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Supplementary Material Available: Crystal data (Table Is), atom coordinates (Tables IIs and IIIs), anisotropic temperature factors (Tables IVs and Vs), and observed and calculated structure factors (Tables VIs and VIIs) (27 pages). Ordering information is given on any current masthead page.

Formaldehyde *O*-Methylide, $[CH_2{=}O^+{-}C^-H_2]$: The Parent Carbonyl Ylide[1]

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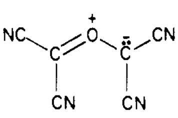
Carbonyl ylides are elusive compared to their sulfur-containing analogues. However, there exists ample evidence for their intermediacy in photochemical ring opening of oxiranes.[2] For example, tetracyanoethylene oxide reacts with a variety of dienophiles such as olefins, acetylenes, and even benzene through the intermediacy of the carbonyl ylide **1** (1,3-dipolar addition).[3]



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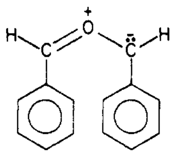

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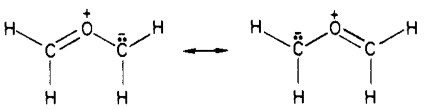


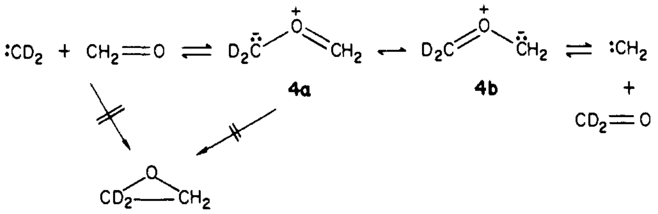
3a **3b**

Stilbene oxides have been photochemically isomerized to the carbonyl ylide **2** at −196 °C.[4] The stereochemistry of ring opening of oxirane to carbonyl ylides has also received considerable attention.[2]

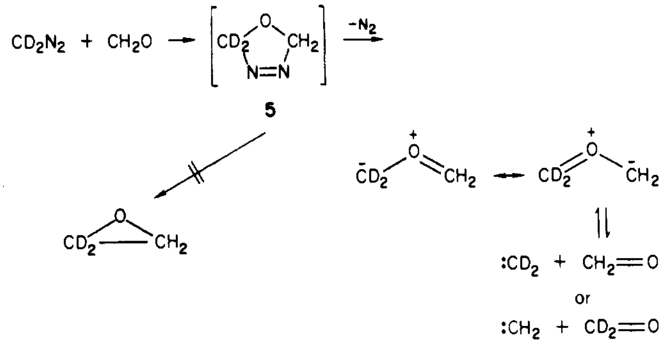
The parent of all carbonyl ylides is formaldehyde *O*-methylide **3**. Although **3** is well-known to theoretical chemists,[5,6] there exists so far no experimental evidence for it.

We would like to report now the intermediacy of the hitherto unknown formaldehyde *O*-methylide (**3**) in the reaction of diazomethane with monomeric formaldehyde in dimethyl ether solution[7a] at −78 °C. To a yellow solution of dideuteriodiazomethane (≈0.24 g, 5 mmol)[7] in 2 mL of dimethyl ether maintained at −78 °C in a dry-ice cooled quartz UV cell under a nitrogen atmosphere is added a precooled solution (−78 °C) of monomeric formaldehyde[8] (0.015 g, 0.5 mmol) in 0.5 mL of dimethyl ether. The resulting yellow solution was irradiated with a Sylvania 275-W sunlamp. The yellow color of the solution gradually disappeared (1–2 min) indicating the photochemical dissociation of diazomethane. After 10 min of irradiation, the dimethyl ether solution already containing precipitated paraformaldehyde[9] was slowly evaporated under a gentle stream of nitrogen gas. The resulting white precipitate was analyzed by mass spectrometry. The mass spectrometric analysis[10] of the product showed 10–12% of dideuterioformaldehyde (observation of peaks at *m/e* 32, M^+ ion, *m/e* 30, $M^+ - 2$ ion) along with formaldehyde and fragmentation peaks of polymethylene. The formation of dideuterioformaldehyde is an indication of the intermediacy of the formaldehyde *O*-methylide **4** in the reaction and its general ambivalent character (Scheme I, **4a** ↔ **4b**).[11] However, one could also account for the observation of dideuterioformaldehyde in the mass spectrometer by the fragmentation of dideuterioethylene oxide formed either by the direct reaction of dideuterio singlet methylene with monomeric formaldehyde or by the irreversible cyclization of the formaldehyde *O*-methylide. The latter two possibilities were clearly ruled out since no parent ion peak at *m/e* 46 for dideuterioethylene oxide was observed.[12] Moreover, ethylene oxide does not photochemically decompose to formaldehyde and methylene (especially under the reaction conditions).

Scheme I



Scheme II



We also considered a direct thermal 1,3-dipolar addition of dideuteriodiazomethane with monomeric formaldehyde (Scheme II) resulting in oxadiazoline **5** which upon nitrogen loss would provide **4**. To test this possibility dideuteriodiazomethane (5 mmol) in 2 mL of dimethyl ether at −78 °C in a cooled glass cell under nitrogen atmosphere was treated with monomeric form-

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(4) (a) For a review, see: Griffin, W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 537. (b) DoMinh, T.; Trozzolo, A. M.; Griffin, W. *J. Am. Chem. Soc.* **1970**, *92*, 1402. (c) Lev, I. J.; Ishikawa, K.; Bhacca, N. S.; Griffin, W. *J. Org. Chem.* **1976**, *41*, 2654.

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(7) (a) Reaction of singlet methylene with dimethyl ether at −78 °C is rather sluggish. Even if there is a slow insertion the product analysis of the formaldehyde reaction is not hampered by it. Also the singlet methylene may be stabilized by solvation by dimethyl ether solvent. (b) Gaseous dideuteriodiazomethane was prepared by treating freshly prepared *N*-(nitrosomethyl)urea with 80% sodium deuteroxide in D_2O solution in a diazomethane-generation apparatus and was predried with NaOD pellets under a slow stream of nitrogen before transferring into cooled dimethyl ether; see: Hecht, S. M.; Kozarich, J. W. *Tetrahedron Lett.* **1972**, 1501.

(8) Paraformaldehyde was obtained from Fisher Scientific Co. and was thoroughly dried before cracking (in an oil bath at +160 °C) into monomeric formaldehyde. Solutions of monomeric formaldehyde in dimethyl ether at −78 °C are indefinitely stable.

(9) The reaction of dideuteriodiazomethane with monomeric formaldehyde in dimethyl ether under both photochemical and thermal conditions produces quite a bit of insoluble paraformaldehyde. Hence in the reaction we seem to get less exchange (≤12%) since most of the monomeric formaldehyde is already polymerized.

(10) Mass spectrum was obtained on a Hewlett-Packard 5985A GC/MS system. The analysis was performed by comparing the mass spectrum of predried prepolymerized sample of monomeric formaldehyde.

(11) We also attempted to observe the formaldehyde *O*-methylide by carrying out the photochemical reaction in a NMR tube with subsequent ^{13}C NMR analysis at low temperature. However, we could not find any spectroscopic evidence for the ylide in accordance with its expected short life time.

(12) Mass spectrum of ethylene oxide shows the molecular ion as the base peak (most abundant peak).

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aldehyde (0.5 mmol) in 0.5 mL of dimethyl ether in total darkness. After 4 h of reaction, the ether solvent was evaporated and the analysis of the resulting white precipitate showed ~6% dideuterioformaldehyde. Again no evidence was obtained for the formation of dideuterioethylene oxide.

These results show that formaldehyde *O*-methylide **4** is formed by the reaction of dideuteriodiazomethane with monomeric formaldehyde under both photochemical and thermal conditions (latter involving oxadiazoline **5**[2]).

The symmetrical nature of formaldehyde *O*-methylide has been probed theoretically by Borden and co-workers.[6] Results of ab initio MCSCF and CI calculations indicate that the formaldehyde *O*-methylide shows strong preference for equal C–O bond lengths, indicating an allyl type resonance interaction (**3a** ↔ **3b**). Our experimental work seems to support the theoretical prediction.

In conclusion we have shown that formaldehyde *O*-methylide is indeed an intermediate in the reaction of diazomethane with monomeric formaldehyde under both photochemical and thermal conditions.

Acknowledgment. Support of our work by National Science Foundation is gratefully acknowledged.

Cubane-Type $Mo_3FeS_4^{4+}$ Aqua Ion and X-ray Structure of $[Mo_3FeS_4(NH_3)_9(H_2O)]Cl_4$

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We have recently reported on the preparation and properties of $Mo_3S_4^{4+}$ aqua ion (I).[1] A sequence of incomplete cubane-type aqua ions of $Mo_3O_4^{4+}$,[2] $Mo_3O_3S^{4+}$,[3] $Mo_3O_2S_2^{4+}$,[4] and $Mo_3OS_3^{4+}$,[5] are known;[6] the second to fourth aqua ions have μ_3-S and the presence of the isomeric forms having μ_3-O has also been reported.[7] Actually, four types of triangular molybdenum(IV) complexes have been reported.[8] However, as far as aqua ions are concerned, only the incomplete cubane-type is known so far.

We describe here the reaction of the aqua ion I with metallic iron as follows:

$$Mo_3S_4^{4+} + Fe \rightarrow Mo_3FeS_4^{4+}$$

This is the first example of a reaction in which the missing corner of the incomplete cubane-type core is filled with another metal.

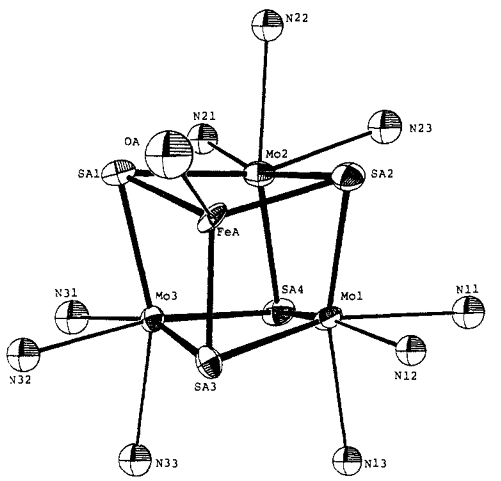

Figure 1. Perspective view of $[Mo_3FeS_4(NH_3)_9(H_2O)]^{4+}$ cation. Bond distances (Å): Mo1–Mo2, 2.766 (8); Mo1–Mo3, 2.783 (3); Mo2–Mo3, 2.830 (8); Mo1–FeA, 2.684 (13); Mo2–FeA, 2.675 (15); Mo3–FeA, 2.691 (13); Mo1–SA2, 2.34 (1); Mo1–SA3, 2.38 (3); Mo1–SA4, 2.30 (3); Mo2–SA1, 2.33 (1); Mo2–SA2, 2.39 (1); Mo2–SA4, 2.36 (3); Mo3–SA1, 2.37 (1); Mo3–SA3, 2.35 (3); Mo3–SA4, 2.42 (3); FeA–SA1, 2.26 (2); FeA–SA2, 2.25 (2); FeA–SA3, 2.25 (3); Mo–N (av), 2.29 (5); FeA–OA, 2.04 (4).

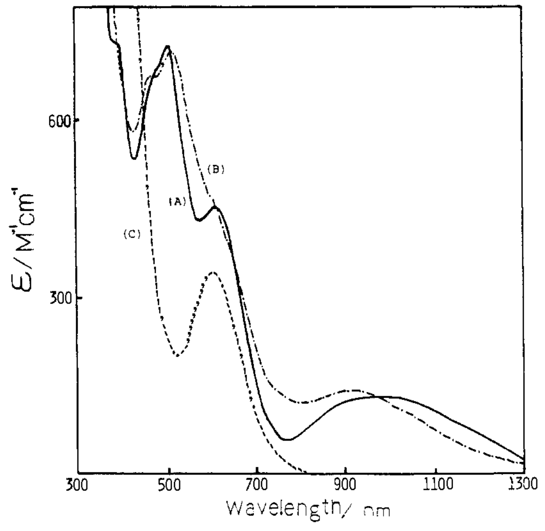

Figure 2. Electronic spectra. (A) $Mo_3FeS_4^{4+}$ in 2 M HPTS; (B) $[Mo_3FeS_4(NH_3)_9(H_2O)]^{4+}$ in concentrated aqueous ammonia (In order to avoid the strong light absorption of ammonia, dilute aqueous ammonia solution (1 M) was used in 800–1300-nm region, although the spectrum is gradually changeable.); (C) $Mo_3S_4^{4+}$ in 2 M HPTS.

There are many clusters with a core like, but none the same as, Mo_3FeS_4; cubane-type clusters of Mo_4S_4,[9] $Mo_2Fe_2S_4$,[10] $MoFe_3$-

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(6) Strictly speaking, the term aqua ion cannot be used for ions containing sulfur atom(s). The term aqua ion, however, will be used here for species in which bridging sulfur atom(s) exist and other ligands are only water.

(7) Personal communication from: Sykes, A. G. *J. Chem. Soc., Chem. Commun.*, submitted for publication.

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