December, 1974] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(12), 3121—3124 (1974) 3121

Molybdenum(V) Chloride as a Reagent for *cis* Chlorination of Olefins

Sakae UEMURA,* Akira ONOE, and Masaya OKANO

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

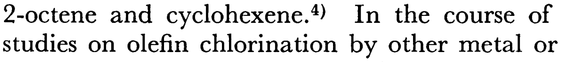
(Received May 27, 1974)

Treatment of nonconjugated olefins such as *cis*- and *trans*-2-butenes, *cis*-2-octene, and cyclohexene with $MoCl_5$ in CCl_4 gave *vic*-dichloroalkanes whose *cis*-isomer was formed predominantly, the ratio of *cis*- to *trans*-addition being 4.9—12.1, together with monochloroalkanes. Preferential formation of *exo-cis*-dichloride was observed in the case of norbornene and norbornadiene. Bromochlorination and chloroiodination of olefins, and aromatic bromination and iodination were carried out with mixtures of $MoCl_5$ and halogens. The reaction scheme for chlorination is discussed.

Chlorine reacts with olefins *via* both homolytic and heterolytic pathways, stereochemistry of the addition depending on the kind of olefins. Thus, the addition occurs non-stereospecifically with conjugated olefins, *cis* addition usually predominating, while with nonconjugated linear olefins it proceeds with high *trans* stereospecificity.[1] Chlorination of nonconjugated olefins by other chlorinating agents, however, shows a somewhat different stereospecificity from that by chlorine; *i.e.*, *cis*-addition sometimes predominates in the reaction of *cis*- or *trans*-2-butene with $CuCl_2$[2] and in the chlorination of 1-alkylpropene with (dichloroiodo)-benzene.[3] $SbCl_5$ is an effective reagent for the *cis*-chlorination of nonconjugated olefins such as 2-butene, 2-octene and cyclohexene.[4] In the course of further studies on olefin chlorination by other metal or metalloidal chlorides we found that *cis*-chlorination also occurred by $MoCl_5$ with higher *cis* stereospecificity than in the case of $SbCl_5$. Although the chlorinating action of $MoCl_5$ was noted in the chlorination of aromatic hydrocarbons,[5] no report seems to have been given on the direct chlorination of olefins. We describe here the results of the chlorination of olefins by $MoCl_5$ in CCl_4, together with those of the mixed halogenation of olefins and aromatic halogenation with mixtures of $MoCl_5$ and halogens.

Results and Discussion

Chlorination. The reaction was carried out by adding or introducing olefinic hydrocarbons into a pale red-brown homogeneous solution of $MoCl_5$ in CCl_4 or CH_2Cl_2 at appropriate temperature, followed by stirring for 0.25—10 hr under N_2 atmosphere. The products were *vic*-dichloroalkanes(**1**) (*cis* and *trans*) and monochloroalkane(**2**) (Scheme 1).



$$\mathrm{RCH{=}CHR'} \xrightarrow[\mathrm{CCl_4}]{\mathrm{MoCl_5}} \underset{\mathrm{Cl}\ \ \ \mathrm{Cl}}{\mathrm{RCH{-}CHR'}} + \underset{\mathrm{Cl}}{\mathrm{RCH_2CHR'}} \qquad (1)$$

(**1**) (**2**)

Some results are summarized in Table 1. Compared to the chlorination by $SbCl_5$,[4] the yield of **1** was lower, while the selectivity for *cis*-chlorination was much higher. Separate experiments using isomeric dichlorobutanes and dichlorocyclohexanes revealed that no interconversion occurred between *cis*-**1** and *trans*-**1** under the present reaction conditions. We see from Table 1 that elongation of the reaction time does not affect so much the ratio of *cis*- to *trans*-addition in the chlorination of cyclohexene despite the increase in the yield of **1** (Compare Runs 6 and 7). This shows that the observed ratio of *cis*- to *trans*-addition is kinetically controlled.

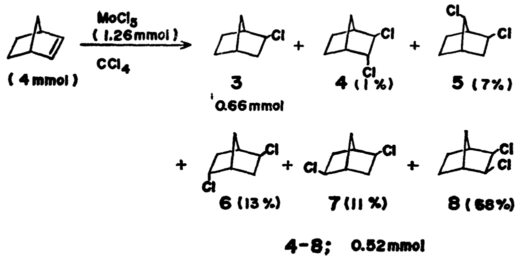
The reaction in other chlorinated solvents such as chloroform and dichloroethane gave no satisfactory results, *viz.*, none of **1** and **2** was obtained in the former solvent, while the yield of **1** and **2** as well as the *cis*-selectivity was quite low in the latter one. No chlorination occurred in more polar solvents such as acetonitrile, nitromethane, alcohols, DMF, and DMSO, probably because of the reactions of $MoCl_5$ with these solvents forming such salts as $Mo_2Cl_6L_3$, $MoOCl_3$ and/or $MoOCl_3L_2$.[6—8] No reaction occurred with ethyl fumarate and ethyl maleate, but a small amount of **1** (<5% yield) was obtained from the reaction of styrene together with a lot of dimeric compound. When the chlorination of cyclohexene was carried out in the presence of *m*-dinitrobenzene or oxygen, no change in the yield or in the *cis*/*trans* ratio of **1** was observed, suggesting that the reaction is not of a radical nature.

In the case of norbornene and norbornadiene the reaction proceeded in CCl_4 at room temperature to give the various chlorinated compounds as illustrated in schemes 2 and 3, the yields of the dichlorinated compounds being 40—45% and 20—25%, respectively. Although the polymerization of norbornene by using $MoCl_5$ as catalyst is known,[9] only a slight amount of polymerization product was obtained under the present reaction conditions. The kind of product and its distribution differed very much from those in the chlorination by Cl_2 or $SbCl_5$. The characteristic feature of this reaction is a preferable formation of **8** and **13**, *exo-cis*-dichlorocompounds, which were hardly obtained at all in the chlorination by $SbCl_5$. **4**—**7** were the main products in the chlorination of norbornene by $SbCl_5$, while nortricyclyl chloride(**9**) and *exo*-2-*syn*-7-dichloronorbornane were mainly obtained by using Cl_2 gas.[7] In the case of norbornadiene chlorination by Cl_2 gave **10**—**12** as the main products,[10] but we found such a case also in the reaction by $SbCl_5$. Thus, although the dissociation of $MoCl_5$ to $MoCl_4$ and Cl_2 has been reported,[11] possible chlorination with chlorine arising from this dissociation can be excluded.

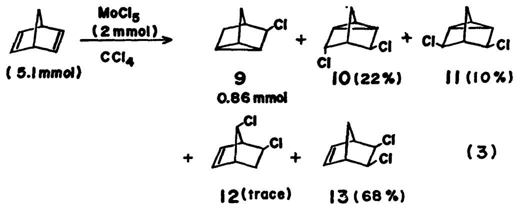
In order to consider the reaction scheme of chlorination, it is desirable to know the structure of $MoCl_5$

---

* To whom correspondence should be addressed.



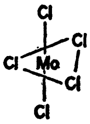
(2)



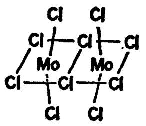
(3)

in solution. It is known that the crystal structure of $MoCl_5$ consists of a dimeric molecule with the chlorine atoms forming two distorted octahedra which have a common edge (**15**).[12] However, different views are given on the nature of $MoCl_5$ in solution; it is monomeric in solution (**14**) and solvated;[7] it preserves its dimeric state in CCl_4.[12] Another kind of dimeric species, namely a polarized dimer complex which may be illustrated as **16**, was also considered in the direct aromatic chlorination by $MoCl_5$ where aromatic compound itself was used as a solvent.[5b] Thus it is possible that such an equilibrium (Scheme 4) is present in the solution of $MoCl_5$. Assuming that this equilibrium is involved in CCl_4, the predominant formation of **8**, **13** and other *cis*-dichlorides can be most reasonably explained by a concerted molecular addition of **14** or **15** to olefins, as has been proposed for the *cis*-chlorination by $SbCl_5$.[4]

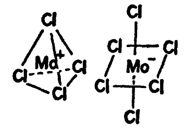
$$2MoCl_5 \rightleftarrows (MoCl_5)_2 \rightleftarrows MoCl_4^+MoCl_6^- \qquad (4)$$



14

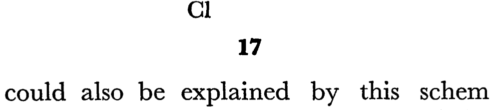


15



16

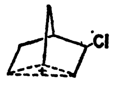
On the other hand, as to the minor formation of *trans*-dichlorides, **16** seems to be the attacking species, reacting with olefin to give carbonium ion intermediate(**17**) followed by the attack of chloride ion (Scheme 5). Formation of the dichlorides, **4**—**7** and **10**—**12**,



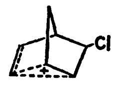
$$>C{=}C< \xrightarrow[16]{} [>\underset{\underset{Cl}{|}}{\overset{}{C}}\overset{+}{\text{—}}C<]MoCl_6^- \rightarrow \mathbf{1}(trans) \qquad (5)$$

17

could also be explained by this scheme where the intermediate carbonium ions would be nonclassical ones; *i.e.*, **18** for **4**—**7** and **19** for **10**—**12**. By comparison of the results of the chlorination by $MoCl_5$ with those by $SbCl_5$, the two following differences are evident. Selectivity for *cis*-chlorination is higher in the former case; *exo-cis*-dichlorides are formed preferably from norbornene and norbornadiene in the former, but none in the latter where the reaction was carried out at various concentrations of $SbCl_5$. The results might suggest that $MoCl_5$ mainly exists in the form of **14** or **15** in CCl_4, while in the case of $SbCl_5$ the more polarized form of **15** seems to have a rather large contribution in the same solvent. The difference could be attributed to the stronger Lewis acidity (the ability of the chloride ion abstraction from another molecule) of $SbCl_5$ than $MoCl_5$.

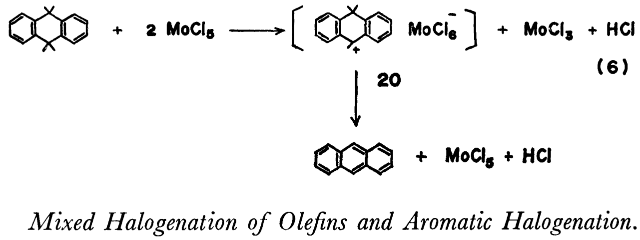


18



19

As to a source of hydrogen chloride which may add to olefin to give **2**, two possibilities are conceivable; the decomposition of $MoCl_5$ to $MoOCl_3$ and HCl[8] by moisture, and hydride ion abstraction by $MoCl_5$ from olefin to give the molybdenum salt of allylic cation, $MoCl_3$, and hydrogen chloride, as was proposed in the case of the reaction with $SbCl_5$.[4] The former possibility does not seem to be important, since even in a careful experiment under N_2 in a dried condition the formation of **2** was observed, its amount being unaffected. Moreover, if hydrogen chloride arises only by the hydrolysis of $MoCl_5$, the amount of **2** in Run 8 (Table 1) should be larger than that in Run 6, since the time before the addition of olefin is much longer in Run 8 than in Run 6. In order to ascertain the latter possibility, we attempted the reaction of dihydroanthracene with $MoCl_5$ in CCl_4 just as in the case of $SbCl_5$.[13] Formation of anthracene was observed (see Experimental), although it was impossible to isolate hexachloromolybdate salt of 9-anthracenium cation. This shows that the molybdenum salt such as **20** can exist in solution (Scheme 6) by considering the reported observation using $SbCl_5$,[13] and consequently that $MoCl_5$ can abstract the hydride ion from certain organic compounds. In the chlorination of cyclohexene and octenes, resinous products were always obtained, probably because of the formation of dienes by elimination of hydrogen from olefin as described in scheme 6, and their polymerization. The reaction of 1,3-cyclooctadiene with $MoCl_5$ readily gave the polymerized product under the same conditions. We thus propose that the important source of hydrogen chloride is the hydride ion abstraction from allylic position of olefins by $MoCl_5$.



(6)

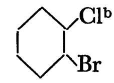
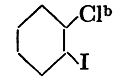
Mixed Halogenation of Olefins and Aromatic Halogenation. Bromochlorination and chloroiodination of olefins[14a] and the aromatic halogenation[14b] were carried out by using mixtures of antimony chlorides and halogens in

Table 1. Chlorination of olefins by molybdenum(V) chloride in CCl_4 (CCl_4 50 ml)

Run	Olefin	mmol	$MoCl_5$ (mmol)	Temp. (°C)	Time (hr)	Products, mmol				Ratio of *cis*- to *trans*- add.
						1			**2**	
						cis-add.	*trans*-add.	total yield, %[a]		
1	*trans*-2-Butene	75	1.4	20	0.33	0.65[b]	0.06[c]	51	0	10.8
2	*trans*-2-Butene	80	2.3	74	0.33	0.81[b]	0.15[c]	85	0	12.1
3	*cis*-2-Butene	70	1.6	21	0.25	0.51[c]	0.09[b]	38	0	5.7
4	*cis*-2-Butene	50	2.0	74	0.33	1.57[c]	0.27[b]	92	0	5.8
5	*cis*-2-Octene	11	2.4	20	10	0.39[d]	0.08[e]	20	2.2	4.9
6	Cyclohexene	20	1.6	22	2	0.46[f]	0.04[g]	32	1.1	11.5
7	Cyclohexene	26	1.2	22	10	0.64[f]	0.06[g]	58	1.4	10.7
8[h]	Cyclohexene	20	1.0	22	2	0.68[f]	0.16[g]	84	0.6	4.3
9[i]	Cyclohexene	10	1.2	22	2	0.58[f]	0.05[g]	53	1.0	11.6
10	1-Octene	50	1.6	18	10	0.92		57	2.1	—

a) Based on $MoCl_5$ and the stoichiometry shown in Scheme 4. b) *dl*. c) *meso*. d) *erythro*. e) *threo*. f) *cis*. g) *trans*. h) Cyclohexene was added after stirring a solution of $MoCl_5$ for 10 hr. i) Solvent, CH_2Cl_2.

Table 2. Bromochlorination and chloroiodination with $MoCl_5$ (solvent, CCl_4 50 ml; at 25 °C for 0.5 hr)

Olefiin	mmol	$MoCl_5$ (mmol)	X_2 (mmol)	Product	Yield[a] (%)
Cyclohexene	10	2.0	Br_2 2.0		63[c]
Cyclohexene	12	1.7	I_2 8.5		37
trans-2-Butene	32	2.0	I_2 2.2	$CH_3CHClCHICH_3$[d]	33
cis-2-Butene	43	2.0	I_2 2.1	$CH_3CHClCHICH_3$[e]	49

a) Based on $MoCl_5$ and the stoichiometry shown in Scheme 7. b) *trans*. c) Other products; *cis*- and *trans*-1,2-dichlorocyclohexane (16% and 7%), *trans*-1,2-dibromocyclohexane (1%), and chlorocyclohexane (0.34 mmol). d) *erythro*. e) *threo*.

Table 3. Aromatic bromination and iodination by $MoCl_5$

(ArH 50-70 mmol; $MoCl_5$ 1.7-2 mmol; halogen 2 mmol; solvent, CCl_4 50 ml)

Substituent in ArH	Halogen	Temp. (°C)	Time (hr)	Yield[a] (%)	Isomer distribution of ArX[b] (%)	
					o-	*p*-
H	Br_2	21	1	93	—	—
CH_3	Br_2	25	0.5	92	26	74[c]
Cl	Br_2	76	1	88	12	88[d]
Br	Br_2	76	1	87	12	88[d]
H	I_2	76	3	93	—	—
CH_3	I_2	76	1	77	52	48[c]
Cl	I_2	76	3	73	16	84[d]
Br	I_2	76	3	68	16	84[d]

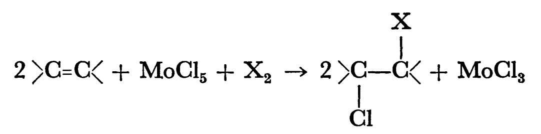
a) Based on halogen and the stoichiometry shown in Scheme 8. b) *meta*- <1%. c) Determined by NMR. d) Determined by glc.

Table 4. Competitive halogenation

(benzene 100 mmol; toluene 20 mmol; halogen 2 mmol; $MoCl_5$ 2 mmol; solvent 50 ml)

Halogenating agent		Solvent	k_T/k_B	*o*/*p* ratio
(a)	Bromination[a]			
	Br_2+MoCl_5	CCl_4	349	0.37
	Br_2+MoCl_5	$ClCH_2CH_2Cl$	28	0.67
(b)	Iodination[b]			
	I_2+MoCl_5	CCl_4	111	1.07

a) At 25 °C. b) At 76 °C.



$$2\,{>}C{=}C{<} + MoCl_5 + X_2 \rightarrow 2\,{>}\underset{\displaystyle Cl}{\underset{|}{C}}-\overset{\displaystyle X}{\overset{|}{C}}{<} + MoCl_3 \qquad (7)$$

$$2\,ArH + MoCl_5 + X_2 \rightarrow 2\,ArX + MoCl_3 + 2HCl \qquad (8)$$

CCl_4 or CH_2Cl_2 as solvent.[14a] We found that similar reactions occurred by using $MoCl_5$ instead of $SbCl_5$. The reactions of olefins with a mixture of $MoCl_5$ and Br_2 or I_2 gave *trans*-bromochloro- or chloroiodo-alkanes respectively according to the stoichiometry shown in scheme 7 (Table 2), and the nuclear halogenation of benzene, toluene, halobenzenes occurred under similar conditions by use of aromatic compounds as substrates instead of olefins (Scheme 8 and Table 3). From a synthetic view point, however, the reactions using $MoCl_5$ were inferior to those with $SbCl_5$: The yield in the mixed halogenation was lower, the bromochlorination was accompanied by side reactions, the selectivity in aromatic halogenation was lower, and the aromatic compounds with electron-withdrawing groups such as nitrobenzene and ethyl benzoate could not be halogenated. In the reactions (Schemes 7 and 8), the mixed halogens such as BrCl and ICl may be formed *in situ*, and the k_T/k_B value and the *o*/*p* ratio in the competitive halogenation (Table 4) suggest that the attacking species is not Br^+ or I^+ but the mixed halogen itself activated by $MoCl_5$, as in the reaction with $SbCl_5$.[14b)] The larger k_T/k_B value and smaller *o*/*p* ratio in the $MoCl_5$ case than in the $SbCl_5$ case show that $MoCl_5$ is a weaker Lewis acid than $SbCl_5$ in line with the results of Friedel-Crafts aromatic acylation.[15)]

Experimental

Commercial *trans*-2-butene(contains 1% of the *cis*-isomer) and *cis*-2-butene(contains 2.4% of the *trans*-isomer) were used without further purification. All the other organic substrates and solvents were purified by distillation before use. Commercial $MoCl_5$ (99% pure), Br_2, and I_2 were used without purification.

All the reactions were carried out by the method reported previously[4,14)] by using $MoCl_5$ in the place of $SbCl_5$ or $SbCl_3$. Identification of the products in Tables 1, 2, and 3 except for 2-chloro-3-iodobutanes was described previously.[4,14)]

Reaction of Norbornene with $MoCl_5$. To a solution of $MoCl_5$ (0.345 g, 1.26 mmol) in CCl_4(50 ml) was added norbornene (0.375 g, 3.99 mmol) at 25 °C and the resulting mixture was stirred for 2 hr under N_2. Aqueous NaOH was then added to stop the reaction. After the usual work-up, the organic layer was evaporated to *ca.* 20 ml. Acetone was added to give a small amount of white organic precipitates of norbornene polymer which were filtered off. The filtrate was analyzed by glc and found to contain **3** (0.664 mmol), **4**(0.006 mmol), **5**(0.035 mmol), **6**(0.068 mmol), **7** (0.060 mmol), and **8**(0.352 mmol) as organic products. The yield of the sum of **4**—**8** was 41.5% based on $MoCl_5$ charged. The identification of **4**—**7** was reported in a previous paper.[4)] An authentic sample of **3** for glc was prepared by the method using norbornene and hydrogen chloride.[16)] **8** was isolated from the combined distillates of several runs by preparative glc, its NMR spectrum being identical with the reported one.[10,17)]

Reaction of Norbornadiene with $MoCl_5$. A similar reaction to that described above by using $MoCl_5$ (2.0 mmol) and norbornadiene (5.1 mmol) in CCl_4 (100 ml) gave **9**(0.86 mmol), **10**(0.088 mmol), **11**(0.040 mmol), **12**(trace), **13**(0.273 mmol), and a slight amount of norbornadiene polymer. The yield of the sum of **10**—**13** was 20.1%. Identification of the products was carried out as follows. Authentic samples of **9** and **12** for glc were prepared by the reported methods from the reactions of Cl_2 with norbornene[18)] and norbornadiene,[10)] respectively. NMR spectrum of **12** which was isolated by preparative glc was identical with the reported one.[19)] Each of **10**, **11**, and **13** was isolated from the combined distillates of several runs by preparative glc. Each NMR spectrum was identical with the reported one.[19,20)]

Reaction of Dihydroanthracene with $MoCl_5$. To a solution of $MoCl_5$ (0.52 g, 1.88 mmol) in CCl_4 (80 ml) was added dihydroanthracene (0.153 g, 0.86 mmol) dissolved in CCl_4 (20 ml) at 25 °C and the resulting mixture was stirred for 1 hr under N_2. Aqueous $NaHCO_3$ was then added. The organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated to *ca.* 20 ml which was revealed by glc to contain 0.31 mmol of unreacted dihydroanthracene and 0.34 mmol of anthracene. A similar reaction by using $MoCl_5$ (2.03 mmol) and dihydroanthracene (1.02 mmol) for 5 hr gave 0.38 mmol of anthracene.

erythro- *and* threo-*2-Chloro-3-iodobutanes.* *trans*-2-Butene (2.2 g, 39.2 mmol) was bubbled at 25 °C for 30 min under stirring into a solution of CH_3CN(50 ml) containing anhydrous $CuCl_2$(1.46 g, 10.9 mmol) and I_2(2.83 g, 11.1 mmol). Glc analysis of ether extract after the usual work-up of the reaction mixture showed the presence of 15.8 mmol of *erythro*-2-chloro-3-iodobutane(72% yield) as porduct. Distillation gave 2.1 g of pure compound; bp 55.5 °C/18 mmHg(lit,[21)] bp 34.8—35.3 °C/5 mmHg). NMR ($CDCl_3$) δ 1.68(d. 3H, J=6.5 Hz), 2.01 (d, 3H, J=6.5 Hz), 3.98 (quintet 1H, J=6.5 Hz), 4.28(quintet 1H, J=6.5 Hz).

A similar reaction of *cis*-2-butene(41 mmol) with $CuCl_2$ (10 mmol) and I_2(10.8 mmol) gave *threo*-isomer in 61% yield. Distillation gave 1.2 g of pure compound; bp 58—58.5 °C/18 mmHg (lit,[21)] bp 33.2—33.5 °C/4 mmHg). NMR($CDCl_3$) δ 1.62(d, 3H, J=6.5 Hz), 1.93(d. 3H, J=6.5 Hz), 4.11(m. 1H), 4.49(m. 1H).

Analytical Instruments. The NMR spectra were determined by means of a Varian A-60 spectrometer in $CDCl_3$ and CCl_4 using TMS as an internal standard. Glc analysis was carried out with two Shimadzu apparatuses 5APTF and 4BMPF[EGSS-X(15%)-Chromosorb-W(3m), PEG 6000 (25%)-Chromosorb-W(3m), and Apiezon-L (30%)-Celite (1m) columns; carrier gas, N_2].

References

1) R. C. Fahey, "Topics in Stereochemistry," Vol. 3, ed. by E. L. Eliel and N. L. Allinger, Interscience, New York (1968), p. 265—278.

2) T. Koyano, This Bulletin, **43**, 1439 (1970).

3) M. Devillier and H. Bodot, *Bull. Soc. Chim. Fr.*, **1972**, 227.

4) S. Uemura, A. Onoe, and M. Okano, This Bulletin, **47**, 692 (1974).

5) a) B. Aronheim, *Chem. Ber.*, **8**, 1400 (1875). b) P. Kovacic and R. M. Lange, *J. Org. Chem.*, **30**, 4251 (1965).

6) C. Miniscloux, G. Martino, and L. Sajus, *Bull. Soc. Chim. Fr.*, **1973**, 2179.

7) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd Ed., Interscience, New York (1972), p. 958—959.

8) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 11, Longmans, London (1930), p. 625.

9) T. Oshika and H. Tabuchi, This Bulletin, **41**, 211 (1968).

10) S. Masson and A. Thuillier, *Bull. Soc. Chim. Fr.*, **1969**, 4368.

11) I. M. Pearson and C. G. Garner, *J. Phys. Chem.*, **65**, 690 (1961).

12) M. L. Larson, *J. Amer. Chem. Soc.*, **82**, 1223 (1960).

13) J. Holmes and R. Pettit, *J. Org. Chem.*, **28**, 1695 (1963).

14) a) S. Uemura, A. Onoe, and M. Okano, This Bulletin, **47**, 143 (1974). b) S. Uemura, A. Onoe, and M. Okano, *ibid.*, **47**, 147 (1974).

15) O. C. Dermer and R. A. Billmeier, *J. Amer. Chem. Soc.*, **64**, 464 (1942).

16) H. Kwart and R. K. Miller, *ibid.*, **78**, 5010 (1956).

17) M. L. Poutsma, *ibid.*, **87**, 4300 (1965).

18) J. D. Roberts, F. O. Johnson, and R. A. Carboni, *ibid.*, **76**, 5692 (1954).

19) R. Hüttel, H. Reinheimer, and K. Nowak, *Chem. Ber.*, **101**, 3761 (1968).

20) D. D. Tanner and G. C. Gidley, *J. Org. Chem.*, **33** 43 (1968).

21) H. J. Lucas and H. K. Garner, *J. Amer. Chem. Soc.* **72**, 2145 (1950).