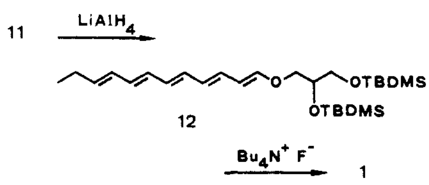
a low-temperature (−20 °C) chromatography on florisil (petroleum ether–ethyl acetate 9:1 and 2:1).

Containing the hydroxy and the tetrahydropyranyloxy function destined to serve as leaving groups properly positioned, **11** was converted by lithium aluminum hydride (5 molar equiv, room temperature, 2.5 h, argon atmosphere[11]) in dry tetrahydrofuran to the pale yellow liquid [(2,3-bis[(*tert*-butyldimethylsilyl)oxy]propyl)oxy]dodeca-1,3,5,7,9-pentaene (**12**) in quantitative crude yield.[12]

As chromatography of the sensitive crude reaction product (**11** → **12**) was fairly inefficient, even at low temperature, it was conveniently used without purification in the final reaction step. With a technique previously employed[4,8] the protecting groups of **12** were removed by tetrabutylammonium fluoride (2.2 molar equiv, room temperature, 1.5 h, argon atmosphere[11]) in tetrahydrofuran–ether. From the resulting crude reaction product the hardly soluble,[13] analytically and isomerically pure *all-trans*-3-(dodeca-1,3,5,7,9-pentaenyloxy)propane-1,2-diol (**1**) crystallized from hot butyl acetate as a pale yellow solid in 47% yield (based on **11**) and thus was easily separated from minor amounts of better soluble isomers and impurities.



With exclusion of air crystalline **1** was found to be stable at room temperature over a months period.[14] The following physical data of **1** are typical: mp 194–196 °C (sealed tube, argon atmosphere);[15] R_f 0.33 (ethyl acetate);[16] Mass spectrum, m/z 250 (M^+); UV (methylene chloride) λ_{max} 323 (ϵ 48 000), 338 (ϵ 74 000), 357 (ϵ 67 000) nm; IR (KBr) 3417, 3012, 2965, 2934, 2879, 1643, 1186, 1115, 1049, 1002 cm^{-1}; 500-MHz ^{1}H NMR (dimethyl sulfoxide-d_6) δ 6.77 (d, J = 12.5 Hz, 1 H, =CHO), 6.05–6.26 (m, 7 H, =CH), 5.73 (dt, $J_{10,11}$ = 7, $J_{9,10}$ = 15 Hz, 1 H, =C*H*CH$_2$CH$_3$), 5.63 (dd, $J_{1,2}$ = 12.5, $J_{2,3}$ = 11 Hz, 1 H, C*H*=CHO), 4.91 (d, J = 5 Hz, 1 H, CHO*H*), 4.65 (t, J = 5.5 Hz, 1 H, CH$_2$O*H*), 3.78–3.84 (m, 1 H, *H*CHOC), 3.62–3.69 (m, 2 H, HC*H*OC, C*H*OH),[17] 3.30–3.40 (m, 2 H, C*H*$_2$OH), 2.08 (dq, $J_{11,12}$ = 7.5, $J_{10,11}$ = 7 Hz, 2 H, C*H*$_2$CH$_3$), 0.96 (t, J = 7.5 Hz, 3 H, CH$_3$).

Acknowledgment. We take pleasure in acknowledging the generous support received from the German Research Society and the Funds of the Chemical Industry. Especially we would like to thank Professor Johann Sonnenbichler (Max Planck Institute of Biochemistry, Munich) for recording and discussion of the 500-MHz ^{1}H NMR spectrum.

Note Added in Proof. In the Ames bacterial assay **1** was found to be a very potent direct mutagen.[18]

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[11] All transformations with polyene derivatives were carried out with strict exclusion of air. Before workup a trace of the radical inhibitor 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide was added to the reaction solution.

[12] A purity of approximately 75% was determined by ^{1}H NMR spectroscopy. In agreement with earlier investigations of the stereochemistry of the Whiting reaction (Demoule, E.; Enggist, P. *Helv. Chim. Acta* **1974**, *57*, 2087–2091), the remaining material is believed to contain the Δ3 and Δ5 cis isomers of **12**. This assignment is supported by additional doublets (J = 12 Hz) near the major doublet at 6.51 ppm in the NMR spectrum in CDCl$_3$ of the crude reaction product (**11** → **12**).

[13] *all-trans*-Polyenes are known to be much less soluble than their cis isomers: Bohlmann, F.; Mannhardt, H. *Chem. Ber.* **1956**, *89*, 1307–1315.

[14] Upon contact with air crystalline **1** deteriorates completely within 30 min at room temperature.

[15] Interestingly **1** retains its UV spectrum after melting and resolidification!

[16] Merck silica gel plate 60 F 254.

[17] The complexity of the glyceryl CH and CH$_2$ resonance signals suggests a hindered rotation of this part of the molecule.

[18] Göggelmann, W.; Maier, F. K.; Pfaendler, H. R. *Mutation Res.*, in press.

Molecular Hydrogen Complexes of the Transition Metals. 2. Evidence for a New Complex, $Mo(CO)(dppe)_2(H_2)$, and for Solution Equilibrium between Dihydrogen and Dihydride Forms, $M\text{-}\eta^2\text{-}H_2 \rightleftarrows H\text{-}M\text{-}H$, in $W(CO)_3(PR_3)_2(H_2)$

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Coordination of molecular hydrogen to transition metals is now firmly established, initially in the stable, structurally characterized complexes $M(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$[1] (M = Mo, W; R = Cy, *i*-Pr), then in low-temperature stable $Cr(CO)_5(H_2)$,[2] and recently in $[IrH(H_2)(PPh_3)_2(C_{13}H_8N)]SbF_6$,[3] $[IrH_2(H_2)_2L_2]^+$,[3] and $[FeH(H_2)(dppe)_2]BF_4$.[4] In order to better define the steric and electronic requirements for H$_2$ to bind in molecular fashion rather than being cleaved to hydride ligands, we report a new stable H$_2$ complex, $Mo(CO)(dppe)_2(H_2)$ (dppe = diphenylphosphinoethane) (**1**). Also, NMR evidence is presented for a dynamic equilibrium between the H$_2$ complex $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(\eta^2\text{-}H_2)$, and an apparent *dihydride* complex, $WH_2(CO)_3(P\text{-}i\text{-}Pr_3)_2$, derived by oxidative addition of the H$_2$ ligand.

The formally 16-electron complex, $Mo(CO)(dppe)_2$, contains a weak, agostic interaction of a phenyl hydrogen with the metal and adds a sixth ligand such as N$_2$.[5] These features are similar to those of $M(CO)_3(PR_3)_2$,[6] the precursors to the first H$_2$ complexes, and suggest that $Mo(CO)(dppe)_2$ is likely to bind H$_2$ also. Addition of H$_2$ (1 atm) to deep brown $Mo(CO)(dppe)_2$ in benzene or toluene gives an orange solution from which well-formed solvated orange prisms of **1** slowly crystallize.[7] Solutions of **1** reversibly lose H$_2$ in a manner similar to $M(CO)_3(PR_3)_2(H_2)$. **1** crystallized in two forms depending on solvent, and both have been examined by single-crystal X-ray methods.[8] Both structures show normal octahedral geometry for the complex with CO trans to the presumed η^2-H$_2$ ligand (Figure 1); i.e., the agostic hydrogen interaction present in the structure of $Mo(CO)(dppe)_2$ is no longer evident. The shortest distance between Mo and phenyl hydrogen (calculated on the basis of idealized hydrogen positions) in **1** is 3.4 Å compared to 2.98 Å for the parent Mo species. In both forms, the CO ligand is disordered across a crystallographic 2-fold axis and obscures the presumed H$_2$ ligand. Although the H$_2$ atom positions were not located, ^{1}H NMR (toluene-d_8, 25 °C, 300

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[1] Part I of this series: Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.

[2] (a) Sweany, R. *J. Am. Chem. Soc.* **1985**, *107*, 2374. (b) Upmacis, R. K.; Gadd, G. E.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; Whyman, R.; Simpson, A. F. *J. Chem. Soc., Chem. Commun.* **1985**, 27. (c) Church, S. P.; Grevels, F.-W.; Hermann, H.; Shaffner, K. *Ibid.* **1985**, 30.

[3] Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 794, 1661.

[4] Morris, R. H.; Sawyer, J. F.; Shiralion, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581.

[5] (a) Sato, M.; Tatsumi, T.; Kodama, T.; Hidai, M.; Uchida, T.; Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 4447. (b) Tatsumi, T.; Tominaga, H.; Hidai, M.; Uchida, Y. *J. Organomet. Chem.* **1980**, *199*, 63. (c) For other examples of agostic interactions, see: Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

[6] (a) Kubas, G. J. *J. Chem. Soc., Chem. Commun.* **1980**, *61*. (b) Part 3 of this series: Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.*, in press.

[7] ν(CO) 1815 cm^{-1} (Nujol) for **1**·3C$_6$H$_6$. We find ν(CO) for $Mo(CO)(dppe)_2$ at 1723 cm^{-1} rather than at 1807 cm^{-1} as previously reported.[5a]

[8] (a) X-ray data for **1**·3C$_6$H$_6$: Space group: $P22_12_1$; cell constants: a = 12.114 (8) Å, b = 14.214 (5) Å, c = 17.491 (6) Å determined from 25 high-order reflections; Z = 4, D_x = 1.28 g/cm^3; crystal size 0.25 × 0.25 × 0.30 mm. Refinement included anisotropic temperature factors on all atoms heavier than hydrogen and converged to an unweighted R value of 0.070. No attempt was made to locate hydrogen atoms. Further details of data collection and the structural determination are presented as supplementary data. (b) X-ray data (−125 °C) for **1**·2C$_7$H$_8$: space group $P2/c(Pc)$; cell constants, a = 12.125 (6) Å, b = 12.154 (8) Å, c = 19.133 (7) Å, β = 96.30 (3)°. *Xtl* size, 0.08 × 0.28 × 0.36 mm, Z = 2, D_x = 1.31 g/cm^3. Least squares refinements including anisotropic thermal parameters for all atoms heavier than carbon converged to an unweighted R value of 0.075.

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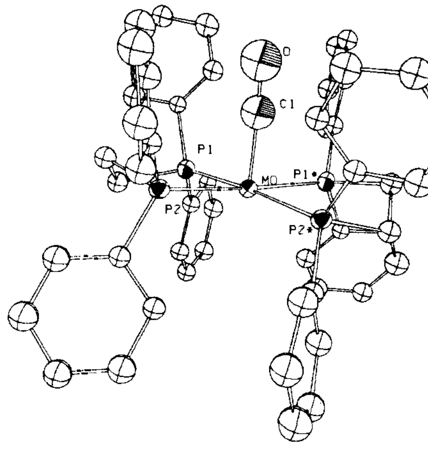

Figure 1. Molecular structure (−125 °C) of $1{\cdot}2C_7H_8$. Principal bond distances (Å): Mo–C1, 1.98 (2); Mo–P1, 2.421 (3); Mo–P2, 2.435 (2); C1–O, 1.20 (2). Selected bond angles (deg): C1–Mo–P1, 95.4 (5); C1–Mo–P1*, 88.3 (5); C1–Mo–P2, 87.7 (5); C1–Mo–P2*, 88.8 (5); P1–Mo–P2, 80.8 (1); P1–Mo–P1*, 95.7 (1); P2–Mo–P2*, 102.9 (1). The distances and angles for $1{\cdot}3C_6H_6$ do not differ significantly.

MHz) of **1** is diagnostic of molecular H_2 coordination.[1] **1** gives a very broad signal (width at half-height = 300 Hz; ^{31}P coupling not observed) near −5 ppm, while the HD isotopomer shows a 1:1:1 triplet with $J(HD)$ = 34 Hz (cf. 33 Hz for $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(\eta^2\text{-}H_2)$[1]). IR spectra of **1** do not exhibit the bands characteristic of coordinated H_2 found for $W(CO)_3(PCy_3)_2(H_2)$,[1] but these were also weak or unobserved for $Mo(CO)_3(PCy_3)_2(H_2)$ and for the recently reported Ir complex.[3]

In regard to the chemistry of the H_2 complexes, $W(CO)_3(PR_3)_2(H_2)$ is unreactive toward ethylene hydrogenation under mild conditions but exchange takes place with D_2 to give a statistical mixture of HD, H_2, and D_2. The exchange does not involve the phosphine ligands and occurs even in the *solid* complexes (8 days, 25 °C, 1 atm of D_2) precluding ligand dissociation from the exchange mechanism. Thus, the H–H bond is susceptible to cleavage, and indeed ^1H NMR and IR indicate that solutions of $W(CO)_3(PR_3)_2(H_2)$ *contain an equilibrium fraction (15–30%) of a hydride*, presumably 7-coordinate $WH_2(CO)_3(PR_3)_2$, formed by oxidative addition of the H_2. For R = *i*-Pr, for example, IR spectra of all isotopomers in hexane show a second set of weaker ν(CO) bands at 1993, 1913, 1867, and 1828 cm^{-1} similar to those reported for 7-coordinate $MoCl_2(CO)_3(PEt_3)_2$,[9] in addition to the H_2 complex bands at 1969 and 1856 cm^{-1}. Solution spectra of $M(CO)_3(PCy_3)_2(H_2)$ (M = Mo, W) also show extra carbonyl bands but some are obscured. Nujol mull spectra of the solid complexes do not show the second set of frequencies, clearly indicating that an equilibrium species and not an impurity is present. Also, the intensity ratio of the two sets of ν(CO) remains approximately the same upon partial decomposition of the sample. ^1H NMR of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ at 25 °C displays, in addition to the broad main signal at −4.48 ppm due to $\eta^2\text{-}H_2$, a 1:2:1 triplet ($J(PH)$ = 37.9 Hz) at −3.68 ppm consistent with a dihydride form (Figure 2). Most importantly, the spectrum of the HD isotopomer displays an identical 1:2:1 triplet (HD coupling is not observed since it would be expected to be small in hydride–deuteride complexes) while the main signal due to η^2-HD *is* split into a 1:1:1 triplet [$J(HD)$ = 33.6 Hz] as expected. This rules out formulation of the minor component as an isomeric H_2-containing species. The hydride and H_2 signals coalesce near 50 °C (at 200 MHz[10]) (Figure 2), and for the HD isotopomer, the large H–D coupling breaks down near 50 °C and only a single broad signal near −4.3 ppm remains. The broadening, disappearance, and reappearance[11] of the triplet hydride signal as two new peaks at −2.40 and −4.93 ppm below 25 °C (Figure 2) and ^{31}P NMR data[12] indicate that $WH_2(CO)_3(P\text{-}i\text{-}Pr_3)_2$ is stereochemically nonrigid, as is common for 7-coordinate complexes.[13] The above findings suggest that solutions of some of the known polyhydride complexes may contain equilibrium amounts of corresponding H_2 complexes. No spectral evidence for a hydride form was found for **1**; thus $W(CO)_3(PR_3)_2(H_2)$ represents a situation wherein the bonding of H_2 is at a near balance point between nondissociative and dissociative (oxidative addition).

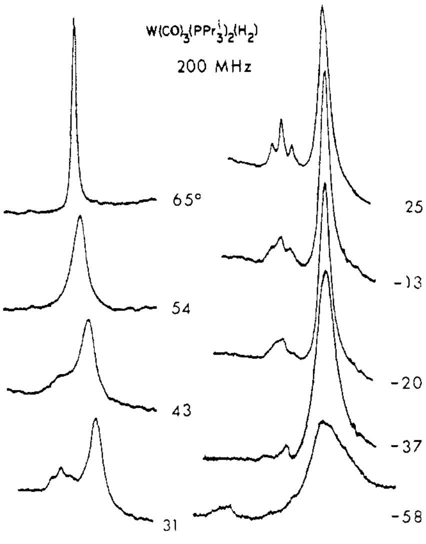

Figure 2. Variable-temperature ^1H NMR (200 MHz, methylcyclohexane-d_{14}) of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$. The broad signal near −2.4 ppm in the −58 °C spectrum is due to one of the now inequivalent hydride ligands in $WH_2(CO)_3(P\text{-}i\text{-}Pr_3)_2$ (see ref 11).

Hoffman[14] and Hay[15] suggest a conventional σ-donor π-acceptor model for H_2 binding. Within the constraints of their calculations, it appears that new H_2 complexes should be searched on TM fragments that present particularly favorable L → M σ-donation plus M → L π-donation capabilities. Complexes displaying agostic C–H interactions are obvious candidates. Note, however, that the known stable complexes are pseudo-6-coordinate d^6 complexes with bulky ligands. The latter feature may provide steric constraints that inhibit dihydride formation. It is interesting that **1** and the other group 6 H_2 complexes all exhibit a strongly π-bonding CO trans to H_2 whereas none of the structurally characterized group 6 polyhydrides,[16] e.g., $MoH_2(PMe_3)_5$,[16a] contain CO. Crabtree's complex[3] and Morris's complex[4] also have a high trans effect ligand trans to H_2. As more H_2 complexes are discovered, the steric and electronic factors which lead to H_2 coordination arrested along the reaction coordinate to dihydride formation will be delineated.

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(9) (a) Westland, A. D.; Muriithi, N. *Inorg. Chem.* **1973**, *12*, 2356. (b) Drew, M. G. B.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1977**, 194.

(10) The coalescence temperature is field-dependent and is near 35 °C at 90 MHz.

(11) The spectrum at −71 °C shows two new broad singlets, one of which is a shoulder on the main, broad H_2 signal at −4.5 ppm. Thus the hydrides apparently are inequivalent at low temperature.

(12) $^{31}P\{^1H\}$ (200 MHz) spectra at 20 °C showed a signal due to the hydride at δ 35.6 (s), ~15% of the intensity of the main signal at δ 33.6 (s). Near −50 °C, the minor signal became a doublet of doublets (δ 39.66, 39.15, 30.90, 30.42), indicative of *inequivalent phosphorus environments*. A fluctional structure would explain the apparent equivalence at room temperature.

(13) Van-Catledge, F. A.; Ittel, S. D.; Jesson, J. P. *Organometallics* **1985** *4*, 18 and references therein.

(14) Saillard, J.; Hoffman, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

(15) Hay, P. J. *Chem. Phys. Lett.* **1984**, *103*, 466.

(16) (a) Hursthouse, M. B.; Lyons, D.; Thornton-Pett, M.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1983**, *476*. (b) Meakin, P.; Guggenberger, L. J.; Peet, W. G.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 1467. (c) Lobkovskii, E. B.; Makhaev, V. D.; Borisov, A. P.; Semenko, K. N. *Zh. Strukt. Khim.* **1979**, *20*, 944. (d) Gregson, D.; Howard, J. A. K.; Nicholls, J. N.; Spencer, J. L.; Turner, D. G. *J. Chem. Soc., Chem. Commun.* **1980**, *572*. (e) Rhodes, L. F.; Zubkowski, J. D.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1982**, *21*, 4185.

Sciences, Office of Basic Energy Sciences.

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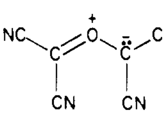
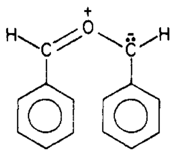
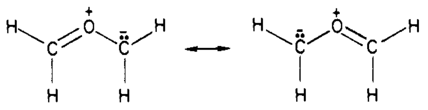
Carbonyl ylides are elusive compared to their sulfur-containing analogues. However, there exists ample evidence for their intermediacy in photochemical ring opening of oxiranes.[2] For example, tetracyanoethylene oxide reacts with a variety of dienophiles such as olefins, acetylenes, and even benzene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



1



2



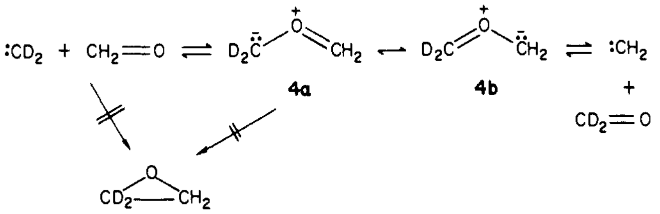
3a **3b**

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]

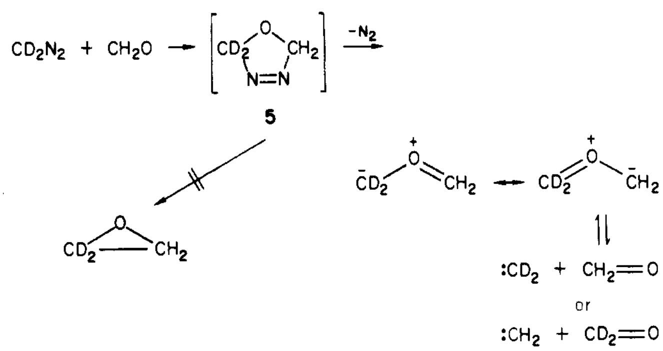
The parent of all carbonyl ylides is formaldehyde *O*-methylide **3**. Although **3** is well-known to theoretical chemists,[5,6] there exists so far no experimental evidence for it.

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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[1] Onium Ylide Chemistry. 5. For part 4, see: Olah, G. A.; Doggweiler, H.; Felberg, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 4975.

[2] Huisgen, R. In "1,3-Dipolar Cycloaddition Chemistry"; Padwa, A., Ed.; Wiley Interscience: New York, 1984; Vol. 1, pp 23.

[3] (a) Linn, W. J.; Benson, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 3657. (b) Linn, W. J. *J. Am. Chem. Soc.* **1965**, *87*, 3665.

[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.

[5] Voltatron, F.; Anh, N. T.; Jean, Y. *J. Am. Chem. Soc.* **1983**, *105*, 2359.

[6] Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1984**, *106*, 2513.

[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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