem. Soc.*, **89**, 5971 (1967).

(11) National Institutes of Health Predoctoral Fellow.

William G. Dauben, Wayne A. Spitzer[11]
Department of Chemistry, University of California
Berkeley, California 94720

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