Triallylheptafluoro-*n*-propyltin was prepared similarly: bp 64–68° (2.7 mm); ir (neat) 1630 ($\nu_{C=C}$), 896 (γ_{C-H}), 497 cm^{-1} ($\nu_{Sn-C(allyl)}$); nmr (CCl_4) 7.73, 7.88 ppm ($SnCH_2$–), J = 69.4, 70.2 cps ($SnCH_2$–). *Anal.* Calcd for $C_{12}H_7F_{15}Sn$: C, 35.07; F, 32.36; H, 3.68; Sn, 28.88. Found: C, 36.09; F, 31.45; H, 3.85; Sn, 27.8.

Alkyl derivatives were prepared from alkyltin chlorides and allylmagnesium halides. New compounds are as follows: triallylmethyltin [bp 100–101° (23 mm); ir (neat) 1620 ($\nu_{C=C}$), 880 (γ_{C-H}), 486 cm^{-1} ($\nu_{Sn-C(allyl)}$); nmr (CCl_4) 9.90 ($SnCH_3$), 8.08, 8.21 ppm ($SnCH_2$–), J = 48.6 ($^{117}SnCH_3$), 50.9 ($^{119}SnCH_3$), 63.9, 64.5 cps ($SnCH_2$–) (*Anal.* Calcd for $C_{10}H_{18}Sn$: C, 46.72; H, 7.06; Sn, 46.21. Found: C, 46.97; H, 7.25; Sn, 46.5)]; triallylethyltin [bp 60–61 (0.6 mm); ir (neat) 1621 ($\nu_{C=C}$), 881 (γ_{C-H}), 487 cm^{-1} ($\nu_{Sn-C(allyl)}$) (*Anal.* Calcd for $C_{11}H_{20}Sn$: C, 48.75; H, 7.44; Sn, 43.80. Found: C, 48.52; H, 7.37; Sn, 44.0)]; triallyl-*n*-propyltin [bp 51–52 (0.2 mm); ir (neat) 1623 ($\nu_{C=C}$), 882 (γ_{C-H}), 487 cm^{-1} ($\nu_{Sn-C(allyl)}$) (*Anal.* Calcd for $C_{12}H_{22}Sn$: C, 50.57; H, 7.78; Sn, 41.65. Found: C, 50.85; H, 7.94; Sn, 42.0)].

Other spectral data are as follows: triallyl-*n*-propyltin [ir (neat) 1623 ($\nu_{C=C}$), 882 (γ_{C-H}), 487 cm^{-1} ($\nu_{Sn-C(allyl)}$)]; diallyldiethyltin [ir (neat) 1621 ($\nu_{C=C}$), 879 (γ_{C-H}), 488 cm^{-1} ($\nu_{Sn-C(allyl)}$)]; diallyldimethyltin [ir (neat) 1622 ($\nu_{C=C}$), 882 (γ_{C-H}), 488 cm^{-1} ($\nu_{Sn-C(allyl)}$); nmr (CCl_4) 9.89 ($SnCH_3$), 8.11, 8.27 ppm ($SnCH_2$–), J = 49.8 ($^{117}SnCH_3$), 52.0 ($^{119}SnCH_3$), 65.3, 65.8 cps ($SnCH_2$–)].

Measurements of Electronic Absorption Spectra.—The solvents were all spectrograde and were used, as supplied, without further purification. The solutions were made under argon, and concentrations were such as to give optical densities between 0.3 and 0.7 at the maximum. The spectra were obtained with a Cary 14 spectrophotometer, using 1-mm cells.

Registry No.—Diallylbis(pentafluoroethyltin), 19647-32-6; triallylpentafluoroethyltin, 19713-76-9; triallylheptafluoro-*n*-propyltin, 19647-33-7; triallylethyltin, 19713-77-0.

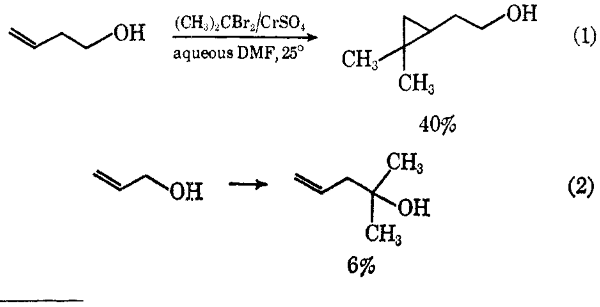
The Reaction of Dimethylmethylchromium Carbenoids with Olefins

A. Zurqiyah and C. E. Castro

Department of Nematology, University of California, Riverside, California 92502

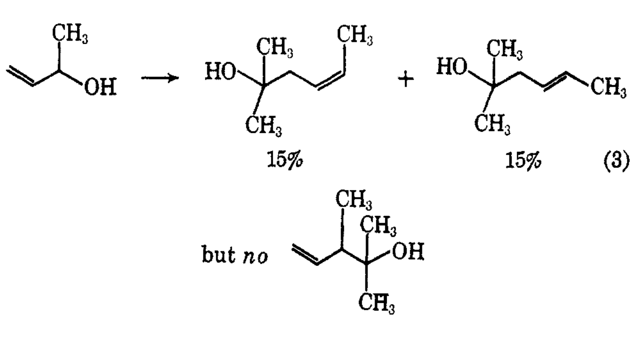
Received November 31, 1968

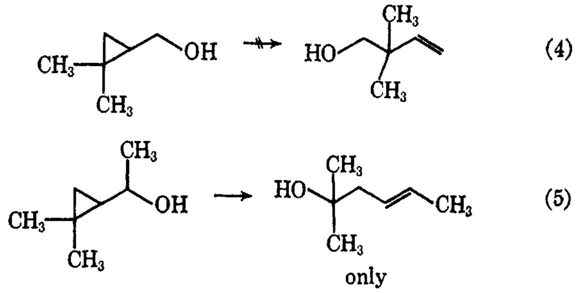
The general chemistry of the reduction of geminal halides and polyhalomethanes with chromous sulfate has been outlined.[1] An important feature of these reactions is the generation of a unique dialkylcarbenoid entity that does have the capacity to react with water and olefins in addition to being reduced and undergoing rearrangement. Adduct formation[2] was typified by eq 1 and 2.

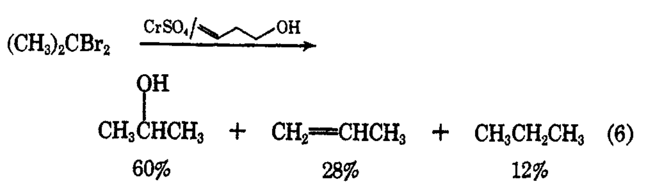


This Note corrects the suggestion that cyclopropanes are intermediates in reactions with allylic alcohols and eliminates a direct C–O insertion.[3]

We have confirmed the results of the reactions with 3-buten-1-ol (eq 1) and allyl alcohol (eq 2). However, reaction with 3-buten-2-ol (eq 3) and an examination of the possible rearrangement of the potential cyclopropane intermediates (under reaction and work-up conditions, eq 4 and 5 are revealing. Moreover, reaction 1 at −5° yields *no* olefinic trapping product[4] (eq 6). The ratio of isopropyl alcohol to propylene and propane produced is constant throughout the run. The over-all kinetics at this temperature (Figure 1) are in accord with the initial buildup of $(CH_3)_2C(Br)Cr^{2+}$.

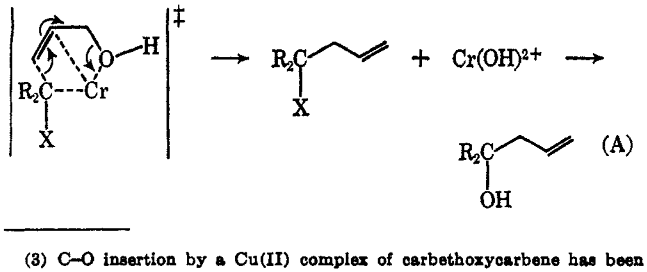






$$CH_3\overset{OH}{C}HCH_3 + CH_2{=}CHCH_3 + CH_3CH_2CH_3 \quad (6)$$

Taken together the data suggest a transition state for olefin insertions that resembles that written for addition by haloalkyllithiums (eq A).[5] In the absence



---

[1] C. E. Castro and W. C. Kray, *J. Amer. Chem. Soc.*, **88**, 4447 (1966).

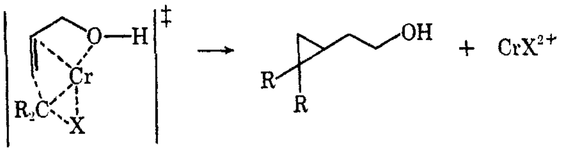
[2] For clarity only adducts are depicted. All yields are based on Cr(II) consumption. Unreacted olefin can be recovered.

[3] C–O insertion by a Cu(II) complex of carbethoxycarbene has been reported: H. Nozaki, S. Moruta, H. Takaya, and R. Noyori, *Tetrahedron Lett.*, **43**, 5239 (1966).

[4] Comparative yields at room temperature in the absence of olefin are propane (2%), propylene (21%), and isopropyl alcohol (76%).

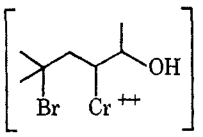
[5] G. L. Closs and J. J. Coyle, *J. Amer. Chem. Soc.*, **87**, 4274 (1965).

of a neighboring leaving group like hydroxyl in the allylic alcohols, bromide is lost in incipient 1,3 fashion (X = halogen, eq B). That is to say, in an extreme



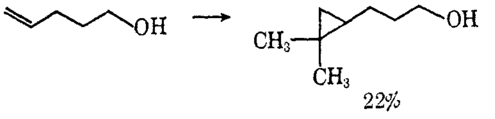
(B)

form, a transient ion like



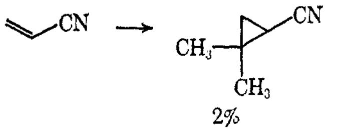
could be considered to eliminate preferentially Cr-$(OH)^{2+}$ rather than undergo 1,3 elimination of Cr-Br^{2+} when it has that option.

Attack of a "free" bromoalkyl radical upon an olefin followed by scavenging with Cr(II) could result in the same products. However, both 3-butenol (eq 1) and 4-pentenol (eq 7) are better "traps" than acrylonitrile



(7)

(eq 8) for the carbenoid. These alcohols would appear to coordinate with the metal ion more favorably for the addition of an adjoining ligand.



(8)

Allyl amine a more strongly bonding ligand, when employed in these reactions, completely suppresses isopropyl alcohol formation. The products from isopropylidene bromide are propane (41%) and propylene (59%). This result is in keeping with the heightened reductive capacity of amine complexes of Cr(II).[6] We are not continuing this investigation.

Experimental Section

Preparation, transfer, storage, and analysis of chromous sulfate was accomplished as previously described. All purchased and prepared starting substances and reference samples had physical constants and infrared spectra that checked the literature. Liquids gas chromatographed as one peak. 1-Cyano-2,2-dimethylcyclopropane was obtained from 2,2-dimethyl-1,3-dihydroxypropane in two steps.[7] In contrast to literature reports, and under a variety of conditions, treatment of lithium dimethylcyclopropylcarboxylate with methyllithium in ether yielded dimethylcyclopropyldimethylcarbinol in addition to dimethylcyclopropyl methyl ketone. Dimethylcyclopropylmethylcarbinol was prepared from the carefully fractionated ketone by lithium aluminum hydride reduction.[8]

Trapping Experiments.—Reactions and product analysis were carried out as previously described.

With 3-Hydroxybutene-1.—To a solution composed of the olefin, 50 g, 50 ml of dimethylformamide, and 9.77 g of 2,2-dibromopropane (0.0484 mol) was slowly added 162.2 ml of 0.97 *M* $CrSO_4$ solution at room temperature. The reaction was allowed to stir at room temperature under nitrogen for 24 hr. At this time 0.141 mol of Cr(II) was consumed. In addition to propane (2.5%), propylene (14%), and isopropyl alcohol (53%), 1.91 g of a fraction of *cis*- and *trans*-1,1-dimethyl-1-hydroxy-3-pentene in equal amounts was obtained. The isomer mixture had bp 68–69° (45 mm), $n^{24}\mathrm{D}$ 1.4337. *Anal.* Calcd for $C_7H_{14}O$: C, 73.63; H, 12.4; Found: C, 73.39; H, 12.18. The olefinic pair was cleanly separated from the isomer 2,3-dimethyl-2-hydroxy-4-pentene. The latter alcohol (8.5 min) emerged before the *cis–trans* pair (12.5 and 11 min, respectively) on a 3-ft DC-710 column at 70°. Pure factions of the *cis* and the *trans* isomers were trapped from a 10-ft 15% DC-710 on firebrick column at 110°. The discerning infrared features were (cm^{-1}) *cis* 680 (strong), 765, 775, 953 and 974 (medium), 1650 (weak); *trans* 960 (s), 1660 (w). Otherwise the spectra were identical. The nmr spectra accord with the structures and are similar. Gas chromatographic analysis of the isomer pair before distillation placed the yield at 30%.

5-Hydroxypentene-1.—Under identical conditions with this olefin, propane (1%), propylene (17), and isopropyl alcohol (59%) were produced. In addition, the other major substance detected was γ-dimethylcyclopropylpropanol. The substance was isolated by trapping the corresponding peak from gas chromatography. *Anal.* Calcd for $C_5H_{10}O$: C, 74.98; H, 12.60. Found: C, 74.48; H, 12.48. The substance had $n^{24}\mathrm{D}$ 1.4391; ir (cm^{-1}) 3300, 2965 (sh), 2919, 2850 (sh), 1432, 1369, 1050, 1010 all strong; nmr (ppm) δ 0.1 s (1 H), 0.42 d(?) (2 H), 1.02 s (6 H), 1.54 m (4 H), 2.25 s (1 H), 3.688 t (2 H).

Acrylonitrile.—In addition to propane (trace), propylene (12%), isopropyl alcohol (35%), and propionitrile (50%),[9] a small amount of dimethylcyclopropylacetonitrile (~2%) was obtained. The substance was identical with authentic materials (*vide supra*) in all respects.

Rearrangement of Dimethylcyclopropylmethylcarbinol.—The carbinol (0.5 g), 3 ml of DMF, 2.7 g of chromic sulfate, and 10 ml of 0.55 *M* chromous sulfate solution were stirred for 24 hr under nitrogen (pH ~2.6) at 25°. The solution was extracted with ether, washed with sodium bicarbonate and water, and dried over sodium sulfate. The concentrated ethereal solution was analyzed by gas chromatography on a 10-ft 20% DC-710 column. The product coemerged only with the *trans*-olefinic alcohol at all temperatures. No trace of the *cis* material could be detected. At 98° the emergence times are dimethylcyclopropylmethylcarbinol (37 min), *trans*-2-methyl-2-hydroxy-4-hexene (40 min), and *cis*-2-methyl-2-hydroxy-4-hexene (45 min). The infrared and nmr spectrum were identical with the *trans* isomer obtained from 3-hydroxybutene-1. An acid-catalyzed rearrangement with DMF (2 ml), water (10 ml), and concentrated H_2SO_4 (0.3 ml) yielded the same result. No isomerizations occurred on the column. Under reaction conditions dimethylcyclopropylcarbinol was unchanged.

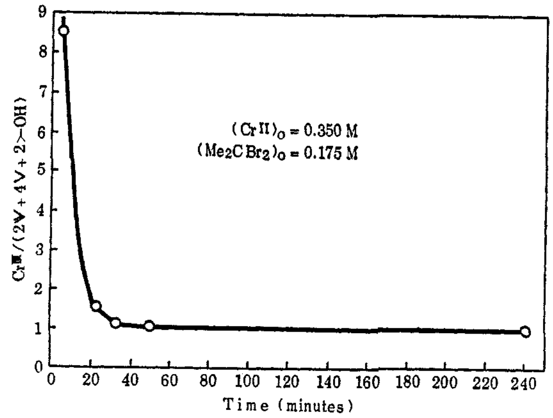


Figure 1.—The relative rates of production of Cr(III) and organic products from the reaction of isopropylidene bromide at −5° in the presence of 3-buten-1-ol.

---

[6] J. K. Kochi and D. M. Singleton, *J. Amer. Chem. Soc.*, **90**, 1582 (1968).

[7] E. R. Nelson, M. Maienthal, L. A. Lane, and A. A. Benderly, *ibid.*, **79**, 3467 (1957).

[8] M. Julia, S. Julia, and J. S. Du Chaffant, *Bull. Soc. Chim. Fr.*, 1736 (1960).

[9] This yield is based on Cr(II) consumption. The reduction of this olefin has been described: C. E. Castro, R. D. Stephens, and S. Moje', *J. Amer. Chem. Soc.*, **88**, 4964 (1966).

Registry No.—*cis*-1,1-Dimethyl-1-hydroxy-3-pentene 19639-96-4; *trans*-1,1-dimethyl-1-hydroxy-3-pentene, 19639-97-5; 5-hydroxypentene-1, 821-09-0.

Acknowledgment.—The authors are indebted to the National Science Foundation for generous support. We are grateful to Professor W. Robert Moore for suspecting the rearrangement of dimethylcyclopropylcarbinol under our reaction conditions.

Aluminum Chloride Catalyzed Arylation of Ferrocene with Hydrazines

GILBERT P. SOLLOTT AND WILLIAM R. PETERSON, JR.

Pitman-Dunn Research Laboratories, Frankford Arsenal,
Philadelphia, Pennsylvania 19137

Received December 5, 1968

The phenylation of aromatic hydrocarbons with diazonium salts proceeds by electrophilic substitution in the case of haloborates,[1] or radical substitution in the case of chlorides.[1,2] In the latter instance, the presence of aluminum chloride changes the character of the reaction to that of electrophilic substitution,[3] and it would appear that, in common with the former, phenyl cation ($C_6H_5^+$) is generated *via* loss of molecular nitrogen by an S_N1 mechanism.

We report a new arylation process in which nitrogen is displaced from the aromatic ring very likely by a concerted displacement mechanism in aluminum chloride catalyzed reactions of arylhydrazines with ferrocene. This appears at the same time to be not only the first indisputable example of the arylation of ferrocene by an ionic mechanism, but also the first arylation of the neutral species.

Beckwith and Leydon[4] have convincingly demonstrated that arylation of ferrocene with diazonium salts (and N-nitrosoacetanilide) proceeds by free-radical attack on ferricinium ion,[5] rather than ionic substitution of the neutral species.[6] Thus

$$\mathrm{FcH} + \mathrm{ArN_2^+} \longrightarrow \mathrm{FcH^+} + \mathrm{ArN_2\cdot}$$

$$\mathrm{ArN_2\cdot} \longrightarrow \mathrm{Ar\cdot} + \mathrm{N_2}$$

$$\mathrm{FcH^+} + \mathrm{Ar\cdot} \longrightarrow [\mathrm{FcArH}]^+ \longrightarrow \mathrm{FcAr} + \mathrm{H^+}$$

This mechanism, besides explaining why ferrocene (FcH) is unaffected by radicals or aryldiazonium salts under experimental conditions precluding the formation of ferricinium ion, explains why diazonium salts do not react with ferricinium ion in the absence of free ferrocene.

We have verified that in contrast to the behavior of aromatic hydrocarbons,[1] ferrocene reacts with *o*-tolyldiazonium fluoroborate[7] by radical rather than electrophilic substitution. Complete inhibition was obtained when the reaction was conducted in the presence of an excess of powdered zinc to preclude the formation of ferricinium ion.

In the present work (Table I), *o*- and *p*-tolyl-, *p*-bromophenyl-, and *α*-naphthylferrocenes were obtained as sole monoarylated products of the reactions of the corresponding hydrazines in *n*-heptane, establishing the ring carbon atom formerly connected to hydrazine nitrogen as the point of attachment of the ferrocene moiety. A reaction with zinc present to reduce any ferricinium ion formed, but otherwise identical with that producing phenylferrocene in 34% yield (Table I), gave the product in 29% yield. This served to establish that attack of aryl radical on ferricinium ion, generated as follows, is not part of the reaction mechanism.[8]

$$\mathrm{FcH} + \overset{\delta+}{\mathrm{Ar}}\mathrm{NHNH_2}\cdot\overset{\delta-}{\mathrm{Al}}\mathrm{Cl_3} \longrightarrow \mathrm{FcH^+} + \mathrm{Ar\cdot} + \mathrm{H_2NNHAlCl_3^-}$$

TABLE I

ARYLATION OF FERROCENE (FcH) WITH HYDRAZINES[a]

Ar in $ArNHNH_2$	Molar ratio, FcH:$ArNHNH_2$:$AlCl_3$	Product (yield, %[b])	Recovd FcH, %
C_6H_5	1:1:1	C_6H_5Fc (4)	77
C_6H_5	1:1:2	C_6H_5Fc (20)	66
C_6H_5	1:2:2	C_6H_5Fc (36)	56
C_6H_5	1:2:3	C_6H_5Fc (34)[c,d]	52
C_6H_5 (HCl)[e]	1:2:3	C_6H_5Fc (23)	54
o-$CH_3C_6H_4$	1:2:3	*o*-$CH_3C_6H_4Fc$ (14)	52
p-$CH_3C_6H_4$(HCl)[e]	1:2:3	*p*-$CH_3C_6H_4Fc$ (7)	33
p-BrC_6H_4	1:2:3	*p*-BrC_6H_4Fc (19)[f]	46
α-$C_{10}H_7$	1:2:3	*α*-$C_{10}H_7Fc$ (16)	60

[a] Solvent: *n*-heptane. [b] Based on starting ferrocene. [c] In the presence of powdered zinc, the yield was 29%. [d] 1,1′-Diphenylferrocene (<1%) was also obtained. A reaction in *n*-octane gave 2% of this compound besides 26% of C_6H_5Fc. [e] The hydrazine was employed as the hydrochloride. [f] Also isolated was 1,1′-bis(*p*-bromophenyl)ferrocene (1%).

The results are consistent with an ionic mechanism involving direct displacement by ferrocene on the benzene ring, with simultaneous removal of hydrazide ion by aluminum chloride. Thus

$$\mathrm{FcH} + \overset{\delta+}{\mathrm{Ar}}\mathrm{NHNH_2}\cdot\overset{\delta-}{\mathrm{Al}}\mathrm{Cl_3} \longrightarrow [\mathrm{FcArH}]^+[\mathrm{H_2NNHAlCl_3}]^- \longrightarrow \mathrm{FcAr} + \mathrm{H_2NNHAlCl_2} + \mathrm{HCl}\ \text{(by-product)}$$

Alkylated ferrocenes were not produced in attempted reactions of methyl- or *t*-butylhydrazines, raising the interesting question of whether or not the attack of ferrocene on aryl may initially involve the ring π system of each.[9,10] The displacement of hydrazide ion from arylhydrazines may be grossly related to Friedel–

---

[1] G. A. Olah and W. S. Tolgyesi, *J. Org. Chem.*, **26**, 2053 (1961), and references cited therein.

[2] The free-radical nature of the Gomberg-Bachman reaction, in which the arylating agent is a diazonium salt and base, is well recognized [C. Rüchardt and E. Merz, *Tetrahedron Letters*, 2431 (1964); E. L. Eliel, J. G. Saha, and S. Meyerson, *J. Org. Chem.*, **30**, 2451 (1965); G. Binsch and C. Rüchardt, *J. Amer. Chem. Soc.*, **88**, 173 (1966)], although perhaps not as well understood [G. R. Chalfont and M. J. Perkins, *ibid.*, **89**, 3054 (1967)].

[3] G. A. Olah in "Friedel-Crafts and Related Reactions," Vol. I, G. A. Olah, Ed., Interscience Publishers, London, 1963, pp 66, 67, and references therein.

[4] A. L. J. Beckwith and R. J. Leydon, *Tetrahedron*, **20**, 791 (1964).

[5] W. F. Little and A. K. Clark, *J. Org. Chem.*, **25**, 1979 (1960).

[6] M. Rosenblum, W. G. Howells, A. K. Banerjee, and C. Bennett, *J. Amer. Chem. Soc.*, **84**, 2726 (1962), concluding that ferrocene is relatively inert toward attack by free radicals, proposed that arylferrocenes are formed *via* intramolecular decomposition of a ferrocene–diazonium salt charge-transfer complex.

[7] W. F. Little, C. N. Reilley, J. D. Johnson, K. N. Lynn, and A. P. Sanders, *ibid.*, **86**, 1376 (1964).

[8] Ferricinium ion could not be detected on work-up of the reaction mixtures, except for trace amounts when the aluminum chloride was present in excess of the hydrazine. R. L. Schaaf and C. T. Lenk, *J. Org. Chem.*, **28**, 3238 (1963), have discussed the oxidation of ferrocene by aluminum chloride.

[9] Nucleophilic attack of ferrocene on silicon and germanium *via* the ring π system was suggested previously.[10]

[10] G. P. Sollott and W. R. Peterson, Jr., *J. Amer. Chem. Soc.*, **89**, 5054, 6783 (1967).