Table I. Radioactivity and ^{3}H/^{14}C Ratio in Malloprenols Biosynthesized from (4*R*)-[2-^{14}C,4-^{3}H]MVA and (4*S*)-[2-^{14}C,4-^{3}H]MVA

		obsd				calcd atom ratio	
MVA (^{3}H/^{14}C ratio)	compd[a]	^{3}H, dpm	^{14}C, dpm	^{3}H/^{14}C ratio	atom ratio[b] ^{3}H:^{14}C	A[c] ^{3}H:^{14}C	B[d] ^{3}H:^{14}C
(4*R*)-[2-^{14}C,4-^{3}H]MVA (4.22)	MPL-9	1045	246	4.25	(9.1 ± 0.2):9	4:9	9:9
	MPL-10	2602	600	4.34	(10.3 ± 0.2):10	4:10	10:10
	MPL-11	5666	1343	4.22	(11.0 ± 0.1):11	4:11	11:11
(4*R*)-[2-^{14}C,4-^{3}H]MVA (13.2)	MPL-10	3797	291	13.1	(9.9 ± 0.2):10	4:10	10:10
	MPL-11	4745	359	13.2	(11.0 ± 0.2):11	4:11	11:11
(4*S*)-[2-^{14}C,4-^{3}H]MVA (5.4)	MPL-9	135	4717	0.03	(0.05 ± 0.02):9	5:9	0:9
	MPL-10	88	548	0.16	(0.30 ± 0.02):10	6:10	0:10
	MPL-11	43	1167	0.37	(0.07 ± 0.01):11	7:11	0:11
(4*S*)-[2-^{14}C,4-^{3}H]MVA (13.2)	MPL-9	658	1133	0.58	(0.40 ± 0.06):9	5:9	0:9
	MPL-10	981	3909	0.25	(0.19 ± 0.02):10	6:10	0:10
	MPL-11	922	4703	0.20	(0.17 ± 0.01):11	7:11	0:11

[a] MPL denotes malloprenol. [b] Normalized ratio. The deviations were calculated from the standard deviation in the radioactivity of each sample. [c] Calculated from the expectation that the (*E*)- and the (*Z*)-isoprene residues are formed by loss of the *pro*-4*S* and *pro*-4*R* hydrogens of MVA, respectively, following the usual isoprenoid pathway. [d] Calculated from the expectation that the (*E*)-isoprene residue results from the usual loss of the *pro*-4*S* hydrogen of MVA, whereas the (*Z*)-isoprene unit results from the unusual loss of the *pro*-4*S* hydrogen.

The elimination of the *pro*-4*S* hydrogen might result from an alternative process, which involves the initial addition of an (*E*)-isoprene residue followed by the redox *E*–*Z* isomerization via the corresponding aldehyde, as previously demonstrated for the biosynthesis of the sesquiterpenoids in fungi.[9] However, all the tritiums originating from [2-^{14}C,5-^{3}H$_2$]MVA were retained in the malloprenols biosynthesized from this double-labeled MVA (Table II).[10] This fact rules out distinctly the participation of the redox *E*–*Z* isomerization in the successive extension of (*Z*)-isoprene units.

The loss of the 4*S* tritium may be due to compartmentalization[11] such that the (*E*)-isoprene residues are assembled in a part of the plant to which is readily accessible external MVA, followed by the addition of (*Z*)-isoprene residues in an area of the plant that external MVA cannot efficiently penetrate. In order to solve this problem, malloprenol-10 (**2**) was biosynthesized from [2-^{14}C,5-^{3}H$_2$]MVA, and the ^{3}H/^{14}C ratio in the aldehyde derived from the malloprenol was examined. The tritium in the malloprenol-10 (**2**) decreased to nineteen-twentieths in the aldehyde (Table II).[10] This decrease in tritium indicates that one-tenth of the total tritium is located on C-1 of malloprenol-10 (**2**). In addition, the uniform distribution of the radioactivity in each of the isoprene units was examined by determining the labeling pattern in the malloprenols biosynthesized from (4*S*)-[2-^{14}C,4-^{3}H]MVA. The radioactive malloprenol was degraded to ^{14}C-labeled acetone and levulinic acid by KMnO$_4$–NaIO$_4$ oxidation. The molar ratios of the acetone to the levulinic acid were in good agreement with the ratios calculated from the expectation that the (*E*)- and (*Z*)-isoprene units are equivalently formed from external MVA (Table III).[10] These examinations demonstrate that compartmentalization does not affect the incorporation of label in the biosynthesis of the malloprenols in the plant. The stereochemistry of formation of the (*Z*)-isoprene unit of the malloprenol thus differs from that observed for the biosynthesis of other isoprenoids.[3-5]

Quite recently, we also observed elimination of the *pro*-4*S* hydrogen atom of MVA in the formation of the (*Z*)-isoprene residues of polyprenols in *Aleurites cordata* (Euphorbiaceae), *Alnus serrulatoides* (Betulaceae), and *Cleome spinosa* (Capparidaceae).[12] It is suggested therefore that elimination of the *pro*-4*S* hydrogen of MVA might be the usual mode in the formation of the (*Z*)-isoprene chain of polyprenols by successive addition of IPP to GGPP in higher plants.

Acknowledgments. We are indebted to Messrs. M. Sakakibara, S. Tominaga, and Y. Yoshioka for a help in part of the experiments. The present work was supported in part by Grant-in-Aids for Scientific Research No. 247027 and 347024, Special Project Research No. 56209019, and Co-operative Research No. 57340031 from the Ministry of Education, Science and Culture and also by the scholarships from the Saneyoshi Scholarship Foundation in 1978, the Kudo Science Foundation in 1978, and the Itoh Science Foundation in 1979.

Supplementary Material Available: Tables of radioactivity, ^{3}H/^{14}C ratios, and degradation product ratios (2 pages). Ordering information is given on any current masthead page.

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[9] (a) Imai, K.; Marumo, S. *Tetrahedron Lett.* **1974**, 4401-4404. (b) Evans, R.; Holton, A. M.; Hanson, J. R. *J. Chem. Soc., Chem. Commun.* **1973**, 465. (c) Overton, K. H.; Roberts, F. M. *J. Chem. Soc., Chem. Commun.* **1974**, 385-386.

[10] This table is relegated to the supplementary material.

[11] Goodwin, T. W. In "Biosynthetic Pathways in Higher Plants"; Prindham, J. B., Swain, T., Eds.; Academic Press: London, 1965; p 57.

[12] Unpublished data. Occurrence of the elimination of *pro*-4*S* hydrogen atom during the formation of the (*Z*)-isoprene chains was also demonstrated for the polyprenols of *A. cordata*, *A. serrulatoides*, and *C. spinosa*. With respect to *C. spinosa*, Suga et al.[13] had reported the elimination of the *pro*-4*R* hydrogen atom of MVA. However, it has recently been found that the previous result was incorrect. Corrections are made elsewhere in the near future.

[13] Suga, T.; Shishibori, T. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2098-2104.

Synthesis and Structure of $Na_4[Mo_8O_{24}(OCH_3)_4]\cdot 8MeOH$: A Novel Isopolymolybdate That Decomposes with the Loss of Formaldehyde

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Recent work in our laboratory has focused on the oxidation of methanol to formaldehyde over a variety of molybdate catalysts[1] with special emphasis on MoO$_3$. Of the physical methods employed to study this reaction, FTIR has been particularly useful in identifying the probable intermediate in this reaction as a surface methoxy group.[2] Efforts have been made to model this system with molecular or ionic species that could be studied by X-ray, single-crystal diffraction techniques. On the basis of the rich and varied chelation chemistry of the oxomolybdenum "core structures"[3,4] and encouraged by the recent crystallographic work on both isopolymolybdates[5,6] and heteropolymolybdates[7] with

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[1] Machiels, C. J.; Sleight, A. W. In "Proceedings of the Climax 4th International Conference on the Chemistry & Uses of Molybdenum"; Barry, H. F., Mitchell, P. C. H., Eds.; Climax Molybdenum Co.: Ann Arbor, MI, 1982.

[2] Groff, R. P. *J. Catal.*, in press.

[3] Knobler, C.; Penfold, B. R.; Robinson, W. T.; Wilkins C. J.; Yong, S. H. *J. Chem. Soc., Dalton Trans.* **1980**, 248-252.

[4] McCarron, E. M., III; Harlow R. L. *J. Chem. Soc. Chem. Commun.* **1983**, 90-91.

[5] Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Liu, R.-S. *J. Am. Chem. Soc.* **1979**, *101*, 491-492.

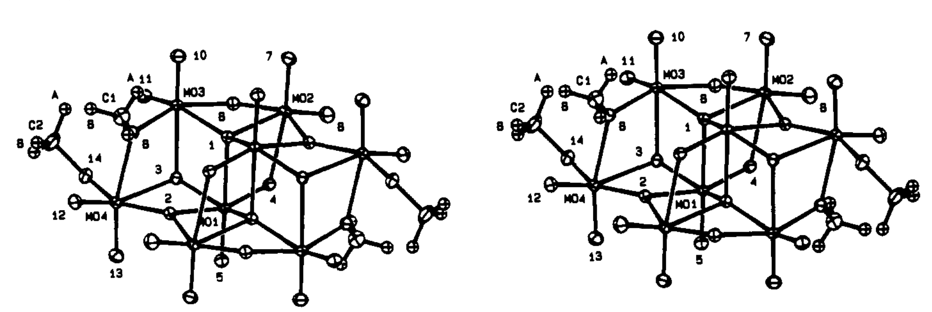


Figure 1. $Mo_8O_{24}(OCH_3)_4^{-4}$ anion.

Table I. Selected Bond Distances (Å) with Estimated Standard Deviations

Mo(1)-O(1)	2.373 (2)	Mo(3)-O(11)	1.711 (2)
Mo(1)-O(1)′	1.938 (2)	Mo(4)-O(2)	2.029 (2)
Mo(1)-O(2)	2.178 (2)	Mo(4)-O(3)	2.241 (2)
Mo(1)-O(3)	1.918 (2)	Mo(4)-O(9)	2.261 (2)
Mo(1)-O(4)	1.759 (2)	Mo(4)-O(12)	1.709 (2)
Mo(1)-O(5)	1.701 (2)	Mo(4)-O(13)	1.713 (2)
Mo(2)-O(1)	2.280 (2)	Mo(4)-O(14)	1.907 (2)
Mo(2)-O(2)′	1.950 (2)		
Mo(2)-O(4)	2.362 (2)	O(9)-C(1)	1.438 (4)
Mo(2)-O(6)	1.929 (2)	O(14)-C(2)	1.440 (4)
Mo(2)-O(7)	1.721 (2)	C(1)-H(1)A	0.91 (5)
Mo(2)-O(8)	1.695 (2)	C(1)-H(1)B	0.96 (6)
Mo(3)-O(1)	2.251 (2)	C(1)-H(1)C	0.91 (6)
Mo(3)-O(3)	2.260 (2)	C(2)-H(2)A	1.06 (4)
Mo(3)-O(6)	1.946 (2)	C(2)-H(2)B	0.93 (6)
Mo(3)-O(9)	1.993 (2)	C(2)-H(2)C	1.01 (7)
Mo(3)-O(10)	1.710 (2)		

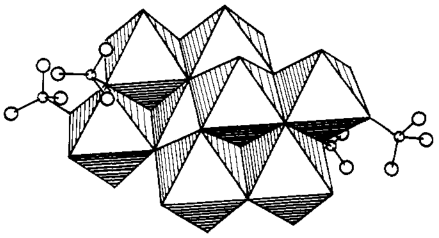
Table II. Selected Bond Angles (Deg) with Estimated Standard Deviations

Mo(3)-O(9)-Mo(4)	111.6 (1)	O(9)-C(1)-H(1)A	111 (3)
Mo(3)-O(9)-C(1)	124.9 (2)	O(9)-C(1)-H(1)B	113 (4)
Mo(4)-O(9)-C(1)	120.9 (2)	O(9)-C(1)-H(1)C	118 (4)
Mo(4)-O(14)-Na(1)	108.9 (1)	O(14)-C(2)-H(2)A	114 (2)
Mo(4)-O(14)-C(2)	126.6 (1)	O(14)-C(2)-H(2)B	112 (4)
Na(1)-O(14)-C(2)	113.3 (2)	O(14)-C(2)-H(2)C	97 (4)

Table III. Short C-H--O Contacts

atoms	O--H, Å	C-H--O, deg	H--O-Mo, deg
C(1)-H(1)A--O(10)	2.49 (5)	116 (4)	90 (1)
C(2)-H(2)A--O(11)	2.48 (4)	120 (3)	109 (1)
C(2)-H(2)A--O(8)″	2.47 (4)	123 (3)	126 (1)

organic substitutents, we have begun to study a wide variety of alkylated isopolymolybdates. We now wish to report our first success, a tetramethylated octomolybdate anion $[Mo_8O_{24}(OCH_3)_4]^{-4}$. This anion is noteworthy not only because it contains methoxy groups which, as noted above, are probable intermediates in the conversion of methanol to formaldehyde but also because it liberates the desired product, i.e., formaldehyde, when heated or exposed to sunlight.



$Na_4[Mo_8O_{24}(OCH_3)_4]\cdot 8CH_3OH$ was prepared by refluxing $MoO_3\cdot 2H_2O$[8] with excess absolute CH_3OH over a 4-Å molecular sieve (Davidson Chemical). The major reaction product, $Mo_2O_5(OCH_3)_2$,[9] a white solid, was separated by filtration. With slow evaporation, the filtrate produced large (1 mm) colorless crystals. The instability of these crystals when removed from the mother liquor precluded conventional CHO analysis. A partial confirmation of the structural formula was provided by thermal analysis.[10]

Irradiation of a sample of $Na_4[Mo_8O_{24}(OCH_3)_4]\cdot 8CH_3OH$ with UV light caused the material to decompose into a blue, amorphous solid. Mass spectrometry performed on gas samples revealed the presence of formaldehyde as a decomposition product. An analogous thermal decomposition at 500 °C gave H_2O in addition to formaldehyde. An X-ray powder diffraction study of the blue residue from the thermal experiment showed the material to be a mixture of Na_2MoO_4, Mo_4O_{11}, and MoO_2, confirming the redox process.

The crystal structure[11] consists of $Mo_8O_{24}(OCH_3)_4^{-4}$ anions and two crystallographically independent $Na_2(CH_3OH)_4^{+2}$ cations, all of which are located at centers of symmetry. Figure 1 shows the anion and the location of the four methoxy groups, two of which bridge neighboring Mo atoms and two of which are nominally in terminal sites (oxygen atoms O(14) and O(14)′ are also bonded to neighboring sodium atoms Na(1) and Na(1)′, respectively). Tables I and II give bond distances and angles respectively. The framework of the anion is very similar to those found for a number of substituted octamolybdates.[6,12-14] The stereochemical positions of the two terminal methoxy groups are identical with those of the two MoO_4^{-2} groups in $Mo_{10}O_{34}^{-8}$ but different from those found for the protons in $H_2Mo_8O_{28}^{-6}$ and the

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(6) Adams, R. D.; Klemperer, W. G.; Liu, R.-S. *J. Chem. Soc., Chem. Commun.* **1979**, 256–257.

(7) Knoth, W. H.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4265.

(8) Prepared as described in: "Handbook of Preparative Inorganic Chemistry"; Vol. 2, Brauer, G., Ed.; Academic Press: New York, 1965; Vol. 2, pp 1412–1413.

(9) McCarron, E. M., III; Staley, R. H.; Sleight, A. W. *Inorg. Chem.* in press.

(10) Thermogravimetric analysis was performed on a Du Pont 951/990 system under flowing argon at a heating rate of 5 °C/min. $Na_4[Mo_8O_{24}(OCH_3)_4]\cdot 8MeOH$ lost 24.5% of its weight upon heating to 500 °C [calculated for $Na_4[Mo_8O_{24}(OCH_3)_4]\cdot 8MeOH \rightarrow Na_4Mo_8O_{22} + 8MeOH\uparrow + 4CH_2O\uparrow + 2H_2O\uparrow$, 25.4%]. The blue solid residue was subsequently heated in oxygen, with a resultant weight gain of 5.3% [calculated for $Na_4Mo_8O_{22} + 2O_2 \rightarrow Na_4Mo_8O_{26}$, 5.3%], the final products being sodium molybdate and molybdenum trioxide.

(11) Crystal structure information: monoclinic, space group $P2_1/c$; at −100 °C, $a = 11.213$ (2) Å, $b = 11.693$ (2) Å, c : 17.622 (3) Å, $\beta = 94.49$ (2)°, $V = 2303$ Å^3, $Z = 2$. Syntex P3 diffractometer, graphite monochromator, Mo Kα radiation, $\lambda = 0.71069$ Å, ω scans of 1.0°, $4 < 2\theta < 55°$, 5288 reflections. An empirical absorption correction based on ψ-scan data was applied; transmission factors ranged from 0.83 to 1.00. The structure was solved by direct methods and was refined by full-matrix, least-squares techniques: 4275 reflections with $I > 3\sigma(I)$, 359 variables (Mo, Na, O, and C with anisotropic thermal parameters; H with isotropic parameters), $R = 0.021$ $R_w = 0.030$. The hydrogen atoms of the methoxide groups [H(1)A–C, H(2)A–C] refined reasonably well; some of the hydrogen atoms of the methanol groups [in particular, those H atoms bonded to C(3), C(4), and C(6)] refined poorly with C–H distances as long as 1.27 Å. The largest peak in the final difference Fourier, 0.60 e Å^{-3}, was located near C(4) and clearly indicated that the hydrogen atoms of that methyl group are partially disordered. The mathematical and computational details can be found in the following reference: Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030–2032.

(12) Böschen, I. V.; Buss, B.; Krebs, B. *Acta Crystallogr., Sect. B* **1974**, *B30*, 48–56.

(13) Isobe, M.; Marumo, F.; Yamase, T.; Ikawa, T. *Acta Crystallogr., Sect. B* **1978**, *B34*, 2728–2731.

(14) Fuchs, J.; Hartl, H.; Hunnius, W.-D.; Mahjour, S. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644.

formyl moieties in $[(HCO)_2(Mo_8O_{28})]^{-6}$. The stereochemical positions of the bridging methoxy groups appear to be unique.

The rate-limiting step in the conversion of methanol to formaldehyde over MoO_3 is the breaking of a C–H bond.[1] Presumably, one of the methoxy protons is transferred to a neighboring oxygen atom on the MoO_3 surface. As a model for the methoxy–MoO_3 intermediate in this reaction, the conformations of the methoxy groups in the $Mo_8O_2(OCH_3)_4^{-4}$ anion of the present structure were thus of particular interest; the formation of short C–H--O contacts[15] would obviously indicate possible paths for proton transfers. There are, in fact, three contacts with H--O distances that are less than 2.5 Å.[16] Interestingly, the methoxy groups adopt conformations that allow *one* hydrogen atom of each group to form a short C–H--O intramolecular contact. One intermolecular contact is also found. All three have terminal oxygen atoms (i.e., Mo=O) as receptors. Table III gives the geometrical details of these contacts.

Registry No. $Na_4[Mo_8O_{24}(OCH_3)_4]\cdot 8CH_3OH$, 86747-45-7; $Na_4[Mo_8O_{24}(OCH_3)_4]$, 86727-42-6; $Mo_2O_5(OCH_3)_2$, 86727-41-5; Na_2MoO_4, 7631-95-0; Mo_4O_{11}, 12033-38-4; MoO_2, 18868-43-4; $Na_4Mo_8O_{26}$, 57455-64-8; MoO_3, 1313-27-5; formaldehyde, 50-00-0; methanol, 67-56-1.

Supplementary Material Available: A listing of positional and thermal parameters, anisotropic thermal parameters, bond distances, and bond angles, figures of the Na(1) and Na(2) environments, and a table of structure amplitudes (45 pages). Ordering information is given on any current masthead page.

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(15) Taylor, R.; Kennard. O. *J. Am. Chem. Soc.* **1982**, *104*, 5063-5070.

(16) Typical of (and inherent in) the X-ray diffraction method, the hydrogen atom positions suffer from systematic errors which lead to C-H bond lengths that are considerably shorter than the true internuclear distances. The calculated H--O distances are consequently somewhat longer than their true values.

Detection by ^{13}C CPMAS NMR of Molecules Photochemically Generated in Organic Glasses at Low Temperature

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Received January 20, 1983

Detection and characterization of matrix-isolated molecules by UV, IR, and EPR spectroscopy has become a powerful method for the study of reactive species.[1] Although it is the most diagnostic spectroscopic tool for structural analysis, NMR has never been used to detect molecules photochemically generated in the solid state. The reason for this has been lack of sensitivity and resolution in the NMR spectra of solids, but the cross polarization–magic angle spinning (CPMAS) experiment has led to significant improvement in both sensitivity and resolution.[2] Therefore, we have explored the potential of low-temperature CPMAS NMR spectroscopy for studies of photolytically generated species and report here on the development of a technique that permits the detection by NMR of molecules photochemically generated in organic glasses.

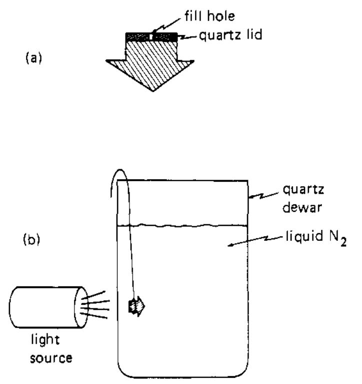


Figure 1. (a) MAS rotor fitted with a quartz lid and fill hole; (b) apparatus for photolyzing precursor in an organic glass in the rotor shown in Figure 1a.

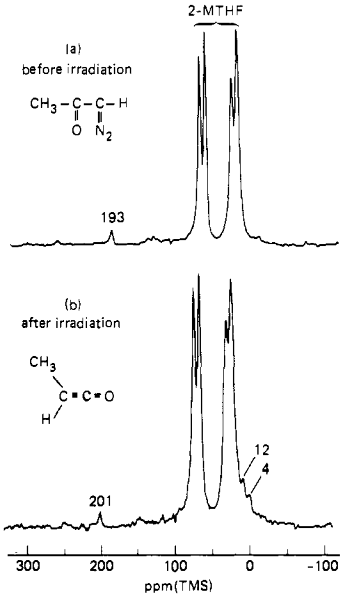
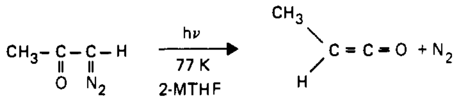


Figure 2. (a) Proton-decoupled ^{13}C CPMAS spectrum at 80 K of the 1-diazo-2-propanone (**1**) in 2-MTHF before photolysis; (b) proton-decoupled ^{13}C CPMAS spectrum of the material in the rotor after photolyzing for 24 h at 77 K, showing conversion to methyl ketene (**2**).

To illustrate the method, we have chosen a particularly simple photochemical reaction, the conversion of 1-diazo-2-propanone (**1**) to methyl ketene (**2**).[3]



$$CH_3-\underset{\overset{\|}{O}}{C}-\underset{\overset{\|}{N_2}}{C}-H \xrightarrow[\text{77 K, 2-MTHF}]{h\nu} (CH_3)(H)C=C=O + N_2$$

1 **2**

A 10 mol % solution of **1** in 2-methyltetrahydrofuran (2-MTHF) was loaded into a rotor fitted with a quartz lid, shown in Figure 1a. The solution was quenched slowly in liquid nitrogen and transferred into the MAS apparatus at temperatures well below the "softening" temperature of the glass (about 100 K for pure 2-MTHF).[4] The proton-decoupled ^{13}C CPMAS spectrum of this sample obtained at 80 K is shown in Figure 2a. The four intense high-field peaks are from the carbons of the solvent, while the single downfield peak at 193 ppm is due to the carbonyl carbon of the diazo ketone precursor (**1**).[5] The resonance of the methyl

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(1) B. Meyer, "Low Temperature Spectroscopy"; Elsevier: New York, 1971.

(2) Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 201.

(3) Meier, H.; Zeller, K. P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32.

(4) Ling, A. C.; Willard, J. E. *J. Phys. Chem.* **1968**, *72*, 1918. Despite the high concentration of precursor, the solid solution was clear before photolysis, but fracturing did occur during the course of irradiation.