Tetrahedron Vol. 44, No. 20, pp. 6295 to 6304, 1988
Printed in Great Britain.

0040-4020/88 $3.00+.00

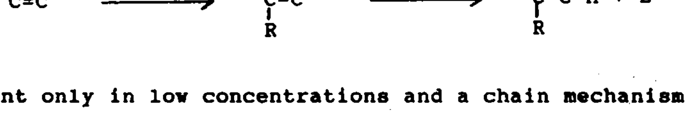
EVALUATION OF TRIBUTYLGERMANIUM HYDRIDE AS A REAGENT FOR THE REDUCTIVE ALKYLATION OF ACTIVE OLEFINS WITH ALKYL HALIDES

Philip Pike, Susan Hershberger, and James Hershberger*
Chemistry Deparment
Miami University
Oxford, Ohio 45056

(*Received in USA* 6 *April* 1988)

Abstract- The reductive alkylation of acrylonitrile and of 2-cyclohexen-1-one by alkyl halides using tributylgermanium hydride was systematically evaluated. The performance of the germanium reagent was compared to that of the more commonly employed tributyltin hydride. For certain applications the germanium reagent afforded improved yields without the use of large excess olefin concentrations. Disadvantages of the germanium reagent include a tendency to hydrogermylate active terminal olefins and a general low reactivity towards alkyl halide substrates. The following series of six other triorganotin and triorganogermanium hydrides were also briefly screened for possible application to reductive alkylations: trimesityltin hydride, trimesitylgermanium hydride, triphenyltin hydride, triphenylgermanium hydride, trineopentyltin hydride, and tricyclohexylgermanium hydride.

Introduction. The free-radical alkylation of active olefins has recently gained prominence as a synthetic transformation. This is due largely to the developmental work of the Giese group. Several excellent reviews of the "Giese" reaction have been published.[1-4] The key mechanistic features are the addition of a carbon-centered free radical to an active olefin, and the subsequent quenching of the resulting free radical by hydrogen atom transfer from an appropriate donor (reaction 1). In the most common form of the alkylation reaction, free radicals are present only in low concentrations and a chain mechanism is operative. The



$$\overset{Y}{C=C} \xrightarrow{R^{\cdot}} \underset{R}{C}-\overset{Y}{C}^{\cdot} \xrightarrow{HZ} \underset{R}{C}-\overset{Y}{C}-H + Z^{\cdot} \qquad (1)$$

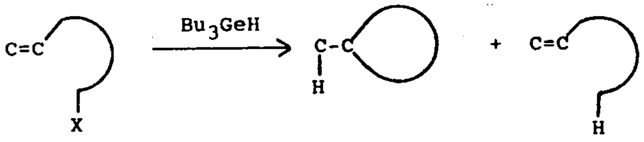
hydrogen atom transfer agent, HZ, is commonly an alkenylmercury halide/$NaBH_4$ or a triorganotin hydride, usually tributyltin hydride. When a tin hydride is used, the carbon-centered radical is derived from the abstraction of an appropriate leaving group from an organic precursor by the metal-centered radical. Common leaving groups include halogens and S- and Se-centered substituents.[5-7]

Simple reduction of the alkyl halide to form a hydrocarbon is a prevalent side reaction in many reductive alkylations. This is caused by hydrogen transfer to the alkyl radical prior to its addition to the active olefin (reaction 2). Strategies aimed at minimizing this process are usually required in order to obtain acceptable yields of the desired addition product[1-4]. In instances which the olefin is readily obtained and can be sacrificed, a large excess of the olefin can be employed to accelerate the rate of alkyl radical trapping. An alternative is to keep the concentration of the HZ low by **in situ** generation (example : conversion of RHgX to RHgH with $NaBH_4$) or by slow addition of the hydride to the reaction mixture. These approaches serve to minimize the rate of reaction 2. Unfortunately, strategies designed to keep the concentration of HZ low can suffer from the difficulty of sustaining a free-radical chain reaction and/or the reactivity of sensitive substrates with $NaBH_4$.

$$R^\cdot + HZ \xrightarrow{k_H} RH + Z^\cdot \qquad (2)$$

We recently published preliminary data indicating that tributylgermaniun hydride is a superior reagent for certain reductive alkylations.[8] Tributylgermanium hydride is significantly less reactive toward alkyl radicals than tributyltin hydride (by a factor of approximately 10)[9,10] and much less reactive than organomercury hydrides (by a factor of at least 100).[11] The germanium reagent derives its principal benefit from the low reactivity of its metal-hydrogen bond. The rate of reaction 2 is suppressed, hence reasonable yields of addition products might be obtained without resorting to high excess olefin concentrations or other special procedures. Very recently, reports have appeared of the use of tributylgermanium hydride for the free radical reductive annulation of unsaturated substrates as shown below.[12,13] The germanium reagent is useful in this application because its lower reactivity towards the carbon-centered radical favors the formation of the cyclic product. It is apparent that tributylgermanium hydride will enjoy increasing popularity as an alternative reducing agent for both "Giese" alkylations and free radical annulations.

$$\xrightarrow[\text{increasing reactivity toward alkyl radicals}]{Bu_3GeH \;<\; Bu_3SnH \;<\; RHgH}$$



In this paper we describe the optimization of conditions for the use of tributylgermanium hydride in the reactions of alkyl halides with acrylonitrile and 2-cyclohexen-1-one. The efficiency of the germanium reagent is compared to that of tributyltin hydride under standardized conditions. We also briefly evaluate the following six metal hydrides for possible applications to reductive alkylation reactions: trimesityltin hydride, trimesitylgermanium hydride, triphenyltin hydride, triphenylgermanium hydride, trineopentyltin hydride, and tricyclohexylgermanium hydride.

Results and Discussion. In order to evaluate the experimental parameters pertinent to the reductive alkylation with germanium hydride, acrylonitrile was selected as the standard acceptor olefin. Acrylonitrile is reputed to be one of the better radical acceptors for alkylations employing tin hydrides.[2,11] The most common solvent for these reactions is benzene. Table I shows that tributylgermanium hydride-induced alkylations proceed well in benzene, but the yields of the desired adducts are generally improved in acetonitrile. This result is surprising as the <u>intramolecular</u> metal hydride-induced addition of carbon-centered radicals to nitriles to form cyclic imines has been reported.[14] Nevertheless, we have adopted acetonitrile as the solvent of choice for intermolecular alkylations with tributylgermanium hydride. In no instance were products attributable to solvent incorporation detected.

Table I[a]

$$RX + CH_2{=}CHCN \xrightarrow[\substack{AIBN \\ 80^\circ C\ (8h)}]{Bu_3GeH} RCH_2CH_2CN + RH$$

	RX	Solvent	%Adduct	%RH
1.	$n\text{-}C_{11}H_{23}I$	acetonitrile	71	11
2.	$n\text{-}C_{11}H_{23}I$	benzene	63	14
3.	$PhCH_2I$	acetonitrile	76	14
4.	$PhCH_2I$	benzene	54	3
5.	$c\text{-}C_6H_{11}I$	acetonitrile	79	<5
6.	$c\text{-}C_6H_{11}I$	benzene	76	<5

a) $[RX]_0=[Bu_3GeH]_0=0.10M$; $[CH_2{=}CHCN]_0=0.15M$; $[AIBN]_0=0.01M$

Table II shows the influence of the leaving group upon the alkylation of acrylonitrile. Less reactive leaving groups (chloro, phenylthio, phenylseleno) fail to yield any addition product. In fact, the only product observed in these reactions is 3-(tributylgermyl)propanenitrile. This is the hydrometalation product of acrylonitrile. It is produced by the free-radical chain process of reactions 3 and 4. The reaction of 1-bromoundecane with acrylonitrile yields only 11% of the addition product (entry 2, Table II). GLC analysis of the reaction mixture showed that a 51% yield of 3-(tributylgermyl)propanenitrile had formed. Reaction of a tributylgermyl radical with the alkyl bromide (reaction 5) and reaction 3 are

Table II[a]

$$RX + CH_2CHCN \xrightarrow[\text{AIBN} \atop 80^\circ\text{C (8h)}]{Bu_3GeH} RCH_2CH_2CN + RH$$

	RX	%Adduct	%RH
1.	$n\text{-}C_{11}H_{23}I$	71	11
2.	$n\text{-}C_{11}H_{23}Br$	11	11
3.	$n\text{-}C_{11}H_{23}Cl$	<5	<5
4.	$n\text{-}C_{11}H_{23}SPh$	<5	<5
5.	$n\text{-}C_{11}H_{23}SePh$	<5	<5

a) Solvent=acetonitrile; $[RX]_0=[Bu_3GeH]_0=0.10M$; $[CH_2=CHCN]_0=0.15M$; $[AIBN]_0=0.01M$

occurring at comparable rates. Of the common leaving groups surveyed in this study, only the alkyl iodides were sufficiently reactive towards germyl radicals to afford good yields of addition products with acrylonitrile. No 3-(tributylgermyl)propanenitrile was detected in reactions of the alkyl iodides. Beckwith has made similar observations concerning the effect of the leaving group in the context of germanium hydride-induced intramolecular cyclization reactions of alkenyl halides.[15]

$$Bu_3Ge^\cdot + CH_2{=}CHCN \longrightarrow Bu_3CH_2CHCN \qquad (3)$$

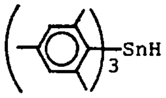
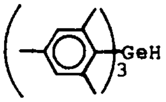
$$Bu_3GeCH_2\dot{C}HCN + Bu_3GeH \longrightarrow Bu_3GeCH_2CH_2CN + Bu_3Ge^\cdot \qquad (4)$$

$$Bu_3Ge^\cdot + n\text{-}C_{11}H_{23}Br \longrightarrow Bu_3GeBr + n\text{-}C_{11}H_{23}^\cdot \qquad (5)$$

The data in Table III permit a comparison of the qualitative reactivity of several triorganotin and triorganogermanium hydrides. Standardized conditions were employed: benzene was used as the reaction solvent in all cases; each reaction was performed for 8h at reflux temperature; all reactions were performed at the same concentrations and were initiated with 10 mol percent AIBN (azobis[isobutyronitrile]). All of the tin hydride reactions with 1-iodoundecane were essentially complete after 8 hours. However, the degree of completion varied widely for reactions with germanium hydrides. The sterically hindered trimesitylgermanium hydride was completely inert, whereas the reaction with triphenylgermanium hydride went to completion. Tributylgermanium hydride and tricyclohexylgermanium hydride exhibited intermediate reactivity. Caution must be used in interpreting this sort of data; the degree of completion merely reflects the ability of a metal hydride to promote the overall chain reaction. Qualitatively

Table III[a]

$$R_3MH + n\text{-}C_{11}H_{23}I \xrightarrow[\text{AIBN/8h}]{\text{benzene/80}^\circ\text{C}} n\text{-}C_{11}H_{24}$$

	R_3MH	$\%n\text{-}C_{11}H_{24}$	$\%n\text{-}C_{11}H_{23}I$[b]
1.	Bu_3SnH	98	4
2.	Bu_3GeH	76	20
3.		93	11
4.		<1	97
5.	Ph_3SnH	93	5
6.	Ph_3GeH	98	5
7.	$(c\text{-}C_6H_{11})_3GeH$	64	25
8.	$[(CH_3)_3CCH_2]_3SnH$	95	2

a) $[R_3MH]_0=[n\text{-}C_{11}H_{23}I]_0=0.10M$; $[AIBN]=0.01M$.

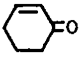
b) GLC yield of remaining alkyl iodide.

however, tributylgermanium hydride is certainly less reactive towards alkyl halides than are the common tin hydrides. In actual preparative reactions using germanium, it may often prove necessary to introduce several charges of AIBN or other initiators in order to ensure complete reaction.

When tin hydrides are employed in reductive alkylation reactions, a large excess of olefin is often useful to optimize the yield of addition product.[1-4] Table IV shows that the nature of the olefin profoundly influences the choice of optimum olefin concentration when tributylgermanium hydride is used. Entries 1-3, 4-5, and 6-7 reveal that, with acrylonitrile as the radical acceptor, a metal hydride:alkyl halide:olefin concentration ratio of 1:1:1 or 1:1:1.5 is preferable to conditions employing high concentrations of olefin. At high olefin concentrations the yield of addition product is precipitously lowered by the competitive formation of the hydrogermylation product via reactions 3 and 4 (see note d in Table IV). The situation is altered when the receptor olefin is 2-cyclohexen-1-one. As shown in entries 8-9, the yield of the addition product is enhanced by the use of a high olefin concentration. Addition of an alkyl radical

Table IV[a]

$$RX + C{=}C \xrightarrow[\substack{\text{AIBN} \\ 80^{\circ}\text{C (8h)}}]{Bu_3GeH} R\text{-}C\text{-}C\text{-}H + RH$$

	RX	olefin (conc.)		%adduct	%RH	%RX[b]
1.	$n\text{-}C_{11}H_{23}I$	$CH_2{=}CH_2CN$	(0.10M)	69	12	<5
2.	"	"	(0.15M)	71	11	<5
3.	"	"	(1.00M)	14[c]	~1[c]	<5[c]
4.	$c\text{-}C_6H_{11}I$	"	(0.15M)	79	<5	14
5.	"	"	(0.40M)	42	<5	<5
6.	$PhCH_2I$	"	(0.10M)	61	4	14
7.	"	"	(0.15M)	76	2	16
8.	$n\text{-}C_{11}H_{23}I$		(0.15M)	21	60	-[d]
9.	"	"	(1.00M)	68	<5	-[d]

a) Solvent=acetonitrile; $[RX]_0=[Bu_3GeH]_0=0.10M$; $[AIBN]_0=0.01M$.

b) GLC yield of recovered alkyl halide

c) A 46% yield of 3-(tributylgermyl)propanenitrile was determined by GLC.

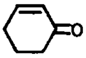
d) Not determined.

to the cyclohexenone is significantly slower than addition to a terminal olefin such as acrylonitrile. High cycloalkenone concentrations are required in order that addition (reaction 1) is favored over simple reduction (reaction 2). Even at high olefin concentration, hydrogermylation of 2-cyclohexen-1-one was not observed.

Table V permits a comparison of the efficacy of tributylgermanium hydride and tributyltin hydride for reductive alkylations of acrylonitrile and 2-cyclohexen-1-one. For each experiment the initial concentrations of hydride, alkyl halide, and olefin were fixed at 0.10M, 0.1M, and 0.15M, respectively. Tributylgermanium hydride is clearly superior for the reaction of 1-iodoundecane with acrylonitrile (entries 1-2). However, the germanium reagent was no improvement over the tin reagent for reactions of acrylonitrile with cyclohexyl iodide or tert-butyl iodide (entries 3-6). The germanium hydride performed significantly better than tin for reactions of 2-cyclohexen-1-one with cyclohexyl iodide or 1-iodoundecane. The tin reagent gave adduct yields of only about 5% whereas tributylgermanium hydride afforded 20-30% yield (entries 7-10). In general the advantage of the germanium reagent will be most pronounced with less reactive olefins, for it is with these applications that the formation of simple reduction products is an obstacle.

Table V[a]

$$RX + C{=}C + Bu_3MH \xrightarrow[80^\circ C\ (8h)]{AIBN} R\text{-}C\text{-}C\text{-}H + RH$$

	RX	olefin	M	solvent	%adduct	%RH
1.	$n\text{-}C_{11}H_{23}I$	$CH_2{=}CHCN$	Ge	acetonitrile	71	11
2.	"	"	Sn	benzene	40	47
3.	$c\text{-}C_6H_{11}I$	"	Ge	acetonitrile	79	-[b]
4.	"	"	Sn	benzene	92	-[b]
5.	$t\text{-}C_4H_9I$	"	Ge	acetonitrile	45	-[b]
6.	"	"	Sn	benzene	72	-[b]
7.	$n\text{-}C_{11}H_{23}I$		Ge	acetonitrile	21	60
8.	"	"	Sn	benzene	5	95
9.	$c\text{-}C_6H_{11}I$	"	Ge	acetonitrile	31	-[b]
10.	"	"	Sn	benzene	7	-[b]

a) $[RX]_0=[Bu_3MH]_0=0.10M$; $[olefin]_0=0.15M$; $[AIBN]_0=0.01M$.

b) Not determined.

Entry 9 in Table V shows that a good yield of 3-undecylcyclohexanone can be obtained by using a ten-fold excess of the enone. Alternatively, one can keep the concentration of tributylgermanium hydride low by employing a controlled addition procedure. For example, a 45% yield of 3-undecylcyclohexanone was obtained by adding a solution of the germanium hydride and AIBN in acetonitrile, by means of a syringe pump over an 8 hour period, to a refluxing acetonitrile solution of 1-iodoundecane and 2-cyclohexen-1-one.

The reductive alkylation of 2-cyclohexen-1-one is a demanding reaction owing to the relatively low reactivity of the carbon-carbon double bond toward alkyl radicals. The predominant side reaction is the simple reduction of the alkyl substrate (reaction 2). For the reaction of the cycloalkenone with 1-iodoundecane with any metal hydride, M-H, the ratio of the simple reduction and addition products is related to the value of k_H as detailed below (assuming that the k_H and k_{add} processes are irreversible). Since the value of k_{add} is not known, and since the concentrations of the metal hydride and the cycloalkenone vary with time, measurement of the product ratio does not permit the extraction of an absolute value for k_H. Nonetheless the product ratio reveals trends in k_H. A large undecane:3-undecylcyclohexanone ratio reflects a relatively large value of k_H. We have employed this reaction to evaluate the properties of eight triorganotin and triorganogermanium hydrides.

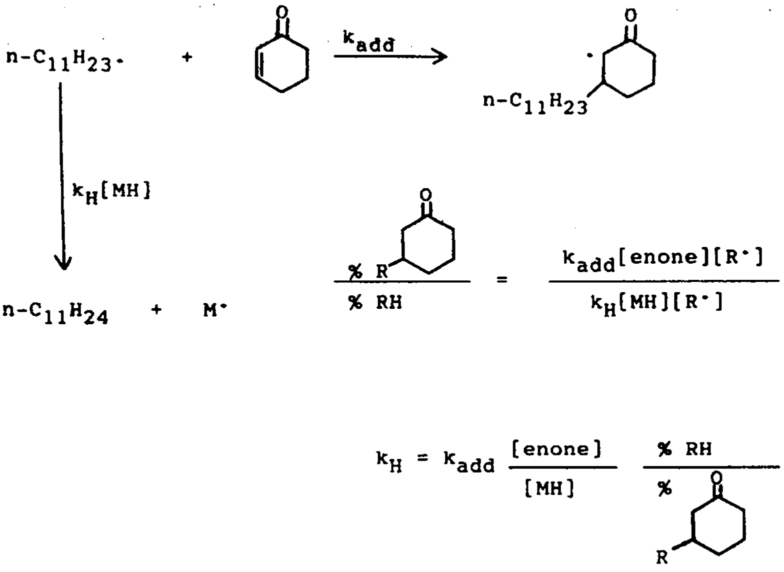
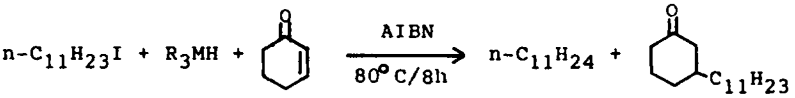
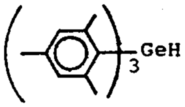
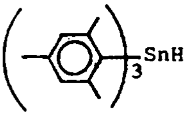


Table VI[a]



	R_3MH	%adduct	%n-$C_{11}H_{24}$	%n-$C_{11}H_{23}I$[b]	R[c]
1.	Bu_3GeH	21	60	25	2.8
2.	Bu_3SnH	5	95	<2	19
3.		<2	<2	100	--
4.		6	80	16	13
5.	Ph_3GeH	13	83	3	6.4
6.	Ph_3SnH	<2	88	10	--
7.	$(c\text{-}C_6H_{11})_3GeH$	16	37	57	2.3
8.	$[(CH_3)_3CCH_2]_3SnH$	3	88	8	29

a) $[n\text{-}C_{11}H_{23}I]_0=[R_3MH]_0=0.10M$; $[\text{2-cyclohexen-1-one}]_0=0.15M$; $[AIBN]_0=0.01M$; Solvent=acetonitrile for M=Ge, benzene for M=Sn.

b) Percent unreacted alkyl halide.

c) R=product ratio = %n-$C_{11}H_{24}$/%adduct.

According to the data in Table VI there is no significant difference between the performances of tributyltin hydride, trimesityltin hydride, triphenyltin hydride, and trineopentyltin hydride. This is consistent with our observation, to be published elsewhere,[16] that the activation parameters for the k_H process are only weakly influenced by the steric and electronic characteristics of the organic ligands on tin. The germanium hydrides, with the exception of the unreactive trimesitylgermanium hydride, all afford higher yields of the addition product and lower amounts of simple reduction product than do the tin hydrides. Minor differences in the performances of the germanium reagents are observed. Triphenylgermanium hydride was less satisfactory that tributylgermanium hydride, but tricyclohexygermanium hydride was somewhat better (after correction for unreacted starting material). this may be due to steric congestion introduced by the cyclohexyl ligands. Any synthetic advantage displayed by tricyclohexylgermanium hydride is attenuated by its sluggish reactivity. Note the large amounts of unreacted alkyl iodide in Table VI, entry 7 and Table III, entry 7.

Conclusion. Tributylgermanium hydride suffers several disadvantages as a reagent for the Giese reductive olefin alkylation reaction. The cost of germanium is relatively high, more than one US dollar per gram for $GeCl_4$. Also, tributylgermanium hydride exhibits a rather low reactivity towards alkyl halides and related substrates. Only the iodide, and in favorable cases the bromide leaving groups are sufficiently labile for use in the alkylation reaction with the germanium hydride. Furthermore, active terminal olefins may react directly with tributylgermanium hydride to give the hydrogermylation side product. Tributyltin hydride is not going to be displaced as the reagent of choice for most olefin alkylations either by tributylgermanium hydride or by the other metal hydrides surveyed in this paper. However, for special applications involving precious olefins or olefins of low reactivity, tributylgermanium hydride may be used to advantage.

Acknowledgment. We thank the Miami University Faculty Research Committee for financial support of this research.

Experimental Section.

General. Benzene and acetonitrile solvents were distilled before use and stored under nitrogen. Azobis[isobutyronitrile] was purchased from Aldrich. The alkyl halides were commercial products. Authentic tetradecanenitrile,[17] 3-(tributylgermyl)propanenitrile,[18] 3-cyclohexylpropanenitrile,[19] 4,4-dimethylvaleronitrile,[20] and 4-phenylbutanenitrile[21] were prepared by literature methods.

Authentic 3-cyclohexylcyclohexanone and 3-undecylcyclohexanone were obtained by silica gel chromatography of product solutions resulting from the AIBN-initiated reactions of tributylgermanium hydride and 2-cyclohexen-1-one with either 1-iodoundecane or cyclohexyl iodide. The isolated yields of GLC-pure products were approximately 20% from reactions run at 0.10M germanium hydride, 0.10M alkyl iodide, and 0.15M olefin. The products exhibited appropriate ^1H-NMR and mass spectra.

Sources of Triorganotin and Triorganogermanium Hydrides. Tributyltin hydride was purchased from Aldrich. Triphenylgermanium hydride,[22] triphenyltin hydride,[23] trineopentyltin hydride,[24-26] trimesitylgermanium hydride,[27-29] trimesityltin hydride,[30,31] tricyclohexylgermanium hydride,[27-29] and tributylgermanium hydride[32,33] were prepared by literature procedures. All metal hydrides were distilled or recrystallized before use and were stored in the freezer under an atmosphere of nitrogen or argon. For general purposes the germanium hydrides require no special handling, but slowly degrade if exposed to air for several days. The tin hydrides are considerably more reactive toward oxygen and exposure to air must be minimized to ensure consistent results.

General Procedure for the Reductive Alkylation of Olefins Using Tributylgermanium Hydride. The alkyl halide (0.50M) and AIBN (0.05M) were dissolved in 5ml of solvent. This solution was purged with a stream of nitrogen or argon. The desired amount of olefin was added via syringe followed by the tributylgermanium hydride (0.50M). The reaction was immediately placed in a heating bath and warmed to 80°C for the prescribed time, usually 8 hours. Product yields were determined by GLC using internal integration standards. Yields reported in Tables I-VI are based upon the limiting reagent(s). The precision of the reported yields is approximately +5%.

References

1. B. Giese, "Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds", Volume 5 in the Organic Chemistry Series, J. E. Baldwin, Ed.; Pergamon, New York: 1986.
2. B. Giese, **Angew. Chem. Int. Ed. Engl.** 1983, **22**, 753.
3. M. Ramaiah, **Tetrahedron** 1987, **43**, 3541.
4. W. P. Neumann, **Synthesis** 1987, 665.
5. S. D. Burke, W. F. Fobare, and D. M. Armistead, **J. Org. Chem.** 1982, **47**, 3348.
6. D. L. J. Clive and D. R. Cheshire, **J. Chem. Soc., Chem. Commun.** 1987, 1520.
7. D. L. J. Clive, T. L. B. Boivin, and G. A. Angoh, **J. Org. Chem.** 1987, **52**, 4943.
8. P. Pike, S. Hershberger, and J. Hershberger, **Tetrahedron Lett.** 1985, **26**, 6289.
9. L. H. Johnson, J. Lusztyk, D. D. Wagner, A. N. Abeywickreyma, A. L. J. Beckwith, J. C. Scaiano, and K. U. Ingold, **J. Am. Chem. Soc.** 1985, **107**, 4594.
10. J. Lusztyk, B. Maillard, D. A. Lindsay, and K. U. Ingold, **J. Am. Chem. Soc.** 1983, **105**, 3578.
11. B. Giese and G. Kretzchmar, **Chem. Ber.** 1984, 3160.
12. A. L. J. Beckwith and D. H. Roberts, **J. Am. Chem. Soc.** 1986, **108**, 5893.
13. A. L. J. Beckwith and P. E. Pigou, **J. Chem. Soc., Chem. Comm.** 1986, 85.
14. D. L. J. Clive, P. L. Beaulieu, and L. Set, **J. Org. Chem.** 1984, **49**, 1313.
15. A. L. J. Beckwith and P. E. Pigou, **Aust. J. Chem.** 1986, **39**, 1151.
16. P. Pike, V. Gilliatt, M. Ridenour, and J. Hershberger, **Organometallics**, in press.
17. F. C. Whitmore, R. W. Schiessler, C. S. Rowland, and J. N. Cosby, **J. Am. Chem. Soc.** 1947, **69**, 235.
18. P. J. Satge, **Annales de Chemie** 1961, 536.
19. J. S. Mihina and R. M. Herbst, **J. Org. Chem.** 1950, 15, 1082.
20. A. Brandstrom, **Acta Chim. Scand.** 1959, 13, 613.
21. P. H. Payot, W. G. Dauben, and L. Replogle, **J. Am. Chem. Soc.** 1957, **79**, 4136.
22. W. H. Nebergall, O. H. Johnson, and D. M. Harris, **Inorg. Syn.** 1959, **5**, 76.
23. G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, **J. Appl. Chem.** 1957, **7**, 366.
24. H. Zimmer, I. Hechenbleikner, O. A. Homberg, and M. Danzik, **J. Org. Chem.** 1964, **29**, 2632.
25. B. V. Fedot'ev, O. A. Kruglaya, and N. S. Vyazankin, **Izv. Akad. Nauk. SSSR Ser. Khim.** 1974, 3, 713.
26. O. A. Kruglaya, B. V. Fedot'ev, I. B. Fedot'eva, and N. S. Vyazankin, **J. Gen. Chem. USSR** 1976 **46**, 1483.
27. M. J. S. Gynane, M. F. Lappert, and P. I. Riley, **J. Organomet. Chem.** 1980, **202**, 5.
28. R. J. Cross and F. Glocking, **J. Organomet. Chem.** 1965, 3, 146.
29. F. Glocking and K. A. Hooton, **J. Chem. Soc.** 1963, 1849.
30. D. H. Lorenz, P. Shapiro, A. Stern, and E. I. Becker, **J. Org. Chem.** 1963, **28**, 2332.
31. I. I. Lapin and V. A. Sedeln'ikova, **Zh. Obschch. Khim.** 1960, **30**, 2771.
32. O. H. Johnson and W. H. Nebergall, **J. Am. Chem. Soc.** 1949, **71**, 1720.
33. M. Lesbre and J. Satge, **Comt. Rend.** 1958, **247**, 471.