

described in terms of three $\text{Fe}(\text{CO})_3$ groups and a dimethylarsenic group being linked together to form a nearly planar square arrangement. The ligand is above this square plane and is coordinated differently to each of the three iron atoms: to Fe(1) by As(5), to Fe(2) by a π bond from the cyclobutene ring, and to Fe(3) by a σ bond from the cyclobutene ring. This nicely meets the valence requirements of each of the groups involved, each iron atom having a (different) distorted octahedral environment. The bonding may be regarded either in terms of a delocalized system involving all the iron and arsenic atoms together with the cyclobutene carbon atoms or, equally well, in conventional valence-bond terms involving d^2sp^3 orbitals on each iron atom. The molecule as a whole has no over-all symmetry either on a molecular or crystallographic basis.

It should be noted that the iron-iron bonds are markedly different in length; the long iron-iron bond involves the iron atom linked to the two arsenic atoms (cf. ref 2), while the shorter ("normal") one involves coordination to a single arsenic atom. These may be compared to the more nearly equal iron-iron distances of 2.69, 2.68, and 2.55 Å found in the parent molecule $\text{Fe}_3(\text{CO})_{12}$.⁵

This structure together with the $[\text{Ni}(\text{diars})(\text{triar})]-(\text{ClO}_4)_2$ compound should indicate the need for caution in the inference of structures for ditertiary arsines even where rearrangement of the ligand may not be expected.

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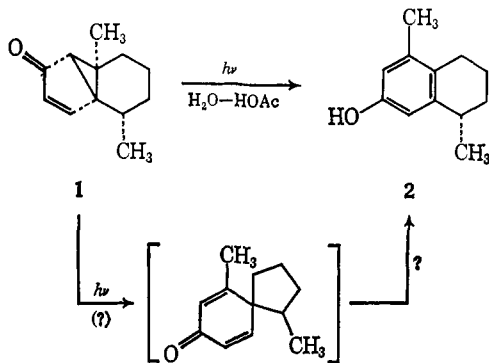
(5) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966).

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Photochemical Formation of a Cyclopropanone¹

Sir:

Kropp and Erman have reported the photoisomerization of 5 α ,8 α -dimethyl-1,5,6,7,8,8 α -hexahydro-1 β ,4 α -cyclo-2(4 α H)-naphthalenone (1) to 4,8-dimethyl-5,6,7,8-tetrahydro-2-naphthol (2) at room temperature in

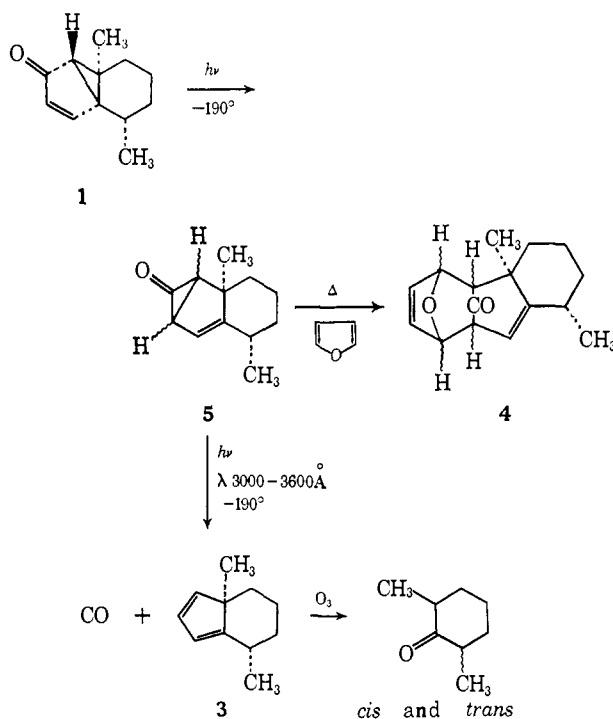


45% aqueous acetic acid.² Analogy with related

(1) Photochemical Transformations. XXXI.

systems suggests that a spirodienone intermediate may be involved³ in this process. We wish to report the nature of the low-temperature (-190°) photochemistry of 1.

Irradiation of neat 1 as a glass at -190° in a liquid nitrogen cooled infrared cell using previously described techniques⁴⁻⁶ produces a photoproduct with intense absorption at 1812 cm^{-1} and weaker absorption at 1840 cm^{-1} , together with a small amount of a ketene derivative with absorption at 2106 cm^{-1} (Figure 1). It is clear from the simultaneous appearance and disappearance that the 1840 - and 1812-cm^{-1} absorptions belong to the same species. Irradiation of 1 with light of $\lambda\ 2537\ \text{\AA}$ or $>3600\ \text{\AA}$ is best for maximum accumulation of the product with the 1812-cm^{-1} absorption. Light in the $3000\text{-}3600\text{-\AA}$ range rapidly converts the photoproduct to carbon monoxide and a hydrocarbon in high yield (65% isolated; >90% by spectroscopic determination). The nmr and infrared spectra, molecular weight, and element analysis of the hydrocarbon are consistent with structure 3.⁷ Ozon-



olysis of the hydrocarbon followed by decarboxylation (and/or decarbonylation) gives a mixture of *cis*- and *trans*-2,6-dimethylcyclohexanones. The formation of 3 represents a novel diversion of the photochemistry of 1 by use of low-temperature techniques. This two-quantum process is a useful synthesis of 3.

The product with the 1812-cm^{-1} band disappears on warming above -115° . No carbon monoxide is evolved

(2) P. J. Kropp and W. F. Erman, *J. Amer. Chem. Soc.*, **85**, 2456 (1963).

(3) P. J. Kropp in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 1.

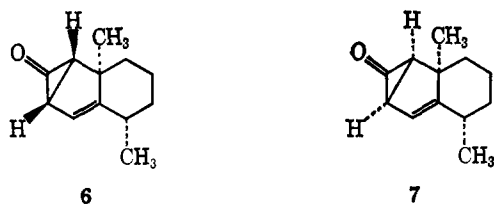
(4) O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, **90**, 2449 (1968).

(5) L. Barber, O. L. Chapman, and J. D. Lassila, *ibid.*, **90**, 5933 (1968).

(6) L. Barber, O. L. Chapman, and J. D. Lassila, *ibid.*, **91**, 531 (1969).

(7) Mass spectrum of the parent ion, $m/e\ 148$; $\nu_{\text{max}}^{\text{diene}}\ 1640, 1600$ (diene), $851, 796$ ($\text{RCH}=\text{CR}'\text{R}''$), 728 cm^{-1} (*cis* $\text{RCH}=\text{CHR}'$); $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}\ 256\text{ nm}$ ($\epsilon\ 3850$); nmr (CCl_4), three olefinic protons ($\delta\ 5.7\text{-}6.2$), allylic methine proton ($m, \delta\ 3.0$), six methylene protons ($m, \delta\ 2.2\text{-}0.8$), and two methyl groups ($s, \delta\ 1.15; d, \delta\ 1.18$).

in the thermal reaction. The photochemical (but not thermal) loss of carbon monoxide and the infrared absorption of the product suggested that the low-temperature photoproduct might be a cyclopropanone.⁸ In accordance with this suggestion, warming the photoproduct in the presence of furan gave an adduct (**4**, mp 131–132°). Structure **4** for the adduct follows from the element analysis, molecular weight, and spectroscopic data, including spin-spin decoupling.⁹ The structure of the adduct **4** defines the structure of the cyclopropanone as **5**. Formation of **5** from **1** can be viewed formally as a $2\pi + 2\sigma$ cycloaddition or a [1,3]-sigmatropic rearrangement.¹⁰ Such a rearrangement is symmetry allowed if it occurs in a suprafacial sense.¹⁰ Either process would lead to stereochemical structure **6** for the cyclopropanone. It is possible, however, that formation of the cyclopropanone involves photochemical electrocyclic opening of the common bond in the bicyclo[3.1.0]hexenone system, demotion, and thermal electrocyclic closure (**8** → **5**) to the cyclopropanone. In this process either of the two stereoisomeric cyclopropanones (**6** or **7**) might be formed. Alterna-



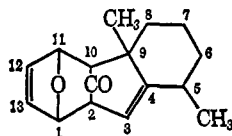
tively, cleavage of the bicyclo[3.1.0]hexenone system in a manner analogous to that observed in umbellulone and lumisantonin⁵ could lead to a ketene carbene which could in turn serve as a precursor of the cyclopropanone.

Concerted, or nearly concerted, loss of carbon monoxide from **5** must occur by a σ -symmetric process.^{11,12} This is reasonable for a photochemical but not for a thermal process.

The relationship between the low-temperature photoproduct (**5**) and the room-temperature photochemistry observed by Kropp² has not been defined. It is clear from the nature of the furan adduct, however, that the principal thermal reaction of the cyclopropanone

(8) The chemical and physical properties of cyclopropanones have been reviewed recently: N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).

(9) Mass spectrum of the parent ion, m/e 244; ν_{\max} 1729 cm^{-1} (C=O); nmr (CDCl₃), δ 6.30 (H₁₃, $J_{12,13} = 6.0$, $J_{1,13} = 1.5$ Hz), 6.20 (H₁₂, $J_{11,12} = 1.5$ Hz), 5.42 (H₃, $J_{2,3} = 6.0$ Hz), 5.00 (H₁₁, $J_{10,11} = 1.5$ Hz), 4.62 (H₁, $J_{1,2} \sim 2$ Hz), 2.75 (H₂, $J_{2,10} \sim 1.5$ Hz), 2.57 (m, allylic methine proton), 2.00 (H₁₀), 2.4–0.8 (m, six methylene protons), 1.23 (s, CH₃), 1.18 (d, CH₃).



All couplings were assigned on the basis of double-resonance experiments. The authors are indebted to Dr. R. W. King for these double-resonance experiments.

(10) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965).

(11) A σ -symmetric process is one in which a plane of symmetry is maintained throughout (D. Lemal and S. D. McGregor, *J. Amer. Chem. Soc.*, **88**, 1335 (1966)). In the present case, the term σ -symmetric is used in reference to the local symmetry about the cyclopropanone ring.

(12) The problem of thermal and photochemical loss of carbon monoxide from cyclopropanones has been discussed.¹⁰

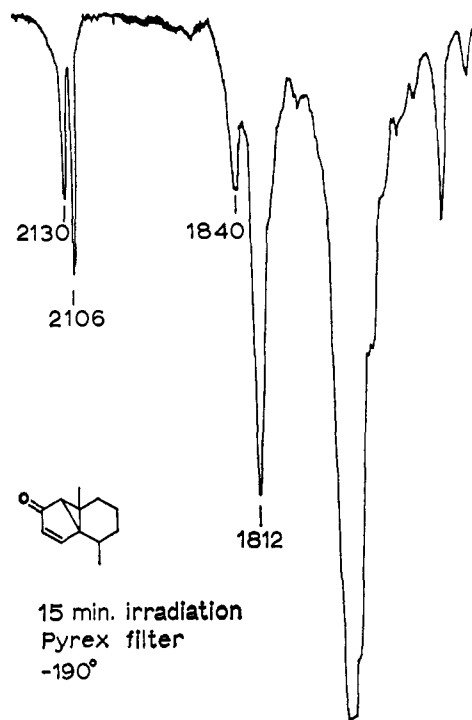
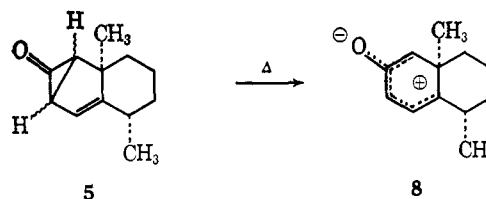


Figure 1. Infrared spectrum of a sample of **1** after 15-min irradiation as a neat film at -190° . The bands at 1812 and 1840 cm^{-1} are due to **5**. The 2130- cm^{-1} band is carbon monoxide, and the 2106- cm^{-1} band is due to a ketene derivative.

5 is the symmetry-allowed heterolysis of the carbon-carbon bond opposite the carbonyl group. The resultant zwitterion (**8** or its protonated form)¹³ would be an ideal precursor for the spirodienone en route to Kropp's phenolic product. Thermal closure of **8** to **1** is symmetry forbidden. Zwitterions analogous to **8**



have been invoked to account for photochemical formation of phenolic products from bicyclo[3.1.0]hex-3-en-2-ones.^{3,14,15}

The small amount of ketene formed in the low-temperature irradiation of **1** has not been identified. It is probably a diene ketene similar to those formed from umbellulone and lumisantonin.⁵

Acknowledgment. This research was supported by Grant GM-14305 from the National Institute of General Medical Sciences, U. S. Public Health Service.

(13) The photochemistry of bicyclo[3.1.0]hexenones is known to depend on the acidity of the medium.^{3,14} This dependence has been ascribed to the difference in chemical behavior of the zwitterion and the protonated zwitterion.¹⁴

(14) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966).

(15) O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963).

(16) National Aeronautics and Space Administration Trainee, 1965–1968; Petroleum Research Fund Fellow, 1968–1969.

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