Bull. Chem. Soc. Jpn., 59, 1195—1199 (1986)

Photochemical Hydroxymethylation of Alicyclic and Aliphatic Alkenes Induced by a Eu^{III}/Eu^{II} Photoredox System in Methanol

Akito Ishida,* Shinya Yamashita, Susumu Toki, and Setsuo Takamuku
The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567
(Received November 1, 1985)

The photoirradiation of a methanol solution of $EuCl_3$ and alkenes such as cyclohexene, cyclooctene, cyclododecene, and tetramethylethylene afforded (hydroxymethyl) alkane. The dihydro dimer of alkene, hydrogen, and ethylene glycol are also formed. Reactions proceed via a radical mechanism induced by hydrogen atoms and hydroxymethyl radicals, which are produced by a photoredox reaction of Eu^{III}/Eu^{II} in methanol.

Transition-metal organometallic chemistry has become important, principally due to the usefulness of members of this class of compounds for catalyzing or assisting in the transformation of organic substrates. However, photochemistry related to this field seems to be restricted to classical coordination compounds in aqueous solutions.[1] In recent years much attention has been paid to the decomposition of water into hydrogen and oxygen using metal catalysts from the viewpoint of the utilization of solar energy.[2] A few photochemical studies have been conducted on the metal compounds or metal complexes which can lead to catalytically and synthetically useful transformations of organic compounds.[3,4] The photochemistry of lanthanoids such as cerium, europium, or samarium has almost been restricted to spectroscopic investigations in aqueous systems,[5] there are a few applications regarding organic syntheses.

We have investigated the photoredox reactions of a Eu^{III}/Eu^{II} system in alcohols in the presence of some organic substrates in order to apply such a redox system of metal ions to organic photochemical reactions. Recently, we reported the formation of a dihydro dimer and a 2:1 styrene–methanol adduct via a radical mechanism when styrene and its derivatives are used as the substrate.[6] On the other hand, when uracil and its derivatives are used, a regioselective hydroxymethylation took place via an electron-transfer mechanism.[7] Here, we report on a photoreaction of europium chloride in the presence of alicyclic or aliphatic alkenes in methanol as a series which shows the scope and limitations for this reaction.

Results and Discussion

Photoreaction of $EuCl_3$ in Methanol. $EuCl_3$ does not absorb light of a longer wavelength than 250 nm in an aqueous solution, but has an absorption band around 280 nm in methanol. This might be due to a solvent-to-metal charge transfer. Upon irradiation of a methanol solution of $EuCl_3$ with a high-pressure mercury lamp through a Pyrex filter, a new absorption band appeared at 320 nm and was assigned to Eu^{II} on the basis of spectroscopic data.[6] Figure 1 shows the absorption spectra before and after irradiation. Hydrogen gas and ethylene glycol were formed monotonously with the irradiation time. The yield of ethylene glycol was less than that of hydrogen (Fig. 2). The formation of formaldehyde was also detected upon the addition of 2,4-dinitrophenylhydrazine to the reaction mixture. After irradiation for 10 h, the yields of these products (based on the $EuCl_3$ used) reached 2000 and 1500%, respectively. This indicates that $EuCl_3$ operated catalytically. Taking the reaction mechanism in an aqueous solution into consideration,[5d] the following reaction scheme is suggested for the present system.

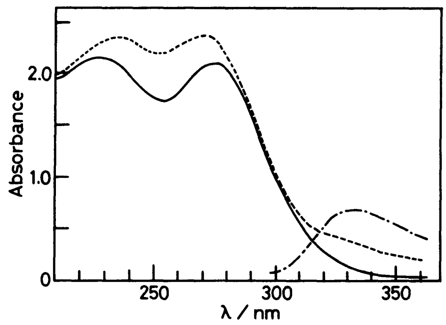


Fig. 1. Absorption spectra of a methanol solution of $EuCl_3$ before and after irradiation. $EuCl_3$ $6H_2O$ 5 mmol dm^{-3} in methanol.
——: Before, -----: atfer 8 h irradiation. —·—·—: differential spectrum enlarged by a factor of 3.

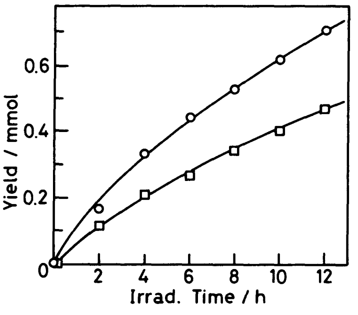


Fig. 2. Yields of hydrogen (—O—) and ethylene glycol (—□—) vs. time plot for the photoreaction of 5 mmol dm^{-3} solution of $EuCl_3$ 5 mL of methanol.

$$Eu^{3+} - CH_3OH \xrightarrow{h\nu} Eu^{2+} + CH_3O\cdot + H^+ \quad (1)$$

$$Eu^{2+} \xrightarrow{h\nu} Eu^{2+*} \quad (2)$$

$$Eu^{2+*} + H^+ \longrightarrow Eu^{3+} + H \quad (3)$$

$$CH_3O\cdot + CH_3OH \longrightarrow CH_3OH + \cdot CH_2OH \quad (4)$$

$$H + CH_3OH \longrightarrow H_2 + \cdot CH_2OH \quad (5)$$

$$2\cdot CH_2OH \longrightarrow HO(CH_2)_2OH \quad (6)$$

$$Eu^{3+} + \cdot CH_2OH \longrightarrow Eu^{2+} + HCHO + H^+ \quad (7)$$

The methoxyl radical formed in Reaction 1 is very reactive because of the large O–H bond-dissociation energy of methanol (435 kJ mol^{-1} [8]) and promptly abstracts H atoms from methanol to give hydroxymethyl radicals (Reaction 4). In the Eu^{III}/Eu^{II} photoredox systems, therefore, it is clear that H atoms and hydroxymethyl radicals are effectively formed. Hydrogen atoms and hydroxymethyl radicals formed by the reactions (Reactions 1—6) should afford equimolecular amounts of hydrogen and ethylene glycol. The hydroxymethyl radical, however, probably reacts with the Eu^{III} ion and decomposes into protons and formaldehyde.

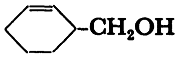
Photoreaction of EuCl$_3$ in the Presence of Alkene in Methanol. The present photoredox system of Eu^{III}/Eu^{II} in methanol was applied to the reaction of alkene. A methanol solution of alkene (**1a**—**d**: 100 mmol dm^{-3}) and EuCl$_3$ (5 mmol dm^{-3}) was irradiated under an argon atmosphere at λ>300 nm. The methanol adduct of **1** (**2**) and the dihydro dimer of **1** (**3**) were obtained as the main products along with a large amount of hydrogen gas and ethylene glycol. In the absence of EuCl$_3$, the alkene was recovered unchanged from methanol after irradiation for 8 h.

$$\underset{\mathbf{1}}{R^1R^2C=CR^1R^2} \xrightarrow[EuCl_3,\ CH_3OH,\ 8h]{h\nu,\ \lambda>300\ nm}$$

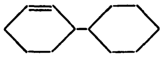
$$\underset{\mathbf{2}}{R^1R^2CHCR^1R^2CH_2OH} + \underset{\mathbf{3}}{(R^1R^2CHCR^1R^2\text{-})_2}$$

a : $R^1 = H$ $R^2\text{-}R^2 = \text{-}(CH_2)_4\text{-}$
b : $R^1 = H$ $R^2\text{-}R^2 = \text{-}(CH_2)_6\text{-}$
c : $R^1 = H$ $R^2\text{-}R^2 = \text{-}(CH_2)_{10}\text{-}$
d : $R^1 = R^2 = CH_3$

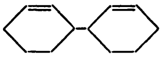
The results are shown in Table 1. **4a**, **5a**, and **6a** from cyclohexene (**1a**) were obtained as minor products. In the case of tetramethylethylene (**1d**), **7d** was formed as one of the main products.



4a



5a



6a

$(CH_3)_2CHCH(CH_3)_2$

7d

The formation of these main products (**2** and **3**) can be reasonably explained as the results of the efficient trapping of primarily formed radicals from methanol (H and $\cdot CH_2OH$) by the added alkene (Reactions 8—10).

Table 1. The Photoreaction of Eu^{III} and Alkene in Methanol[a]

Alkene	Concn/ mmol dm^{-3}	Conv/%	Product yield/%[b] 2	3	H$_2$	(CH$_2$OH)$_2$
1a[c]	100	71	49	22	197	40
1a[d]	500	49	3	7	12	0
1b	100	78	52	25	128	23
1b	500	50	8	31	12	—[g]
1c	100	64	42	36	250	—
1c	300	43	7	61	55	—
1d[e]	100	81	37	4	44	—
1d[f]	500	50	13	7	3	—

a) EuCl$_3$ 6H$_2$O 5 mmol dm^{-3}, methanol 5 mL, 8 h irrad. b) The yields are based on **1** consumed. c) Yields of minor products **4a**: 1, **5a**: 16, **6a**: 2%. d) **4a**: 2, **5a**: 15, **6a**: 15%. e) **7d**: 26%. f) **7d**: 25%. g) Not determined.

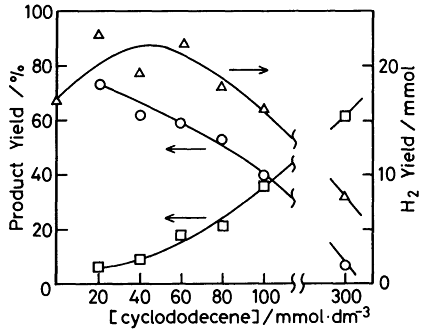


Fig. 3. Dependence of yields of hydrogen (—△—), **2c** (—○—), **3c** (—□—) on the concentration of cyclododecence for the photoreaction of EuCl$_3$ 6H$_2$O (5 mmol dm^{-3}) in methanol (5 mL) for 8 h.

$$H + \mathbf{1} \longrightarrow \cdot RH \quad (8)$$

$$\cdot CH_2OH + \mathbf{1} \longrightarrow \cdot R\text{-}CH_2OH \quad (9)$$

$$2\cdot RH \longrightarrow RH\text{-}RH\ (\mathbf{3}) \quad (10)$$

$$\cdot R\text{-}CH_2OH \xrightarrow{[H]} H\text{-}R\text{-}CH_2OH\ (\mathbf{2}) \quad (11)$$

The addition of a H atom to alkene (Reaction 8) competes with the abstraction of a H atom from methanol (Reaction 5). These competitive processes depend on the concentration of the alkene used, The product ratio (**2**:**3**) was found to be very sensitive to the concentration of the alkene (Fig. 3). At a low alkene concentration, hydrogen mainly abstracts the hydrogen from methanol, producing hydrogen molecules and hydroxymethyl radicals. Thus, the main reaction becomes the hydroxymethylation of the alkene. With an increase in the concentration of alkene, the addition of a hydrogen atom to alkene becomes competitive and the yield of the dihydro dimer (**3**) increases to 61% at 0.3 mol dm^{-3} in the case of cyclododecene (**1c**). These reulsts are also consistent with the estimation on the basis of the kinetic data reported.[9]

The unsaturated products, **4a**—**6a** formed consider-

Table 2. Deuterium Isotope Effects in Photoreaction of $EuCl_3$ and Cyclododecene in Isotopic Methanols[a)]

Solvent	Concn	Product yield/%[b)]		Product Ratio	
	1c/mmol dm^{-3}	**2c**	**3c**	**2c**/**3c**	H_2/mL
CH_3OH	60	59	19	3.1	17
CH_3OD	60	58	16	3.6	16
CD_3OH	60	21	28	0.75	14

a) $EuCl_3$ $6H_2O$ 5 mmol dm^{-3}, Solvent 2 mL, 8 h irrad. b) Based on **1c** consumed.

ably in the case of cyclohexene. It has been known that the allylic hydrogens of cyclohexene are much more reactive toward abstraction than those of other alkenes. This fact had been explained by the coplanarity of the cyclohexenyl radical and was substantiated by results reported by Mayo et al.[10)] The ratios of k_{ab} (rate of H atom abstraction from alkene) to k_{ad} (rate of addition to alkene) were 16, 0.4, 1.5, and 1.2 for cyclohexene, cyclooctene, cyclododecene, and tetramethylethylene, respectively. The unsaturated products (**4a**, **5a**, and **6a**) might have been formed via the cyclohexenyl radicals. In the case of tetramethylethylene, the reduction of **1d** took place to afford 2,3-dimethylbutane (**7d**). The radical **8d** formed by the addition of a hydrogen atom to **1d** was a tertiary alkyl radical. The steric repulsion by an isopropyl and two methyl groups was anticipated as making the coupling reaction difficult. For a *t*-butyl radical (similar to **8d**), the disproportionation prevailed over the coupling in solution, whereas for alicyclic alkyl radicals, the former was interior to the latter.[11)] These facts suggest that the hydrogenation of alkene occurs mainly in tetramethylethylene and are consistent with the experimental results.

$$(CH_3)_2\dot{C}CH(CH_3)_2$$

8d

In order to obtain an insight into this reaction, experiments were carried out using deuterium-labelled compounds. The results are summarized in Table 2.

The europium chloride used contained 6 gram-equivalent H_2O as the water of crystallization. However, its quantity was less than 0.1 wt% of the methanol and the effects of the water are presumed to be negligible. The yields of **2c** and **3c** did not differ greatly in CH_3OH and CH_3OD. When CD_3OH was used, however, **2c** decreased significantly with an increase of **3c**. The evolution of hydrogen gas was also reduced in the case of CD_3OH. The initial processes (Reactions 1—3) were regarded as not being influenced by the deuterium labelling. A reaction for which deuterium-isotope effects are expected is the hydrogen atom abstraction from methanol by hydrogen atom (Reaction 5) among the initial processes. The retardation of Reaction 5 in CD_3OH leads to a decrease in the yields of the hydroxymethyl radical as well as the hydrogen evolution with corresponding increases in the yields of the cyclododecyl radical. These explanations are in accord with the experimental results given in Table 2.

Concerning the hydrogen source for the formation of **2c** from the 2-(hydroxymethyl)cyclododecyl radical (**9c**) (Reaction 11), there are three possibilities: (1) recombination with a hydrogen atom, (2) disproportionation with other radicals, and (3) the abstraction of hydrogen from methanol. The first case seems to be not so important because the concentrations of hydrogen atoms and the radical **9c** are very low. The second and the third cases are of some importance for the present reaction conditions. Especially, considering the dissociation energies of the C–H bond in cyclohexane (402 kJ mol^{-1})[12)] and the C–H bond in methanol (394 kJ mol^{-1}),[13)] hydrogen abstraction from methanol becomes more exothermic than that from cyclohexane by 8 kJ mol^{-1}. Therefore, for this process, the effects of deuterium isotopes might be important. This interpretation is in accord with the fact that in the case of styrene, a 2:1 styrene–methanol adduct and a dihydro dimer were obtained as the main products, however, a 1:1 adduct was not detected. The benzyl-type radical derived from styrenes can not abstract H atom from methanol because the C–H bond energy of the benzylic C–H bond is low, 356 kJ mol^{-1}.[13)] Therefore, the benzyl radical can only terminate by coupling with another benzyl radical.

An example of photochemical hydroxymethylation is known for norbornene in which hydroxymethylation proceeds by a xylene-sensitization in methanol via a radical mechanism.[14)] On the contrary, cyclohexene and cycloheptene undergo a dipolar addition of methanol to give methoxy products.[14)] The reactions are selective for cyclic six- and seven-membered rings. The present photoreactions of Eu-alkene systems in methnol are able to efficiently transform aliphatic and alicyclic alkenes to (hydroxymethyl) alkanes, in which europium ions act as an efficient sensitizer. The photoreaction of Eu(III) and alkene in methanol is useful as a general synthetic method for the hydroxymethylation of alkenes.

Experimental

Instruments. GLC analyses were carried out on a Shimadzu GC-7A gas chromatograph with OV-17 (2 m) for cyclohexene, cyclooctene, and cyclododecene, with a Porapak-type QS (40 cm) or a Porapak-type T (40 cm) for tetramethylethylene and ethylene glycol. ^{1}H and ^{13}C NMR spectra were recorded in a CDCl$_3$ solution on a Bruker WM-360 spectrometer using TMS as an internal standard. The mass spectra were run on a JEOL JMS-DX300 (Gas chromatograph–Mass spectrometer) using the same columns as for the GC analysis. UV-spectra were recorded on a Hitachi 323 spectrophotometer.

Materials. Cyclohexene, cyclooctene, cyclododecene, and tetramethylethylene (Nakarai) were distilled over sodium prior to use and EuCl$_3$ 6H$_2$O (Nakarai) was used without further purification. Methanol was distilled over CaH$_2$. Isotopically labelled methanols (Merck) were used without further purification.

Spectral Change for the Eu$^{\text{III}}$—Methanol System by Irradiation. A methanol solution of EuCl$_3$ (2 mmol dm^{-3}) was irradiated under an argon atmosphere through a Pyrex filter with a 350-W high-pressure mercury lamp at running-water temperature. Absorption spectra were measured before irradiation and subsequently at regular time intervals. During the irradiation evolution of hydrogen gas was observed.

General Procedure. Photoreaction of a Methanol Solution of Eu$^{\text{III}}$ and Alkenes. A methanol solution of alkene (**1**: 100 mmol dm^{-3}) and EuCl$_3$ (5 mmol dm^{-3}) was placed in a Pyrex cell connected to a gas syringe through a capillary tube to collect evolved hydrogen gas and irradiated under an argon atmosphere with a 350-W high-pressure mercury lamp for 8 h. After irradiation, the solution was concentrated under reduced pressure. The identification of products was carried out by a direct comparison of GLC and MS with those of available authentic samples. The following products were isolated by means of preparative gas chromatography (OV-17, 2 m) or the column chromatography on silica gel with hexane and benzene and were identified by spectral data.

Hydroxymethylcyclohexane (2a): Viscous oil; MS *m/z* (rel intensity) 96 (M$^+$—18, 7%), 83(16), 81(13), 67(28), 55(63), 41(100), 39(96), 31(66).

3-Hydroxymethylcyclohexene (4a): Viscous oil; **4a** was transformed into **2a** by hydrogenation of the reaction solution mixture by palladium–carbon. MS *m/z* (rel intensity) 94 (M$^+$—18, 2%), 81(11), 79(21), 66(5), 53(11), 41(12), 39(32), 31(100).

Bicyclohexyl (3a), 2-Cyclohexyl-cyclohexene (5a), 3,3′-Bicyclohexene (6a): **6a** was obtained by a photoreaction of **1a** and benzophenone, and hydrogenated by palladium–carbon to give new peaks coinciding with **3a** and **5a** at an early stage and concentrated at one peak after the end of the reaction.

3a: Viscous oil; MS *m/z* (rel intensity) 166 (M$^+$, 45%), 109(19), 96(29), 83(97), 82(100), 67(90), 53(39).

5a: MS *m/z* (rel intensity) 164(M$^+$, 2%), 91(13), 82(22), 81(54), 79(72), 77(35), 67(24), 55(100), 53(54), 41(94), 39(81).

6a: MS *m/z* (rel intensity) 162(M$^+$, 1%), 91(11), 82(7), 81(100), 79(89), 77(43), 66(20), 55(22), 53(51), 41(92), 39(69).

Hydroxymethylcyclooctane (2b): ^{1}H NMR (CDCl$_3$) δ=1.33 (m, 14H), 1.83 (m, 1H), 2.47 (bs, 1H), 3.42 (d, J=6 Hz, 2H), 2,4-dinitrobenzoate of **2b**: mp 63—64 °C; MS *m/z* (rel intensity) 336(M$^+$, vw), 306(3), 195(12), 149(13), 124(15), 111(21), 96(100).

Bicyclooctyl (3b): Colorless needles; mp 46—47 °C; MS *m/z* (rel intensity) 222(M$^+$, vw), 111(100), 110(40), 82(36), 69(98), 55(42), 41(22); ^{1}H NMR (CDCl$_3$) δ=1.26—1.72(m); ^{13}C NMR (CDCl$_3$, off-resonance) δ=44.5(d), 30.9(t), 27.0(t).

Hydroxymethylcyclododecane (2c): Viscous oil; ^{1}H NMR (CDCl$_3$) δ=1.32 (m, 22H), 1.63 (t, J=6 Hz, 1H), 1.90 (bs, 1H), 3.47 (d, J=6 Hz, 2H); MS *m/z* (rel intensity) 198(M$^+$, vw), 180(7), 166(6), 152(6), 137(6), 123(11), 111(37), 97(70), 83(87), 69(73), 55(100). ^{13}C NMR (CDCl$_3$, off-resonance) δ=69.27(t), 40.67(d), 30.04(t), 29.73(t), 27.36(t), 26.88(t), 25.99(t).

Bicyclododecyl (3c): Needles; mp 117—118 °C; MS *m/z* (rel intensity) 334(M$^+$, 30), 166(100), 111(26), 97(48), 96(37), 83(43), 82(30), 69(30), 55(41); ^{13}C NMR (CDCl$_3$, off-resonance) δ=33.46(d), 26.26(t), 24.14(t), 23.93(t), 23.74(t), 22.92(t), 22.86(t); Found: C, 86.14; H, 13.86%. Calcd for C$_{24}$H$_{46}$: C. 86.13; H, 13.62%.

2,3-Dimethylbutane (7d) and 2,3,3,4,4,5-Hexamethylhexane (3d): **4d** was identified by the comparion of GC and MS with those of authentic sample obtained by a hydrogenation of tetramethylethylene. **3d** was identified based on GC–Mass data.

2,2,3-Trimethyl-1-butanol (2d): Viscous oil; ^{1}H NMR (CDCl$_3$) δ=0.82 (s, 6H), 0.85 (d, J=7 Hz, 6H), 1.64 (q, J=7 Hz, 1H), 1.90 (bs, 1H), 3.37 (s, 2H); ^{13}C NMR (CDCl$_3$, off-resonance) δ=17.40(q), 30.00(q), 32.65(d), 37.36(s), 70.92(t).

The authors wish to thank the members of Material Analysis Center in the Institute of Scientific and Industrial Research, Osaka University, for the NMR and mass-spectra measurements and the elemental analyses.

References

1) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York (1970).

2) M. Graetzel, *Acc. Chem. Res.*, **14**, 376 (1981), and references cited therein; D. G. Whitten, *Acc. Chem. Res.*, **13**, 83 (1980).

3) G. L. Geoffroy and M. S. Wrighton, "Organometallic Photochemistry," Academic Press, New York (1979), Chap. 3.

4) T. Sato, H. Kaneko, and S. Yamaguchi, *J. Org. Chem.*, **45**, 3778 (1980); E. Murayama, A. Kohda, and T. Sato, *J. Chem. Soc., Perkin Trans. 1*, **1980**, 947; A. Kohda, K. Ueda, and T. Sato, *J. Org. Chem.*, **46**, 509 (1981).

5) a) P. C. Ford, R. E. Hinze, and J. D. Peterson, "Concepts of Inorganic Photochemistry," ed by A. W. Adamson and P. D. Fleischauer, Wiley (Interscience), New York (1974), p. 203; b) G. Adachi, K. Tomokiyo, K. Sorita, and J. Shiokawa, *J. Chem. Soc., Chem. Commun.*, **1980**, 914; G. Adachi, K. Sorita, K. Kawata, K. Tomokiyo, and J. Shiokawa, *J. Less-Common Met.*, **93**, 81 (1983); c) Y. Hass, G. Stein, and M. Tomkiewicz, *J. Phys. Chem.*, **74**, 2558 (1970); d) M. Brandys and G. Stein, *J. Phys. Chem.*, **82**, 852 (1978); e) N. Azuma, A. Matsumoto, and J. Shiokawa, *Polyhedron*, **2**, 63 (1983).

6) A. Ishida, S. Toki, and S. Takamuku, *Chem. Lett.*, **1985**, 893.

7) A. Ishida, S. Toki, and S. Takamuku, *J. Chem. Soc., Chem. Commun.*, **1985**, 1481.

8) G. Baker, J. H. Littlefair, R. Shaw, and J. C. Thynne, *J. Chem. Soc.*, **1965**, 6970.

9) Rate of addition of H atom to ethylene is 3.2×10^9 mol^{-1} dm^3 s^{-1} [J. K. Thomas, *J. Phys. Chem.*, **71**, 1919 (1967)] and one of abstraction of H atom from methanol by H atom is 2.9×10^6 mol^{-1} dm^3 s^{-1} [P. Neta, G. R. Holdren, and R. H.

Schuler, *J. Phys. Chem.*, **75**, 449 (1971)]. When the olefin is ca 0.02 mol dm^{-3} the reactions of addition and abstraction are suggested to be comparable.

10) F. R. Mayo, *Acc. Chem. Res.*, **1**, 193 (1968); D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Am. Chem. Soc.*, **87**, 4824 (1965).

11) M. J. Gibian, R. C. Corley, *Chem. Rev.*, **73**, 441 (1973); R. A. Scheldon and J. K. Kochi, *J. Am. Chem. Soc.*, **92**, 4395 (1970).

12) K. C. Ferguson and E. Whittle, *Trans. Faraday Soc.*, **67**, 2618 (1976).

13) D. M. Golden, and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

14) P. J. Kropp, *J. Am. Chem. Soc.*, **91**, 5783 (1969).