Our data, on the other hand, indicate a preference for formation of an α-sulfinyl carbanion whose conformation is that expected from the theoretical calculations.[24]

Acknowledgment. This work was supported by the National Science Foundation [GP-9599, GP-29497 (BBJ), and GP-15791 (HLA)]. Computer time was obtained through the facilities of the Computer Science Center, University of Maryland.

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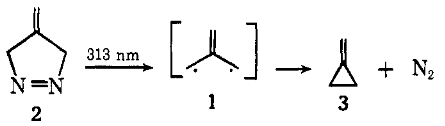
Received December 14, 1971

Trimethylenemethane. Direct and Benzene-Sensitized Vapor-Phase Photolysis of 4-Methylene-1-pyrazoline

Sir:

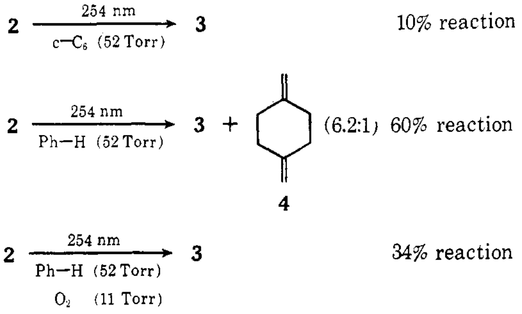
As a result of general[1] as well as personal[2] interest in trimethylenemethane (**1**), the vapor-phase photochemistry of 4-methylene-1-pyrazoline (**2**) has been investigated preparatory to flash photolytic experiments designed to detect the intriguing species.



Irradiation of **2** (λ_{max}^{vap} 327 nm)[3] in the vapor phase through Pyrex at room temperature gave methylenecyclopropane (**3**) as the only condensable product at 78°K. Assuming that photochemical reversion to allene and diazomethane followed by photolytic generation of methylene which could add to allene to give **3** does not occur,[4] **1** is a likely intermediate in the reaction. Incomplete photolysis (40% decomposition) of 3,3-dideuterio-**2** (63% *d* on C_8) gave **3** with an *exo*-methylene to ring hydrogen ratio of 0.5 ± 0.05, suggesting that symmetrization of the peripheral carbons in **1** occurred; furthermore, recovered **2** was unchanged.

The quantum yield for the direct photolysis was 0.37 ± 0.1 at room temperature with 1.52 Torr of **2**. The apparatus and technique have been described[5a] and diethyl ketone ($\Phi = 1.0$ at 125°) was the actinometer.[5b] Corrections were made for the relative absorption characteristics of **2** and the actinometer in relation to the emission of the source and Pyrex filter system. There was about 10% decrease in the relative quantum yield upon addition of 570 Torr of nitrogen and a slight increase when the pyrazoline pressure was lowered to 1.14 Torr. The addition of 72 Torr of piperylene had the same effect as nitrogen at that pressure.

Attempts were made to triplet sensitize the reaction of **2** with biacetyl ($E_T = 54.9$ kcal/mol) with no success, presumably because the triplet energy of *cis*-azo compounds is higher than 60 kcal/mol.[6] Because the spectrum of **2** has somewhat of a window at 254 nm (ϵ 80), it was possible to use benzene as a sensitizer. Thus, while direct photolysis of **2** (2.28 Torr) in the presence of 52 Torr of cyclohexane at 254 nm gave 10% reaction to **3**, replacement of the cyclohexane with benzene (52 Torr) gave 60% decomposition under the same conditions. Furthermore, not only was **3** formed but also 1,4-dimethylenecyclohexane (**4**) in a 6.2:1 ratio, respectively, as determined by nmr and mass spectrometry.[7] At lower pressures of **2** less **4** was formed (*e.g.*, at 0.42 Torr of **2** the **3**:**4** ratio was 14). Importantly, 254-nm irradiation of **2** (2.2 Torr) with benzene (52 Torr) and 11 Torr of oxygen under the same conditions resulted in only 34% decomposition giving only **3**.



These results suggest that (a) direct photolysis of 4-methylenepyrazoline (**2**) gives a singlet trimethylenemethane species, **1**, which closes to methylenecyclopropane (**3**); (b) benzene-sensitized photolysis of **2** is both triplet and singlet sensitized possibly leading to **4** and **3**, respectively; (c) oxygen quenches triplets of **2** or **1** before production of dimer; and (d) oxygen partly quenches benzene singlets.

Since most pyrazolines and cyclic azo compounds appear to decompose from their singlet states upon direct excitation, suggestion a is reasonable. However, unclear is whether **3** is formed *via* electronically excited states of **1** or a vibrationally excited ground state of **1** like the orthogonal biradical apparently involved in the thermal self-interconversions of **3**. It is of interest that direct photolysis of 3-methylenecyclobutanone in furan at 15° gave **3** with small amounts of **4**.[8] In addition, the amount of **4** produced increased with decreasing temperature, and, of course, at very low temperatures Dowd[9] elegantly demonstrated by esr that the triplet of **1** was produced. Thus, Dowd's solution experiments may indicate that intersystem crossing of singlet **1** to triplet **1** occurs competitively with a thermally activated process of closure of singlet **1** to **3**, which is consistent with the expectation of a 13-kcal/mol activation energy[2] for closure of the orthogonal singlet ground state of **1**. It should also be noted that Borden[10] has suggested on theoretical grounds that electronically excited **1** can close only to excited states of **3** although conversion of excited **1** to the ground state of **3** is not an unexpected process.[11]

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[1] (a) For a review, see F. Weiss, *Quart. Rev., Chem. Soc.*, **24**, 278 (1970); (b) see also M. J. S. Dewar and J. S. Wasson, *J. Amer. Chem. Soc.*, **93**, 3081 (1971).

[2] J. J. Gajewski, *ibid.*, **93**, 4450 (1971).

[3] (a) P. Dowd, *ibid.*, **88**, 2587 (1966); (b) R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2589 (1966).

[4] Photolysis in the presence of cyclopentene gave no bicyclo[3.1.0]-hexane, thus lending support to this assumption.

[5] (a) H. Webster III and E. J. Bair, *J. Chem. Phys.*, **53**, 4532 (1970); (b) K. O. Kutschke, M. H. J. Wijnen, and E. W. R. Steacie, *J. Amer. Chem. Soc.*, **74**, 714 (1952).

[6] P. S. Engel, *ibid.*, **89**, 5031 (1967).

[7] All products were stable to the photoconditions, and all reactions proceeded quantitatively.

[8] P. Dowd, G. Sengupta, and K. Sachdev, *J. Amer. Chem. Soc.*, **92**, 5726 (1970).

[9] P. Dowd, A. Gold, and K. Sachdev, *ibid.*, **90**, 2715 (1968).

[10] W. T. Borden, *Tetrahedron Lett.*, 259 (1967).

[11] G. S. Hammond, *Advan. Photochem.*, **7**, 373 (1969).

The benzene-sensitized photolysis of **2** proceeds six times more efficiently than direct photolysis at 254 nm, but the major product appears to be derived by a singlet pathway. In fact, under our conditions excited singlet benzene should collide with **2** with $k = 2.6 \times 10^7$/sec and the known rate of decay of benzene singlets is 1.2×10^7/sec,[12] so there is opportunity for singlet sensitization of **2**, especially considering the high collision cross sections for such sensitization when the fluorescence spectrum of the sensitizer overlaps the absorption spectrum of the acceptor.[13] Of importance in this connection is the fact that intersystem crossing of singlet benzene ($k_{\text{isc}} = 1.1 \times 10^7$ sec)[12] is about half as fast as collisions of singlet excited benzene with **2** under conditions of our experiment, so the fact that a mixture of **3** and **4** is produced with more of the former in these reactions is not unreasonable if **4** is formed from triplet **1** or triplet **2**. The suggestion that **4** is a triplet-derived product is a conclusion reached by Skell in attempting to explain the presence of **4** (and *p*-xylene) and the absence of **3** in the reaction of 2-iodomethylallyl iodide with potassium vapor.[14] Similarly, Berson found only dimeric products upon attempted generation of 5-isopropylidenebicyclo[2.1.0]pentane[15] and these products exhibited strong nmr emission signals when initially produced, consistent with their formation *via* at least one triplet species according to Closs.[16] It is unclear why Andrews and Day did not obtain dimeric products in the triplet ketone sensitized photolyses of 4-chloromethylene-3,3,5,5-tetramethyl-1-pyrazoline although steric effects may be important.[17]

The oxygen-quenched, sensitized photolyses of **2** suggest that both singlet and triplet reactions are being quenched. Oxygen quenches singlet benzene with $k = 1.2 \times 10^{11}$ l./(mol sec)[18] so under our conditions each benzene singlet is quenched with $k = 8 \times 10^7$/sec. Since oxygen apparently quenched only 28% of the reaction (34% of **3** *vs.* 48% of **3**), singlet energy transfer from benzene to pyrazoline would have to be approximately ten times faster than collisions, a possibility in light of ref 13. However, oxygen quenching of benzene singlets appears to give benzene triplets[18] which should be quenched by oxygen with a frequency of 7×10^6/sec under our conditions.[18] Under these conditions benzene triplets can collide with **2** with $k = 2.6 \times 10^7$/sec giving triplet **2** which could give triplet **1**. Apparently oxygen also quenches these species before they can give dimeric material, **4**, and, quenching of triplet **1** could give **3** directly in which case the suggestion that singlet sensitization is faster than collision rates and that the 34% of **3** in the oxygen-quenched sensitized photolyses comes from singlet sensitization may not be valid.

We put forward these mechanistic hypotheses recognizing that more complicated alternatives exist and that important questions remain unanswered. Do the states of **1** produced here resemble the singlet and triplet ground states of **1**? What are the geometries of these species? Wherein lies the inefficiency of the direct photolyses of **2**, and how are the dimeric products formed? These are being investigated with effort being focused on direct spectroscopic observation of the trimethylenemethane species.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund (2754-AC1; 4), the National Science Foundation (GP 27621), and the Alfred P. Sloan Foundation for partial support of this work.

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[12] Teh-hsuan Chen and E. W. Schlag in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969.

[13] Th. Förster in "Modern Quantum Chemistry," Part III, O. Sinanoglu, Ed., Academic Press, New York, N. Y., 1965.

[14] P. S. Skell and R. G. Doerr, *J. Amer. Chem. Soc.*, **89**, 3062, 4688 (1967).

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[16] G. L. Closs, *ibid.*, **93**, 1546 (1971).

[17] S. D. Andrews and A. C. Day, *J. Chem. Soc. B*, 1271 (1968).

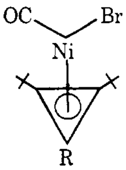
[18] A. Morikawa and R. J. Cvetanovic, *J. Chem. Phys.*, **52**, 3237 (1970).

Trialkylcyclopropenium Metal Compounds[1]

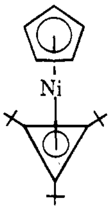
Sir:

Several triphenylcyclopropenium compounds with transition metals have been prepared[2–5] since the initial report by Gowling and Kettle[6] of a substance formulated as $[h^3\text{-}C_3(C_6H_5)_3Ni(CO)Br]_2$ (**1**). Trihapto-alkyl-substituted cyclopropenium compounds of transition metals have not as yet been observed; the only reported reaction involving a trialkylcyclopropenium compound results in carbonyl ring insertion to produce h^3-trimethylcyclobutenone–cobalt tricarbonyl from $C_3(CH_3)_3^+$ and $Co(CO)_4^-$.[7]

The chemical properties of the cyclopropenium group acting as a trihapto ligand are not as yet clear, because the phenyl derivatives prepared thus far have generally low solubility. It is of particular interest to compare the cyclopropenium and allyl groups, which are closely related electronically. We report here syntheses of the first alkylcyclopropenium metal compounds and several observations which clarify the nature of the cyclopropenium–metal bonding.



2, R = $t\text{-}C_4H_9$
3, R = CH_3



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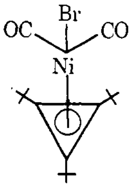

5

Addition of excess nickel carbonyl to a methanolic solution of tri-*tert*-butylcyclopropenium fluoroborate[8] and sodium bromide under nitrogen and recrystallization of the product from toluene yields crystals of **2** [*Anal.* Calcd for $NiC_{16}H_{27}OBr$: Ni, 15.70; C, 51.38; H, 7.28; Br, 21.36; mol wt, 373. Found: Ni, 16.00; C, 50.66; H, 7.41; Br, 21.69; mol wt, 332, 337

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[1] This research was supported by the National Science Foundation through Grant NSF 6396X.

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[5] R. M. Tuggle and D. L. Weaver, *ibid.*, **10**, 2599 (1971).

[6] E. W. Gowling and S. F. A. Kettle, *ibid.*, **3**, 604 (1964).

[7] R. B. King and A. Efraty, *J. Organometal. Chem.*, **24**, 241 (1970).

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