K_{eq} (k_1/k_{-1}) = 1.88 ± 0.04 (CD_3CN), 1.61 ± 0.04 (CH_2Cl_2), 1.55 ± 0.02 (CCl_4).[11] In analogy with **5**, azirines **9** and **10** afforded 2,3-pentanedione and a mixture of methoxyazirines upon treatment with water and methanol, respectively.

The thermal nature of the isomerization of the initially formed azirines **9** and **10** was revealed by conducting the photolyses at low temperature. Irradiation of **7** at −40° afforded exclusively azirine **9** by nmr. Similarly, **8** gave exclusively **10**. Warming solutions of pure **9** and **10** in the nmr probe resulted in the appearance and growth of new peaks corresponding to **10** and **9**, respectively. In a given solvent, solutions of pure **9** and **10** exhibited identical nmr spectra after thermal equilibration.

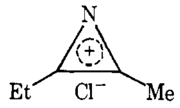
The kinetic data for the isomerizations of **9** and **10** are summarized in Table I;[12] activation parameters (CH_2Cl_2) are:[13] forward process (**9** → **10** (k_1)), E_a = 15 kcal/mol, $\Delta S^{\ddagger}$ (−15°) = −15 eu; reverse process (**10** → **9** (k_{-1})), E_a = 15 kcal/mol, $\Delta S^{\ddagger}$ (−15°) = −16 eu.

Table I. Kinetic Data for the Isomerization $\mathbf{9} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathbf{10}$

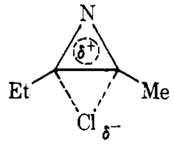
Solvent	Temp, °C	$k_1 \times 10^4$, sec^{-1}	$k_{-1} \times 10^4$, sec^{-1}	k_1, rel
CCl_4	−10	0.180[a]	0.116[a]	1
CH_2Cl_2	−10	2.13[b]	1.33[b]	12
CD_3CN	−10	14.2[b]	7.54[b]	79

[a] Extrapolated from rate data at +22 and +33°. [b] Average value of k calculated from forward and reverse results.

The dependence of rate on solvent polarity (see Table I) clearly establishes the polar nature of the transition state and is consistent with the intermediacy of an azacyclopropenyl ion–chloride ion pair **11** in the isomerizations of **9** and **10**.[14–16] However, an alternative mechanism involving polar bridged transition state **12** cannot be excluded.



11



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Reaction of **5** or **9** and **10** with silver salts results in the immediate precipitation of silver chloride but thus far work-up has afforded only intractable material.[17,18]

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for partial support of this research. Helpful discussions with Professors J. O. Edwards, R. G. Lawler, and L. A. Spurlock are gratefully acknowledged. Finally we thank Mr. J. G. Henkel for the use of his computer program.

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[11] Determined by nmr integration; errors represent standard deviations.

[12] Obtained by nmr by following the change in intensity of the methyl singlet of **9** and 10 with time.

[13] Determined from Arrhenius plots of rate data on forward and reverse processes at four different temperatures, −18, −10, 0, and +15°.

[14] The solvolysis of 1,2-diaryl-3,3-dichloroaziridines involves a 1,2-intramolecular chlorine migration *via* an aziridinyl cation–chloride ion pair intermediate: R. E. Brooks, J. O. Edwards, G. Levey, and F. Smyth, *Tetrahedron*, **22**, 1279 (1966). See also, J. A. Deyrup and R. B. Greenwald, *J. Amer. Chem. Soc.*, **87**, 4538 (1965). Similarly, the thermal rearrangement of 2-chloro epoxides to 2-chloro ketones involves a 1,2-intramolecular chlorine shift: R. N. McDonald and R. N. Steppel, *ibid.*, **92**, 5664 (1970), and previous papers in the series.

[15] The degenerate isomerization of 3-chlorocyclopropene, a process which is believed to proceed *via* the cyclopropenyl cation, is not only orders of magnitude faster in similar solvents but also appears to exhibit a much larger rate dependence on solvent polarity: R. Breslow, G. Ryan, and J. T. Groves, *ibid.*, **92**, 988 (1970).

[16] Mechanisms involving elimination–addition or addition–elimination of HCl were excluded on the basis of the fact that these processes would not exhibit simple first-order kinetics. Control experiments in which HCl was added to pure solutions of **9** and 10 afforded good first-order kinetic plots and a small decrease in the first-order rate constants k_1 and k_{-1} was observed.

[17] A reported attempt by Hassner to prepare diphenylazacyclopropenyl iodide was likewise unsuccessful.[4a]

[18] Salts of the cyclopropenyl cation have been prepared from 3-chlorocyclopropene: R. Breslow and J. T. Groves, *J. Amer. Chem. Soc.*, **92**, 984 (1970).

[19] Petroleum Research Fund Graduate Fellow, 1969–1970.

The Mechanism of the Silver-Catalyzed Reaction of Grignard Reagents with Alkyl Halides

Sir:

The coupling of alkyl groups by the reaction of Grignard reagents and alkyl halides (eq 1) is induced by

$$R'MgX + R\text{–}X \xrightarrow{MX_n} R\text{–}R' + MgX_2 \qquad (1)$$

a variety of transition metal halides (MX_n).[1] The mechanism of this facile transformation is of interest for catalytic processes generally, and has been the subject of extensive investigations.[2] The multiplicity of reactions possible with various metal catalysts, however, has precluded a general and systematic description of the elementary steps involved in the catalytic sequences. Thus, the roles of the metal catalysts, the reactions of the organometallic intermediates, and the presence of transient alkyl radicals have remained unclear.

We examined initially the *stoichiometric* reduction of transition metal salts by Grignard reagents, and then studied the *catalytic* coupling of Grignard reagents with alkyl halides. Thus, Grignard reagents in tetrahydrofuran (THF) solution reacted with stoichiometric amounts of silver(I) salts (halides, acetate, perchlorate) on mixing at 2° according to eq 2.[3,4] Similarly, when

$$RMgX + AgY \longrightarrow RAg + MgXY \qquad (2a)$$

$$2RAg \longrightarrow R\text{–}R + 2Ag \qquad (2b)$$

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[1] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Englewood Cliffs, N. J., 1954, p 122.

[2] M. H. Abraham and M. J. Hogarth, *J. Organometal. Chem.*, **12**, 1, 497 (1968); D. I. Davies, J. N. Done, and D. H. Hey, *J. Chem. Soc. C*, 1392, 2021, 2506 (1969); W. B. Smith, *J. Org. Chem.*, **26**, 4206 (1961); L. H. Slaugh, *J. Amer. Chem. Soc.*, **83**, 2734 (1961); G. Costa, G. Mestroni, and G. Boscarato, *Ric. Sci.*, **7**, 315 (1964); R. O. C. Norman and W. A. Walters, *J. Chem. Soc.*, 950 (1957).

[3] (a) *Cf.* J. H. Gardner, *et al.*, *J. Amer. Chem. Soc.*, **51**, 3375 (1929); **59**, 2583 (1937); 61, 2551 (1939); *J. Org. Chem.*, **5**, 61, 126 (1940); (b) *cf.* also C. E. H. Bawn, *et al.*, *J. Chem. Soc.*, 3923 (1960); F. Glocking and D. Kinston, *ibid.*, 3001 (1959); and H. C. Brown, *et al.*, *J. Amer. Chem. Soc.*, **83**, 1001, 1002 (1961).

[4] (a) Hereafter solvation by THF will not be explicitly included. (b) Organometals are generally more stable in THF than in diethyl ether. (c) K. Wada, M. Tamura, and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 6656 (1970).

Table I. Reaction of Grignard Reagents with Silver(I) Bromide[a]

Grignard reagent[b]		Alkyl dimers[c]			
RMgBr	R′MgBr	R–R	R–R′	R′–R′	Σ[d]
Et–	Et–		92		92[e]
Et–	*n*-Pr–	47	37	12	96
Et–	*i*-Pr–	41	28	10	79[f]
Et–	*tert*-Bu–	36	5	19	60[f]
Et–	$CH_2{=}CH$–	22	68	7	97

[a] In 21 ml of THF at 2° for 60 min with 1.7–2.2 mmol of AgBr. [b] 3.5 mmol each. [c] Yield (per cent) based on silver(I) according to eq 2. [d] Total dimer yield. [e] In addition to 2% ethylene and 6% ethane. [f] In addition to 7% propylene and 10% propane. [g] In addition to 17% isobutane and 17% isobutylene.

Table II. Structural Effects of the Alkyl Halide on the Rate of Coupling with Ethylmagnesium Bromide Catalyzed by Silver[a]

Alkyl halide[b]	Rates of formation of products[c]			
R′–Br	Et–Et	Et–R′	R′–R′	ΣEt, R′[d]
Et–Br	15.4			35
n-Pr–Br	7.7	1.2	0.3	33[e]
i-Pr–Br	15	17	5.4	101
tert-Bu–Br	95	112	10	660

[a] In THF solutions at 2.0°, Ag = 4.5×10^{-4} *M*, EtMgBr = 0.18 *M*. [b] 0.30 *M*. [c] Initial rate given as 3.6×10^{6} *M*/sec. [d] Rate of formation of all products = $C_2H_6 + C_2H_4 + RH + R(-H) + 2$ (coupled products). [e] Reaction somewhat complicated by alkyl exchange.

two Grignard reagents were simultaneously exposed to the same conditions, a mixture of three dimers was formed as shown in Table I.

$$RAg,\ R'Ag \longrightarrow [R_2,\ R'_2,\ R\text{–}R] + 2Ag \qquad (3)$$

The oxidative dimerization of Grignard reagents with silver *nitrate* was unique in that less than stoichiometric amounts of silver(I) was required (25% based on eq 2), since nitrate was capable of reoxidizing silver. Analogously, if lithium nitrate, nitrogen dioxide, or methyl nitrate was deliberately added, only catalytic amounts (less than 10 mol %) of silver(I) bromide were required for oxidative dimerization. More importantly, the use of silver nitrate rendered a large amount of the reduced silver in a soluble form.[5] The latter, which has an absorption maximum at 415 nm (ϵ 1.5 × 10^4),[6] could be reversibly precipitated with diglyme as a 1:1 Ag–Mg complex to which we ascribe the oxidation state of silver as 0.

The soluble silver complex is an efficient catalyst at concentrations as low as 10^{-5} *M* for the production of *n*-butane from ethylmagnesium bromide and ethyl bromide. We deduce from kinetic experiments (utilizing initial slopes) that the rate of formation of butane can be approximated within 10% by eq 4. The rate

$$\frac{d[C_4H_{10}]}{dt} = k[\text{Ag complex}]^{1.0}[\text{EtBr}]^{0.8}[\text{EtMgBr}]^{0.1} \qquad (4)$$

of coupling, thus, can be described as roughly first order in alkyl halide and zero order in Grignard reagent. The rate of the catalytic coupling of ethylmagnesium bromide with other alkyl halides is given in Table II, the last column of which shows that the rate of overall reaction is *tert*-BuBr > *i*-PrBr > *n*-PrBr in a ratio of 20:3:1. Structural changes in the Grignard reagent led to no apparent systematic variation in the reaction rate.[7] On the basis of these studies we propose the following catalytic mechanism.[8]

$$R'MgX + AgX \longrightarrow R'Ag + MgX_2 \qquad (2')$$

$$RAg,\ R'Ag \longrightarrow [R\text{–}R,\ R'\text{–}R,\ R'\text{–}R'] + 2Ag \qquad (5)$$

$$Ag + R\text{–}X \xrightarrow{\text{slow}} R\cdot + AgX \qquad (6)$$

$$R\cdot + Ag \longrightarrow RAg,\ \text{etc.} \qquad (7)$$

The rate-limiting step in this mechanism is given by eq 6 in which the alkyl halide is responsible for the reoxidation of silver produced in eq 5.[9] This slow step is closely akin to the production of alkyl radicals by the ligand-transfer reduction (eq 8) of alkyl halides

$$R\text{–}X + M^{n+} \longrightarrow R\cdot + M^{(n+1)+}X \qquad (8)$$

with other reducing metal complexes such as those derived from chromium(II), cobalt(II), and tin(III) complexes.[9b] These reductants show the same variation in rates with the structures of the alkyl halide as that presented in Table II for Ag.

More direct evidence for the selective formation of alkyl radicals from the alkyl halide is shown by trapping experiments. Thus, the catalytic coupling of ethylmagnesium bromide and *tert*-butyl bromide at 2° can be carried out in the presence of styrene as a radical scavenger (Table III). The total rate of formation of all products derived from the ethyl (Grignard) moiety was virtually unchanged up to 0.4 *M* styrene under these conditions. On the other hand, the total rate of formation of all those products from the *tert*-butyl (bromide) moiety, excluding adducts to styrene, was

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(5) This silver complex contained no silver(I) extractable with concentrated ammonia. It reacted with dilute aqueous sulfuric acid to precipitate silver metal quantitatively, but liberated no alkane in the process. It was capable of oxidatively dimerizing allyl and benzyl bromides quantitatively to biallyl and bibenzyl, respectively (silver bromide was formed). (b) We will refer hereafter to this as a soluble silver complex, although repeated and various attempts to isolate a pure compound have not yet been successful; compare, *e.g.*, R. R. DeWald, J. M. Brooks, and M. A. Trickey, *Chem. Commun.*, 963 (1970), and R. S. Eachus and M. C. R. Symons, *ibid.*, 1336 (1970).

(6) (a) The visible absorption spectrum of the silver complex is independent of the Grignard reductant employed. The same species is formed from silver nitrate and diethylmagnesium or ethyllithium, or alternatively from ethylmagnesium bromide and silver bromide (perchlorate) with lithium nitrate or nitrogen dioxide. The degree of aggregation of the silver in the complex is unknown. (b) A new species absorbing at 400 nm (ϵ 2.0 × 10^4) is formed in the presence of excess Grignard reagent or dialkylmagnesium. It is probably a complex of silver with the Grignard reagent, and it is the active species reacting with alkyl bromides under conditions in which the soluble silver absorbing at 415 nm is unreactive.

(7) The relative order of reactivity (*n*-PrMgBr = 100) was qualitatively determined by measuring the extent of reaction between *n*-PrBr (0.15 *M*) and various Grignard reagents (0.20 *M*) for an arbitrary length of time in the presence of silver catalyst (7.9 × 10^{-4} *M*) at 25°: CH_3 (40), Et (200), *n*-Pr (100), *i*-Pr (450), *tert*-Bu(100), neopentyl (20), vinyl (20), and phenyl (5).

(8) (a) Fluoroalkylsilver(I) species have been recently identified: W. T. Miller, *et al.*, *J. Amer. Chem. Soc.*, **90**, 7367 (1968); **91**, 6532 (1969); V. R. Polishchuk, *et al.*, *Tetrahedron Lett.*, 3933 (1970); see also, C. D. M. Beverwijk, *et al.*, *Organometal. Chem. Rev.*, **5**, 215 (1970). (b) The participation of other processes involving homolytic displacements and substitutions on alkylsilver such as

$$R'\cdot + RAg \longrightarrow R'R + Ag$$

cannot be excluded at this point [*cf.* J. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940, 3942 (1969)].

(9) (a) Initiation of vinyl polymerization by silver powder and aralkyl halides has been shown [M. Kinoshita and N. Yoshizumi, *J. Chem. Soc. Jap.*, **71**, 409, 892 (1968)]; (b) J. K. Kochi and J. W. Powers, *J. Amer. Chem. Soc.*, **92**, 137 (1970); P. B. Chock and J. Halpern, *ibid.*, **91**, 5802 (1969); H. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968). (c) Studies of spin trapping and chemically induced dynamic polarization are in progress [*cf.* E. G. Janzen, *ibid.*, **4**, 31 (1971), and H. R. Ward, R. G. Lawler, and T. A. Marzilli, *Tetrahedron Lett.*, 521 (1970)].

Table III. Trapping the *tert*-Butyl Radical from the Ag-Catalyzed Reaction of EtMgBr and *tert*-BuBr[a]

[Ag], 10^4 *M*	[Styrene], *M*	Rates of formation of products[b] ΣEt[c]	Σ*tert*-Bu[d]	Σ*tert*-Bu/ΣEt
2.9	0	212	207	0.98
2.9	0.415	162	53	0.33
2.9	2.08	122	41	0.33
8.9	0.415	397	262	0.66

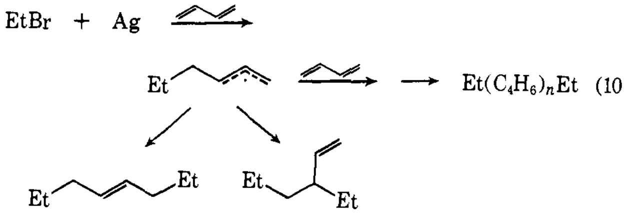
[a] In THF solution containing 0.18 *M* EtMgBr and 0.30 *M* *tert*-BuBr at 2°. [b] Initial rate given as 3.6×10^6 *M*/sec. [c] $C_2H_4 + C_2H_6 + 2C_4H_{10} + CH_3CH_2C(CH_3)_3$. [d] $i\text{-}C_4H_8 + i\text{-}C_4H_{10} + 2\text{-}[(CH_3)_3C]_2 + CH_3CH_2C(CH_3)_3$.

decreased to 25% of its value in the absence of styrene. It is clear that styrene was able to trap most of the *tert*-butyl radicals[10] formed as intermediates in eq 6′.

$$tert\text{-BuBr} + \text{Ag} \longrightarrow tert\text{-Bu}\cdot + \text{AgBr} \qquad (6')$$

$$tert\text{-Bu}\cdot + \text{PhCH{=}CH}_2 \longrightarrow \text{Ph}\underset{\cdot}{\text{C}}\text{HCH}_2\text{-}tert\text{-Bu, etc.} \qquad (9)$$

In a similar experiment a mixture of telomeric adducts (eq 10) was isolated from the catalytic reaction of ethylmagnesium bromide and ethyl bromide in the presence of butadiene as scavenger.



(10)

The catalytic reaction of *cis*-propenylmagnesium bromide with methyl bromide yielded *cis*-butene-2 (>94%), in agreement with the work of Whitesides and Casey,[11] who showed that the coupling of vinylsilver(I) complexes occurred stereoselectively. On the other hand, *cis*-propenyl bromide and methylmagnesium bromide were catalytically converted to a mixture of *cis*-butene-2 (70%) and *trans*-butene-2 (30%). The latter resulted from the inversion of configuration of the 1-propenyl radical.

Finally, we wish to comment on the formation of alkyl dimers according to eq 5. Previous studies[11] showed that the decomposition of 1-alkenylsilver(I) did not occur *via* dimerization of vinylic radicals[3b] and are supported by the observation (Table I) that styrene has no effect on the decomposition of alkylsilver(I). Furthermore, our results obtained from catalytic studies are also consistent with a concerted bimolecular mechanism since the rate of the coupling process relative to disproportionation increased with the bulk concentration of the silver catalyst.[12,13]

Acknowledgment. We wish to thank the National Science Foundation for granting financial support and R. A. Bailey for preliminary studies.

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(10) (a) The *tert*-butyl adducts to styrene showed characteristic bands at 1357 and 1385 cm^{-1} in the infrared spectrum but were not analyzed quantitatively since high molecular weight polymers were also formed. (b) The *tert*-butyl radicals were not completely trapped even at higher styrene concentrations. They may have been directly trapped by another silver, particularly if the latter is aggregated, *e.g.*

$$\text{R–X} + (\text{Ag})_n \longrightarrow \text{RAg} + \text{AgX} + (\text{Ag})_{n-2}$$

(11) G. M. Whitesides and C. P. Casey, *J. Amer. Chem. Soc.*, **88**, 4541 (1966).

(12) (a) This assumes that alkane and alkene are formed by processes first order in organosilver(I) [*cf.* G. M. Whitesides, *et al.*, *ibid.*, **92**, 1426 (1970)]. (b) It is not clear whether di- and polynuclear alkylsilver(I) species are also important intermediates.[6] The degree of aggregation would also influence the relative rates on dilution since coupling may also occur in the aggregate.

(13) The mechanism of the coupling of aryl Grignard reagents with alkyl halides is unique. Thus, phenylsilver(I) is significantly more stable than alkylsilver(I) and could be readily isolated under our conditions. It reacted with alkyl Grignard reagents to yield only *dialkyl*, and with ethyl bromide only on heating (60°) to produce biphenyl and Ag, exclusively. Cross coupling was observed with the allyl bromide. The catalyzed reaction of ethylmagnesium bromide and bromobenzene was complicated by the exchange reaction.

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Alkylcopper(I) in the Coupling of Grignard Reagents with Alkyl Halides

Sir:

Copper complexes have been used as catalysts in the reaction of Grignard reagents with alkyl halides in ethereal solutions.[1] The mechanism of the catalysis, however, has been obscured by the occurrence of several simultaneous homolytic and heterolytic processes. In this report the various competing reactions have been clearly differentiated by the use of tetrahydrofuran (THF) as solvent in which the key organocopper(I) intermediates are more stable. Further, we wish to show that catalysis of the coupling reaction by silver[2] and copper, despite their similarity, occurs by fundamentally different mechanisms.

Alkylcopper(I) species were readily formed at temperatures less than −10° in THF by metathesis between copper(I) salts and Grignard reagents.[3,4] The same alkylcopper(I) was also produced from copper(II)

$$\text{RMgX} + \text{Cu}^{\text{I}}\text{Y} \longrightarrow \text{RCu}^{\text{I}} + \text{MgXY} \qquad (1)$$

salts at temperatures as low as −78°, accompanied spontaneously by 0.5 mol of dialkyl.

$$2\text{RMgX} + \text{Cu}^{\text{II}}\text{Y}_2 \longrightarrow \text{RCu}^{\text{I}} + 2\text{MgXY} + 0.5\text{R}_2 \qquad (2)$$

Solutions of alkylcopper(I) showed varying stability and underwent autocatalytic disproportionation according to eq 3[4,5] (Table I) in sharp contrast to the

$$2\text{RCu}^{\text{I}} \longrightarrow \text{RH} + \text{R}(-\text{H}) + 2\text{Cu} \qquad (3)$$

behavior of alkylsilver(I).[2] The disproportionation reaction (3) was unaffected by radical traps such as styrene in accord with Whitesides' observation[6] of the

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(1) V. D. Parker, L. H. Piette, R. M. Salinger, and C. R. Noller, *J. Amer. Chem. Soc.*, 86, 1110 (1964); V. D. Parker and C. R. Noller, *ibid.*, **86**, 1112 (1964).

(2) M. Tamura and J. Kochi, *ibid.*, **93**, 1483 (1971).

(3) (a) H. Gilman and J. M. Straley, *Recl. Trav. Chim. Pays-Bas.*, **55**, 821 (1936); (b) see also K. H. Thiele and J. Kohler, *J. Organometal. Chem.*, **12**, 225 (1968); G. Costa, G. Alti, and L. Stefani, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Natur., Rend.*, **31**, 267 (1961); C. E. H. Bawn and R. Johnson, *J. Chem. Soc.*, 3926, 4162 (1960).

(4) K. Wada, M. Tamura, and J. Kochi, *J. Amer. Chem. Soc.*, **92**, 6656 (1970).

(5) It was also possible to carry out the decomposition of Grignard reagents (eq 1 or 2 and 3) with less than stoichiometric amounts of copper if lithium nitrate or NO_2 was used as a mild oxidant to reconvert copper to copper(I,II). Some of the copper remained in solution as a metastable species (λ ≈ 575 nm) which quantitatively precipitated copper metal on standing or on treatment with dilute sulfuric acid [*cf.* silver, ref 2].

(6) (a) G. M. Whitesides and C. P. Casey, *J. Amer. Chem. Soc.*, **88**, 4541 (1966); (b) G. M. Whitesides, J. San Filippo, Jr., E. R. Stedronsky, and C. P. Casey, *ibid.*, **91**, 6542 (1969); **92**, 1426 (1970).