5216-32-0; *trans*-α,α'-dichlorostilbene, 951-86-0; iron, 7439-89-6; copper, 7440-50-8; zinc, 7440-66-6.

Acknowledgments.—We thank Mrs. A. B. Richmond for the preparative gas chromatography, Dr. T. L. Pugh for the mass spectra, Dr. E. Bromels for the Raman spectra, and Dr. E. G. Brame and Professor Bryce Crawford for advice on spectral interpretation, and Mr. L. L. Burchfield for skillfully performing the experimental work.

Regiospecificity and Stereochemistry in the Hydralumination of Unsymmetrical Acetylenes. Controlled Cis or Trans Reduction of 1-Alkynyl Derivatives[1]

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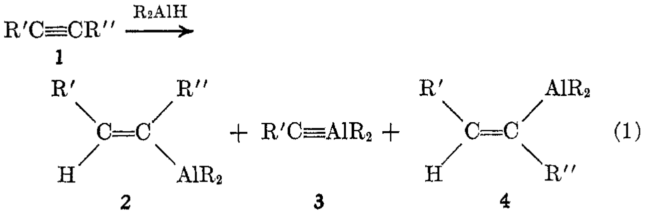
The regiospecificity and stereochemistry for the addition of aluminum–hydrogen bonds to unsymmetrical acetylenes were examined in order to evaluate the steric and electronic factors of this important reaction. Phenylethynyl derivatives of the type $C_6H_5C{\equiv}CE$ (**5**), where E = CMe_3, $SiMe_3$, $GeMe_3$, $GeEt_3$, $SnMe_3$, PMe_2, H, and Br, were treated with 1 equiv of diisobutylaluminum hydride (**6**) in hydrocarbon solution. Hydrolytic work-up was employed to determine the cis or trans nature of the addition or the extent of C–E bond cleavage; alternative work-up with deuterium oxide permitted the labeling of the carbon–aluminum bond site and hence the determination of the regiospecificity of hydralumination. With E = SiR_3 or GeR_3, the hydralumination proceeded almost completely in a trans manner; use of 1 equiv of a tertiary amine with **6** gave almost exclusively cis addition. These controlled trans or cis reductions were also found to be general for other trimethylsilyl derivatives of terminal acetylenes, and hence this method has considerable promise for stereospecific chemical transformations of acetylene derivatives. The patterns observed for the cis or trans hydraluminations and the C–E bond cleavages, taken together with the regiospecificity, are most consistent with a transition state involving electrophilic attack by the aluminum center, culminating in a cis addition. Trans hydralumination seems to ensue from the isomerization of the cis adduct.

Although the hydralumination of internal acetylenic linkages leads cleanly to the cis adduct (**2a**),[2] terminal acetylenes can yield both the hydralumination adduct (**2b**) as well as the substitution product (**3b**).[3] Since the synthetic utility of such vinylaluminum adducts (**2b**) is curtailed by contamination with varying amounts of **3b** (*ca.* 30% with $C_6H_5C{\equiv}CH$),[4] we investigated the possible use of trimethylsilyl derivatives of terminal acetylenes (**1c**) in achieving hydralumination without substitution. Such a derivative did, in fact, yield exclusively the hydralumination product,[5a] but the trans stereochemistry of the reaction,[5b] forming almost solely **4c**, was an arresting contrast to that of previously reported cis hydraluminations with dialkylaluminum hydrides.[2] Moreover, the direction or regiochemistry of Al–H bond addition to the acetylenic linkage of **1c** was opposite[5a] that observed for related disubstituted acetylenes (**1a**).[2b] These interesting orientational and stereochemical observations have encouraged us to examine the hydralumination of a series of 1-alkynyl derivatives bearing metalloidal or nonmetallic functional groups adjacent to the triple bond (**1d**). By assessing the relative amounts of hydralumination (cis and trans, **2d** and **4d**) and of metalation (**3d**), we hoped to understand better the steric and electronic factors of this important reaction.



(1)

a, R' and R'' = alkyl
b, R' = alkyl; R'' = H
c, R' = alkyl or aryl; R'' = $SiMe_3$
d, R = alkyl or aryl; R'' = E

Results

The hydraluminations of a series of phenylethynyl derivatives, $C_6H_5C{\equiv}CE$ (**5**) (where E = CMe_3, $SiMe_3$, $GeMe_3$, $GeEt_3$, $SnMe_3$, PMe_2, H, and Br) were performed in heptane solution with 1 equiv of diisobutylaluminum hydride (**6**). Hydrolytic work-up of the reaction mixtures with deuterium oxide and nmr analyses of the deuterated reduction or cleavage products permitted a determination of the proportion of aluminum derivatives, *e.g.*, **2**, **3**, and **4**. Because of the novel trans hydraluminations observed with the trialkylsilyl and -germyl derivatives of phenylacetylene, the hydraluminations of these compounds were examined under other experimental conditions. Even when the hydralumination of phenylethynyl(trimethyl)silane (**5b**) was carried out at −10° to only 5% conversion, the hydrolyzed[6] product was still 95% *trans*-β-styryl(trimethyl)silane (**9b**). However, earlier work

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[1] Part XIX of the series, "Organometallic Compounds of Group III," devoted to carbometalation and hydrometalation. Previous part: J. J. Eisch and J. M. Biedermann, *J. Organometal. Chem.*, **30**, 167 (1971).

[2] (a) G. Wilke and H. Müller, *Justus Liebigs Ann. Chem.*, **629**, 222 (1960); (b) J. J. Eisch and W. C. Kaska, *J. Amer. Chem. Soc.*, **88**, 2213 (1966).

[3] H. Lehmkuhl, K. Ziegler, and H. G. Gellert in "Houben-Weyls Methoden der Organischen Chemie," Band XIII/4, E. Müller, Ed., Georg Thieme, Stuttgart, 1970, pp 159–164.

[4] J. J. Eisch and W. C. Kaska, *J. Organometal. Chem.*, **2**, 184 (1964).

[5] (a) J. J. Eisch and M. W. Foxton, *ibid.*, **11**, P24 (1968). (b) The trans hydralumination of alkynes with lithium aluminum hydride was first reported by L. H. Slaugh and E. F. Magoon [*Tetrahedron*, **23**, 4509 (1967)] and, independently, by the present authors (ref 5a). Lithium diisobutylmethylaluminum hydride has been found to effect trans hydralumination of alkynes very smoothly in nonpolar media [G. Zweifel and R. Steele, *J. Amer. Chem. Soc.*, **89**, 5085 (1967)].

[6] In this and other cases of measuring the ratio of cis and trans aluminum adducts by hydrolysis, a low temperature and vigorous stirring had to be maintained during quenching, in order to avoid thermal isomerization of the aluminum adducts. N.B: Ordinarily, vinylaluminum compounds are hydrolyzed with retention of stereochemistry.[2]

TABLE I

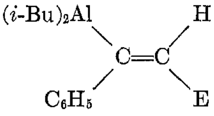
HYDRALUMINATIONS OF PHENYLETHYNYL DERIVATIVES, $C_6H_5C{\equiv}CE$ (5), BY $(i\text{-}Bu)_2AlH$ (6)

Substrate $C_6H_5C{\equiv}CE$				Products			
Compd	E	C≡C, μ	Conditions[a]	7β	9	7α	8
5a	CMe_3	4.61 (w)	50°			100	
5b	$SiMe_3$	4.65 (s)	20°	4	96		
5b	$SiMe_3$		60°, R_3N[b]	96	4		
5b	$SiMe_3$		35°, Et_2O[c]	65	35		
5c	$GeMe_3$	4.65 (m)	50°	6	94		
5c	$GeMe_3$		100°, R_3N[b]	98	2		
5d	$GeEt_3$	4.65 (m)	50°	7	93		
5e	$SnMe_3$		20°				100
5e	$SnMe_3$		20°, R_3N[b]				100
5f	PMe_2	4.63 (m)	50°	85		15	
5f	PMe_2		50°, R_3N[b]	85		15	
5g	H	4.72 (sh)	20°	71			29
5h	Br	4.55 (s)	100°				100

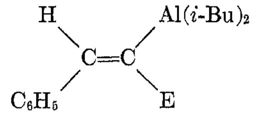
[a] In pentane or heptane using a 1:1 ratio of equivalents of 5 and 6. [b] With 1 equiv of N-methylpyrrolidine. [c] In diethyl ether solution.

in this laboratory had shown that tertiary amine adducts of diisobutylaluminum hydride achieved a slower but cleaner cis hydralumination of tolane (2, R′ = R″ = C_6H_5), with no trans adduct or dimerized product. Consequently, the hydraluminating properties of a 1:1 adduct of *N*-methylpyrrolidine and **6** were examined. Although *tert*-butyl(phenyl)acetylene (**5a**) simply underwent the previously observed cis addition at a slower rate, the silyl and germyl derivatives of phenylacetylene (**5b–d**) now underwent almost completely cis addition, a behavior exactly opposite that observed in the absence of the amine. Diethyl ether was not as effective in redirecting the hydralumination to a cis course, since a 65:35 cis:trans ratio resulted.

As to the regiospecificity of the addition reactions, the deuterium labeling in the hydrolysis products showed that hydralumination of *tert*-butyl(phenyl)acetylene (**5a**) placed the diisobutylaluminum group exclusively α to the phenyl group (**7α**). With the silyl and germyl derivatives **5b–d**, and phenylacetylene itself, **5g**, the aluminum group was placed exclusively β to the phenyl group in both cis and trans hydraluminations (**7β** and **9**). Dimethyl(phenylethynyl)phosphine (**5f**) on the other hand, yielded regioselective, cis hydralumination in proportions of 85% β and 15% α to the phenyl group.



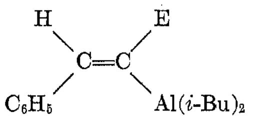
7α



7β

$C_6H_5C{\equiv}CH$

8



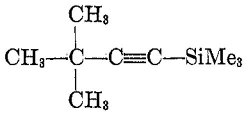
9

Cleavage of the C–E bond in $C_6H_5C{\equiv}CE$ (**1d** → **3d**) was observed only for E = $SnMe_3$ (**5e**), H (**5g**), and Br (**5h**). In **5e** and **5h** only cleavage and no discernible hydralumination was achieved; with phenylacetylene cleavage amounted to 29% of the total reaction. The behavior of these phenylethynyl derivatives is summarized in Table I.

The possible generality of the controlled cis or trans hydralumination of silyl derivatives of 1-alkynes was investigated for the cases **10–12**. Both **11** and **12** behaved exactly like **5b**, giving the trans reduction product with **6** alone and the cis product with **6** combined with *N*-methylpyrrolidine. On the other hand, for reasons not yet understood, **10** led to no detectable monomeric reduction product (cis or trans), despite diligent variation in experimental conditions. Instead, only two isomers of 1,3-bis(trimethylsilyl)-2-methyl-1,3-pentadiene were isolated.

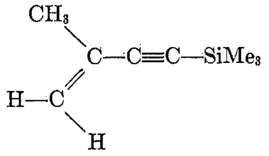
$CH_3{-}C{\equiv}C{-}SiMe_3$

10



$$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}C{\equiv}C{-}SiMe_3$$

11



12

The cis hydralumination adducts of these silyl and germyl acetylenes (**5b–d**, **11** and **12**) could be smoothly isomerized into their more stable trans structures either by adding 1 equiv of diisobutylaluminum chloride at 25° or by heating with a catalytic amount of **6**. In both cases it appears that the isomerizing agent acts as a Lewis acid toward the *N*-methylpyrrolidine.

Also bearing on the interpretation of these results are the observations that lithium aluminum hydride in THF effected only the cleavage of **5b** to yield phenylacetylene on hydrolysis, but that the same reagent smoothly hydraluminated *cis*-β-styryl(trimethyl)silane.

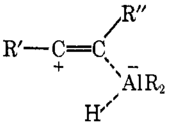
$$C_6H_5C{\equiv}CH \xleftarrow[2.\ H_2O]{1.\ C_6H_5C{\equiv}CSiMe_3} LiAlH_4 \xrightarrow[2.\ H_2O]{1.\ C_6H_5CH{=}CHSiMe_3} C_6H_5CH_2CH_2SiMe_3$$

Finally, it should be mentioned that the substituted vinylsilanes resulting from these reductions show considerable promise as precursors for other organic derivatives. The highly stereoselective bromodesilylation of β-styryl(trimethyl)silane has encouraged us to continue work on the synthetic aspects of these reactions.

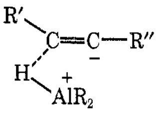
$$\underset{\text{trans:cis} = 95:5}{C_6H_5CH{=}CHSiMe_3} \xrightarrow[-20^\circ]{Br_2\text{-}CCl_4} \underset{\text{trans:cis} = 88:12}{C_6H_5CH{=}CHBr\ (90\%)}$$

Discussion

The regiospecificity, the stereospecificity, and the isomerization processes observed in these hydraluminations call for some further mechanistic consideration. The regiospecificity or direction of Al–H bond addition to these alkynes could be rationalized, either electronically in terms of an electrophilic attack by aluminum (**13**) or a nucleophilic attack by hydrogen (**14**), or sterically in terms of a four-center trasition state (**15**). The pronounced retarding effect of tetrahydrofuran on the hydralumination rate of 4-octyne[7] and of *N*-methylpyrrolidine on the reactions of these alkynes (**5**) is consistent with the importance of a tricoordinate hydraluminating species, as in **13** or **15**, in nondonor media. Thus, some type of electrophilic attack by aluminum seems to be involved when **6** is used in hydrocarbon solution in the absence of Lewis bases.[8] A further choice between transition state models **13** and **15** can be made by considering the behavior of *tert*-butyl(phenyl)acetylene (**5a**) *vs.* that of its silyl and germyl counterparts (**5b–d**). If the exclusive formation of **7a** from **5a** were explained on steric grounds (*i.e.*, smaller nonbonded interactions between R″ = C_6H_5 and R = *i*-C_4H_9 in **15**), then the exclusive placement of the (*i*-C_4H_9)$_2$Al group next to the R_3Si or R_3Ge in **5b–d** (either cis or trans) to yield **7** or **9b**,**c** must be a source of bewilderment. On the other hand, a superior explanation applicable to all cases is that electrophilic attack by **6** will be favored, so as to place the electron deficiency on that carbon (**15**) better able to sustain it. The polarization of the carbon–carbon linkage in the transition state, shown in **16**, would be especially fostered in **5a**, where R″ = C_6H_5 and R′ = *tert*-C_4H_9, and in **5b–d**, where R′ = C_6H_5 and R″ = R_3Si, R_3Ge, R_2P, and H. For the C_6H_5, *tert*-C_4H_9, and H substituents, their σ_{para} could be invoked to rationalize their electron release; for the organometalloidal groups R_nE a particularly effective p_π–d_π interaction with E could be noted. Even in the ground state of **5b–d** and **5f**, their infrared spectral C≡C stretches display shifts and accentuated intensities consistent with dative bonding and marked polar character[9,10] (Table I).



13



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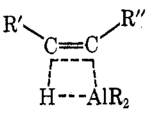

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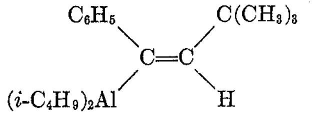
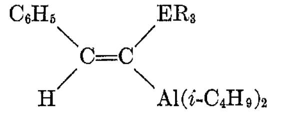
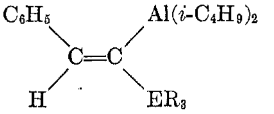


7a

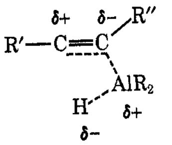


7b–d



9b–d

ER_3 = $SiMe_3$, $GeMe_3$, $GeEt_3$



16

$$C_6H_5C\equiv CE \longleftrightarrow C_6H_5\overset{+}{C}=\overset{-}{C}E \longleftrightarrow C_6H_5\overset{+}{C}=C=\overset{-}{E}$$

5, E = Me_3Si, Me_3Ge, Et_3Ge, and Me_2P

The stereochemistry and the isomerization processes of these additions deserve joint treatment, for the question arises whether the observed trans hydralumination of $C_6H_5C\equiv CSiMe_3$ and $C_6H_5C\equiv CGeR_3$ might have occurred by an initial cis addition followed by isomerization to the more stable trans adduct. If this be the actual pathway for **9b–d**, such isomerization must be very fast indeed, for at 5% conversion of **5b** at −10°, the product was already 95% trans adduct. A scrutiny of the first 5% of reaction and a complete kinetic analysis of initial rates are underway,[7] in order to distinguish the isomerization possibility from a kinetically controlled trans hydralumination,[5] presumably of different kinetic order than a cis process. However, it is clear from the present studies that cis adducts **7b–d**, in the absence of Lewis base complexation (*N*-methylpyrrolidine), are readily converted into the trans adducts **9b–d**. Addition of a Lewis acid, **6** or (*i*-C_4H_9)$_2$AlCl, to the amine adduct of **7b** causes formation of **9b**.

Two mechanistic possibilities come to mind:[2b,11] after removal of the amine by complexation with the Lewis acid, (*i*-Bu)$_2$AlCl, either Lewis acid catalyzed isomerization (path a) or uncatalyzed, thermal isomerization of **7b** by virtue of an exceptionally low C=C rotational barrier arising from combined p_π–d_π (C–Si) and p_π–p_π (C–Al) effects.[10] The observation that just 1 equiv of (*i*-C_4H_9)$_2$AlCl causes a prompt isomerization of **7b** at 25° is in better accord with path b, since the Lewis acid should be essentially tied up as its *N*-methylpyrroline complex and hence not available for path a. This rapid isomerization of uncomplexed **7b** suggests that the trans hydraluminations of **5b–d** do proceed *via* cis adducts. It is noteworthy that the phosphine derivative **5f** undergoes cis hydralumination, with or without the presence of an amine. Presumably the basic character of the Me_2P group provides the system with an internal Lewis base to protect **7f** from isomerization.

Finally, the C–E bond cleavages observed with $C_6H_5C\equiv CE$, where E = Me_3Sn, Br, or H, may well proceed by differing mechanisms. However, it can be observed that slight modification of transition state **16** could permit the hydridic group to attack group R″, instead of the β carbon. Another noteworthy cleavage is that of the C–Si bond in **5b** by $LiAlH_4$. This finding

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[7] J. J. Eisch and S. G. Rhee, unpublished studies.

[8] In the presence of Lewis bases, an electrophilic attack by aluminum on the unsaturated hydrocarbon (S), with displacement of the base (B), may also obtain.

$$R_2AlH{\cdot}B + S \longrightarrow [R_2HA\overset{\cdot B}{\underset{\cdot S}{<}}] \longrightarrow \text{adduct}$$

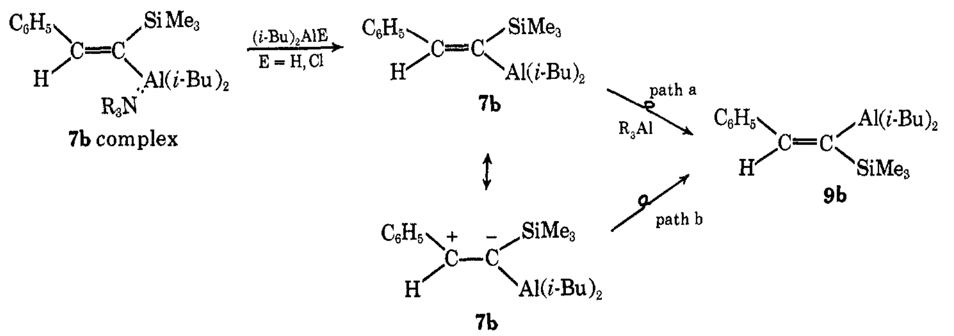
However, kinetic studies[7] have yet to rule out a nucleophilic attack by the hydridic complex.

$$B{\cdot}\overset{\delta+}{AlR_2}\cdots\overset{\delta-}{H} + S \longrightarrow \text{adduct}$$

[9] R. West and C. S. Kraihanzel, *Inorg. Chem.*, **1**, 967 (1962).

[10] J. J. Eisch and J. T. Trainor, *J. Org. Chem.*, **28**, 487 (1963).

[11] A third possibility, addition of (*i*-Bu)$_2$AlE to **7b** (ref 2b) and reelimination, seems unlikely to play a role under the relatively mild conditions employed here.



shows that a recognized nucleophilic attack by hydride takes place in an entirely different manner than the attack of **6** or **6**-NR$_3$ on the same substrate. This is further reason to dismiss **13** as a suitable model for these hydraluminations by reagent **6**.

Experimental Section

Melting points were determined with a Thomas–Hoover "Unimelt" apparatus and are corrected. Infrared spectra were recorded of samples as potassium bromide disks, mineral oil suspensions, or solutions in pure solvents, by means of a Perkin-Elmer spectrophotometer, Model 137. Proton magnetic resonance spectra were measured with a Varian spectrometer, Model A-60, on samples dissolved as 10% solutions in pure solvents containing tetramethylsilane as an internal standard. Signals are reported using the δ scale in parts per million, followed by the integrated intensities of the proton signals and the coupling constants (J) in hertz. Vpc analyses were performed on an F & M dual-column equipped with 2-ft columns packed with 10% silicone gum rubber on firebrick. Elemental analyses were carried out by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

All preparations and reactions involving either air- and moisture-sensitive organometallic reagents were conducted under an atmosphere of dry, oxygen-free nitrogen. Appropriate techniques for such manipulations, including the necessary purification of solvents, have already been described.[2b]

Preparation of Starting Materials.—Several of the substituted phenylacetylenes were prepared from phenylethynylmagnesium bromide and the appropriate organometalloidal halide in general accordance with the following specific procedure for phenylethynyl(trimethyl)silane. Thus, a stirred solution of ethylmagnesium bromide prepared from 12.2 g (0.50 g-atom) of magnesium turnings and 54.5 g (0.50 mol) of ethyl bromide in 250 ml of anhydrous diethyl ether was treated dropwise with 51.0 g (0.50 mol) of freshly distilled phenylacetylene and the resulting mixture was further stirred for 16 hr at 25°. Thereupon, a solution of 55.0 g (0.505 mol) of chlorotrimethylsilane in 50 ml of ether was added dropwise over the course of 4 hr. After a 24-hr reflux period, the semisolid mixture was cooled in ice and stirred while 100 ml of water was cautiously introduced. The separated organic layer was stored over anhydrous calcium sulfate, the solvent was evaporated, and the residue was distilled under reduced pressure. Phenylethynyl(trimethyl)silane (**5b**) was obtained in 80% yield, bp 46–47° (0.4 mm), $n^{22.5}\mathrm{D}$ 1.5272 [lit.[12] bp 59–60° (1.0 mm), $n^{25}\mathrm{D}$ 1.5255], and proved to be pure by vpc.

Phenylethynyl(trimethyl)germane (**5c**) was prepared by a similar procedure, except that tetrahydrofuran was used as the solvent. On a 0.035-molar scale, 95% of the germane was obtained, bp 54–55° (0.5 mm) [lit.[13] bp 70° (1.5 mm)].

Phenylethynyl(triethyl)germane (**5d**) was analogously synthesized in 60% yield from a 0.080-molar run, bp 90–91° (0.40 mm) [lit.[14] bp 115° (1.5 mm)].

Phenylethynyl(trimethyl)tin (**5e**) was prepared on a 0.10-molar scale in only 35% yield when diethyl ether was employed as the solvent. Better yields were subsequently obtained by conducting the reaction in tetrahydrofuran, bp 72–74° (0.50 mm) [lit.[15] bp 60° (0.2 mm)].

Dimethyl(phenylethynyl)phosphine[16] (**5f**) was synthesized on a 0.080-molar scale in 67% yield by permitting chloro(dimethyl)phosphine to interact with phenylethynylmagnesium bromide in diethyl ether and maintaining the reaction mixture at room temperature at all times. The reaction product was worked up and then distilled under a nitrogen atmosphere, bp 58–59° (0.30 mm).

***tert*-Butyl(phenyl)acetylene** (**5a**).—A solution of 41.0 g (0.50 mol) of *tert*-butylacetylene in 200 ml of 95% ethanol was added to a solution of 71.3 g (0.50 mol) of cuprous bromide in 800 ml of concentrated ammonium hydroxide. After standing overnight the blue-green precipitate was collected and washed, in turn, with ten 100-ml portions of water and then with three 50-ml portions of ethanol. The resulting orange powder, upon drying *in vacuo*, amounted to only 5.5 g (8%) of *tert*-butylethynylcopper(I). However, its subsequent reaction with iodobenzene proceeded well.

Thus, the foregoing cuprous acetylide (0.038 mol) and 7.66 g (0.038 mol) of iodobenzene were heated for 16 hr in 100 ml of refluxing anhydrous pyridine (general procedure of Stephens and Castro).[17] The cooled solution was diluted with 300 ml of water and extracted with four 100-ml portions of ether. The ether extracts were washed successively with 2 *N* hydrochloric acid, sodium bicarbonate solutions, and water. After drying over anhydrous calcium sulfate the ether solution provided, upon fractional distillation, 5.9 g (84%) of *tert*-butyl(phenyl)acetylene, bp 76–77° (1.5 mm) [lit.[18] bp 84° (10 mm)]. A vpc examination showed the presence of <1% of iodobenzene.

An effective modification to circumvent the difficult isolation and purification of the *tert*-butylethynylcopper(I) consisted in using the silver salt. Thus, a solution of 20.5 g (0.25 mol) of *tert*-butylacetylene in 100 ml of 95% ethanol was mixed with a solution of 42.5 g (0.50 mol) of silver nitrate in 100 ml of aqueous ethanol (1:1 v/v). The precipitated *tert*-butylethynylsilver was collected, washed with water and then with ethanol, and dried *in vacuo*, yield 45 g (94%). This silver acetylide (45 g, 0.24 mol), 48 g (0.24 mol) of iodobenzene, and 30.4 g (0.24 mol) of cuprous bromide were heated for 16 hr in 800 ml of refluxing anhydrous pyridine. Usual work-up afforded 23 g (57%) of pure *tert*-butyl(phenyl)acetylene.

Bromo(phenyl)acetylene (**5h**).—A solution of 20.4 g (0.20 mol) of phenylacetylene in 10 ml of tetrahydrofuran was added to a sodium hypobromite solution that was prepared from 11 ml of bromine, 50 ml of 10 *N* sodium hydroxide solution, and 100 g of ice. After a 5-hr stirring period, the reaction solution was treated with sufficient ammonium chloride solution to destroy the residual hypobromite ion. The solution was then extracted with ether, the extracts were dried over anhydrous calcium sulfate, and the ether solvent was evaporated. Distillation yielded 29.0 g (81%) of bromo(phenyl)acetylene as a pale yellow oil, bp 37–39° (0.35 mm), $n^{24}\mathrm{D}$ 1.6088 [lit.[19] bp 96° (15 mm)].

1-Propynyl(trimethyl)silane (**10**), **3,3-dimethylbut-1-ynyl(trimethyl)silane** (**11**), and **2-methylbut-1-en-3-yn-4-yl(trimethyl)silane** (**12**) were prepared from chlorotrimethylsilane and the corresponding alkynes, namely propyne, *tert*-butylacetylene, and

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2-methylbut-1-en-3-yne, respectively, by following the procedure for phenylethynylsilane. Because of the volatility of the alkynes, the yields of silanes ranged from 30 to 60%. Physical constants of $RSiMe_3$ follow: (a) R = $CH_3C{\equiv}C$, bp 96–97°, $n^{26}D$ 1.4153 (lit.[20] bp 100°); (b) R = $Me_3CC{\equiv}C$, bp 52–54° (55 mm) [lit.[21] 57° (60 mm)]; and [c) R = $CH_2{=}CMeC{\equiv}C$, bp 49–50° (33 mm), 120–122° (750 mm), $n^{25}D$ 1.4451 [lit.[22] bp 32° (15 mm)].

Reactions of Phenylethynyl Derivatives with Diisobutylaluminum hydride. Trans Hydralumination of Phenylethynyl(trimethyl)silane (5b).—A solution of 20.0 g (0.141 mol) of diisobutylaluminum hydride (**6**) in 25 ml of pentane was added dropwise to a stirred solution of **5b** (24.5 g, 0.141 mol) in 35 ml of pentane maintained at 20°. After a 15-hr stirring period, the solution was chilled in an ice bath and cautiously treated with 7.6 ml of water. The resulting suspension was filtered and the solvent was removed from the filtrate. Distillation of the residue gave 23.5 g (96%) of *trans*-β-styryl(trimethyl)silane, bp 90–91° (13 mm) [lit.[12] bp 80–83° (3 mm)]. A vpc analysis showed this sample to contain less than 5% of an equal mixture of the cis isomer and **5b**. Redistillation and spectral analysis established that trans reduction of the silylacetylene had occurred: ir (liquid film) 6.25 and 6.35 (C=C conjugated with aromatic) and 10.16 μ (*trans* CH=CH); nmr (neat) δ 0.14 [s, $(CH_3)_3Si$], 6.33 (d, 1-CH, *J* = 19 Hz), 6.88 (d, 2-CH, *J* = 19 Hz), 7.07–7.41 (m, 5 H).

When a 1:1 molar ratio of triisobutylaluminum and **5b** (0.04-molar scale) was heated at reflux in 50 ml of heptane for 15 hr, hydrolysis gave a mixture of 90% trans and 3% cis products and 7% of a higher isomeric mixture possibly involving Al–C bond addition.

Trans Hydralumination of 5b and Treatment with Deuterium Oxide.—Repetition of the foregoing hydralumination but treatment of the reaction mixture with deuterium oxide (99.8%), instead of water, yielded a monodeuterated *trans* product, nmr (neat) 6.88 (t, *J* = 3 Hz). There was no trace of the doublet centered at 6.33 ppm, due to the β hydrogen. Therefore, it is concluded that the aluminum was attached exclusively to the carbon adjacent to the Me_3Si group.

Trans Hydralumination of 5b at −10° under Partial Conversion.—To check whether any large amount of cis hydralumination occurred under kinetically controlled conditions, the foregoing hydraulumination was conducted at −10° (insignificant reaction <−10°), samples periodically withdrawn with a hypodermic syringe and squirted immediately into ice water. A vpc analysis showed that, even at 5% conversion of alkynylsilane into alkenylsilane, the *trans*-β-styryl(trimethyl)silane accounted for 95% of the products. It was observed that any time lag due to inefficient hydrolysis of the aliquots permitted further hydralumination during hydrolysis and led to spurious results.

Cis Hydralumination of 5b in the Presence of *N*-Methylpyrrolidine.—Admixture of 4.8 g (0.056 mol) of *N*-methylpyrrolidine with a solution of 8.0 g (0.056 mol) of diisobutylaluminum hydride in 40 ml of heptane gave a slight exotherm. This reagent solution was then added dropwise to a stirred solution of **5b** (9.8 g, 0.056 mol) in 20 ml of heptane and the resulting solution was heated for 24 hr at 55–60°. After cooling, 3.1 g of water were cautiously added, the suspension was filtered, and the filtrate was distilled. The main fraction (9.4 g, 96%) boiled at 43–45° (0.50 mm) [lit.[12] bp 50–52° (0.2 mm)] and was shown by vpc analysis to contain 96% *cis*-β-styryl(trimethyl)silane and 4% of the trans isomer. Redistillation through a 40 × 2 cm spinning-band column afforded a pure cis product: nmr (neat) δ 0.03 [s, $(CH_3)_3Si)$], 5.83 (d, 1-CH, *J* = 15, Hz), 7.36 (d, 2-CH, *J* = 15 Hz), 7.2 (s, sh, 5 H).

When a 1:1 molar ratio of **5b** and the hydride were permitted to interact in diethyl ether solution for 12 hr, a 65:35 ratio of cis and trans isomers were obtained upon hydrolysis.

Cis Hydralumination of 5b and Treatment with Deuterium Oxide.—The cis hydralumination was performed as described above, but the hydrolysis was performed with deuterium oxide (99.8%), nmr (neat) δ 7.36 (t, *J* = 2.2 Hz). Thus, it is concluded that again the aluminum in the hydralumination adduct was attached exclusively to the carbon adjacent to the Me_3Si group.

Trans Hydralumination of 5b *via* Cis Hydralumination. A. Diisobutylaluminum Chloride.—The cis hydralumination of **5b** was carried out on a 0.012-molar scale in the manner described above. A vpc analysis of a hydrolyzed aliquot showed the presence of 99% of the *cis*-styrylsilane and 1% of the trans isomer. Diisobutylaluminum chloride (2.0 g, 0.012 mol) was now added to the main reaction solution maintained at 20–25°. After 30 min the vpc analysis of a hydrolyzed aliquot showed a cis:trans styrylsilane ratio at 5:95; an aliquot analyzed after a further 15 hr of contact gave the same ratio of isomers.

Repetition of this isomerization experiment at −70° revealed that after 150 min a cis:trans ratio of 79:21 was obtained. Again in analyzing these aliquots care must be taken to achieve prompt hydrolysis at low temperatures (chilled $CH_2OH–H_2O$), in order to avoid additional, spurious isomerization.

B. Diisobutylaluminum Hydride.—As before, a 0.012-molar run of the cis hydraluminated adduct of **5b** was performed and again a vpc analysis of the hydrolyzed aliquot revealed 99% of the cis isomer. Diisobutylaluminum hydride (0.40 g, 0.003 mol) was added to the reaction solution and the solution was heated under reflux for 66 hr. Again a cis:trans styrylsilane ratio of 5:95 was obtained.

Trans Hydralumination of Phenylethynyl(trimethyl)germane (5c) and of Phenylethynyl(triethyl)germane (5d).—Conducted on a 0.017-molar scale, the individual hydraluminations of these compounds were performed as with **5b**. After 3 hr at 50° the reaction mixtures were hydrolyzed, worked up, and distilled (90–93% yield). In both cases, the vpc analysis of the distilled products showed 94 ± 1% of the *trans*-β-styryl isomer and 6% of the cis product. Redistillation through a spinning-band column (40 × 2 cm) afforded the pure *trans* isomer: (a) *trans*-β-styryl(trimethyl)germane, bp 60–62° (0.5 mm);[23] (b) *trans*-β-styryl(triethyl)germane, bp 96–97° (0.50 mm), nmr (neat) δ 0.75–1.32 [m, $(C_2H_5)_3Ge$], 6.57 (d, 1-CH, *J* = 18.5 Hz), 6.84 (d, 2-CH, *J* = 18.5 Hz), and 7.1–7.5 (m, 5 H).

Anal. Calcd for $C_{14}H_{22}Ge$: C, 63.95; H, 8.44. Found: C, 64.03; H, 8.30.

Trans Hydralumination of Phenylethynyl(triethyl)germane and Treatment with Deuterium Oxide.—Hydralumination was conducted on a 0.005-molar scale, as previously described for **5b**. Treatment with deuterium oxide (99.8%) and distillative work-up gave 93% of the *trans*-β-styryl(triethyl)germane, whose neat nmr spectrum showed a triplet at 6.84 ppm (*J* = 2 cps) but showed the absence of the doublet at 6.57 ppm; thus, in the hydraluminated adduct, the aluminum was attached exclusively to the carbon adjacent to the Et_3Ge group.

Cis Hydralumination of 5c or 5d in the Presence of *N*-Methylpyrrolidine.—As with **5b**, but on a 11.3-millimolar scale, the *N*-methylpyrrolidine and hydride were mixed in 20 ml of heptane. This solution was added dropwise to the germane (**5c** or **5d**) in 20 ml of heptane. After 15 hr at 60° and 5 hr at reflux, the usual work-up gave the corresponding β-styryl(trialkyl)germanes in 90–94% yield, each of which was shown by vpc to be 98% ± 1 of the cis isomer and 2% of the trans isomer. *cis*-β-Styryl(trimethyl)germane boiled at 59–60° (0.5 mm) and displayed the typical vinyl signals at 5.85 and 7.45 ppm (*J* = 14 Hz); *cis*-β-styryl(triethyl)germane boiled at 93–94° (0.5 mm) and had vinyl nmr signals at 5.92 and 7.50 ppm (*J* = 14 Hz). Only the methyl analog was analyzed for carbon and hydrogen, since the *cis*-β-styryl(triethyl)germane could be converted by an isomerization into the already analyzed *trans*-β-styryl(triethyl)germane (*cf. infra*).

Anal. Calcd for $C_{11}H_{16}Ge$: C, 59.82; H, 7.30. Found: C, 60.04; H, 7.55.

Cis Hydralumination of 5d and Isomerization of the Hydralumination Adduct.—The foregoing procedure was repeated for **5d**, but on a 22-millimolar scale. At the close of the heating period, one-half of the solution was treated with deuterium oxide and worked up in the usual way. The distilled product was identified as >98% of *cis*-β-styryl isomer by vpc analysis. Examination of its nmr spectrum (neat) showed only an unresolved triplet resonance at 7.50 ppm and hence proved that the product is fully deuterated at the vinyl carbon adjacent to the Et_3Ge group.

The remaining one-half of the reaction solution was treated with 13 mmol of diisobutylaluminum chloride and the solution was

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stirred at 20–25° for 1 hr. Customary work-up gave *trans*-β-styryl(triethyl)germane which contained 4% cis isomer.

Attempted Hydralumination of Phenylethynyl(trimethyl)tin (5e).—The interaction of 1.6 g (11 mmol) of the hydride with 2.98 g (11 mmol) of **5e** in 40 ml of heptane led to the formation of reddish solution during the 48-hr reaction period at 20–25°. No gas evolution or metal deposition was noticed. Usual work-up and solvent removal through a fractionation column gave a liquid residue (1.2 g) which by vpc analysis was shown to contain 92% of phenylacetylene, 5% of **5e**, and 3% of an unidentified component of much higher retention time.

Repetition of the experiment with a 1:1 mixture of the hydride and *N*-methylpyrrolidine at 60° for 15 hr gave identical results.

Hydralumination of *tert*-Butyl(phenyl)acetylene (5a).—A solution of 4.0 g (28.2 mmol) of the hydride and 4.40 g (28 mmol) of *tert*-butyl(phenyl)acetylene in 40 ml of heptane was heated at 50° for 18 hr. Usual hydrolytic work-up gave 3.76 g (84%) of *cis*-β-*tert*-butylstyrene:[24] bp 73–75° (13 mm); nmr (neat) δ 0.95 [s, $(CH_3)_3C$], 5.57 (d, 2-CH, J = 12.5 Hz), 6.43 (d, 1-CH, J = 12.5 Hz), and 7.12 (s, 5 H).

An identical run was performed but the hydralumination adduct was treated with deuterium oxide (99.8%). The distilled product displayed an nmr spectrum having a triplet (J = 1.5 Hz) with peaks of equal intensity centered at 5.57 ppm. Since no vinyl peaks were detectable at 6.43 ppm, the product was fully deuterated at the vinyl carbon adjacent to the phenyl group.

Hydralumination and Concurrent Metalation of Phenylacetylene.—Diisobutylaluminum hydride (8.0 g, 56.4 mmol) was added dropwise to 12.5 g (122 mmol) of fresly distilled phenylacetylene and the resulting orange liquid was stirred for 4 days at 20–25°. The excess phenylacetylene (6.4 g, 63 mmol) was then removed *in vacuo* and caught in a trap cooled in ethanol–solid carbon dioxide. The residual red syrup was treated with 3.4 g of deuterium oxide, the suspension was diluted with hexane, and the mixture was filtered. Removal of the solvent from the filtrate gave, by vpc analysis, a mixture of phenylacetylene (29%) and styrene (71%). By means of nmr analysis, the acetylene was shown to be 1-deuterio-2-phenylacetylene (free of undeuterated acetylene) and the styrene to be exclusively *trans*-β-deuteriostyrene (triplets centered at 4.77 and 5.36 ppm). No deuteron could be detected on the cis-β or the α-vinyl position.

Attempted Hydralumination of Bromo(phenyl)acetylene (5h).—No reaction occurred, as determined by vpc analysis, when 8.0 g (56.4 mmol) of the hydride and 10.2 g (56.4 mmol) of bromo(phenyl)acetylene in 25 ml of heptane was stirred at 20–25° for 5 days. Reflux for 24 hr caused darkening of the solution and usual hydrolytic work-up gave only phenylacetylene.

Hydralumination of Dimethyl(phenylethynyl)phosphine (5f).—A solution of 3.28 g (23.1 mmol) of the hydride and 3.74 g (23.1 mmol) of **5f** in 25 ml of heptane was heated for 15 hr at 45–50°, during which time a colorless precipitate formed. By warming briefly to 90°, the solid redissolved and thereupon the solution was divided into two parts. One part upon hydrolytic work-up yielded 70% of dimethyl(*cis*-β-styryl)phosphine: bp 69–71° (0.85 mm); nmr (neat) 0.98 [d, $(CH_3)_2P$, J_{HP} = 3.0 Hz], 6.00 (d of d, 1-CH, $J_{H_1H_2}$ = 12.5 Hz, J_{HP} = 1.2 Hz), 6.74 (d, 2-CH, J = 12.5 Hz), 7.15–7.4 and 7.5–7.75 (m, 5 H).

Anal. Calcd for $C_{10}H_{13}P$: C, 73.15; H, 7.98. Found: C, 73.32; H, 7.85.

The other part of the reaction mixture was treated with deuterium oxide to give 75% of this distilled styrene, whose nmr spectrum (neat, triplets centered at 6.00 and 6.74 ppm) showed deuteration on both vinylic carbon atoms in the ratio of cis-β:α 85:15 in the resulting dimethyl(*cis*-β-styryl)phosphine.

Attempts to change the stereochemistry of addition were unsuccessful. (a) A run was conducted on the foregoing scale, and then 2.3 mmol of **6** were added. Refluxing for 16 hr and hydrolytic work-up gave only the cis isomer, and no sign of the trans addition. (b) Using a 1:1 ratio of the hydride and *N*-methylpyrrolidine for the reduction of **5f** for 16 hr at reflux gave 60% of the cis product and 40% of **5f** upon hydrolytic work-up.

Hydralumination of Other Alkynylsilanes. A. 1-Propynyl(trimethyl)silane (10).—This alkyne could not be smoothly hydraluminated despite a studied variation of experimental procedures, including the use of equimolar amounts of *N*-methylpyrrolidine. Either the alkyne remained unreacted or it underwent reductive dimerization to yield a mixture of 1,3-bis(trimethylsilyl)-2-methyl-1,3-pentadienes,[25] bp 173–176°. No trace of the known, stable monomeric *cis*- or *trans*-1-propenyl(trimethyl)silanes could be detected by vpc analysis of reaction hydrolysates.

B. 3,3-Dimethylbut-1-ynyl(trimethyl)silane (11).—Hydralumination on a 28-millimolar scale in 20 ml of hexane gave a 65% yield of *trans*-dimethybut-1-en-1-yl(trimethyl)silane: bp 128–130°; nmr (neat) 0.05 [c, $(CH_3)_3Si$], 0.98 [s, $(CH_3)_3C$], 5.57 (d, 1-CH, J = 19 Hz), and 6.07 (d, 2-CH, J = 19 Hz).

Repetition on the foregoing scale with a hydrolytic work-up of deuterium oxide yielded a product which by nmr analysis was shown to have the deuteron exclusively on the vinyl carbon α to the Me_3Si group (triplet at 6.07, 2.7 Hz).

The use of a 1:1 hydride–*N*-methylpyrrolidine mixture on a 14-millimolar scale with 48-hr heating gave, upon hydrolysis, 72% of *cis*-dimethylbut-1-en-1-yl(trimethyl)silane:[26] bp 109–110°; nmr (neat) 0.14 [s, $(CH_3)_3Si$], 1.07 [s, $(CH_3)_3C$], 5.37 (d, 1-CH, J = 16 Hz), and 6.37 (d, 2-CH, J = 16 Hz).

C. 2-Methylbut-1-en-3-yn-4-yl(trimethyl)silane (12).—Treatment of an excess of the silane (16.0 g, 0.116 mol) with 8.0 g (0.056 mol) of the hydride at 20–25° produced a yellow solution exothermically. After 4 days the excess **12** was removed *in vacuo*. Hydrolysis with pentane–water and distillative work-up yielded 5.4 g (67%) of *trans*-2-methylbuta-1,3-dien-4-yl(trimethyl)silane: bp 138–139°; nmr (CCl_4) δ 0.09 [s, $(CH_3)_3Si$], 1.83 (s, CH_3), 5.03 (br s), 5.81 (d, 4-CH, J = 19.5 Hz), and 6.60 (d, 3-CH, J = 19.5 Hz).

Anal. Calcd for $C_8H_{16}Si$: C, 68.48; H, 11.50. Found: C, 68.49; H, 11.59.

A 0.10-molar run employing a 1:1 mixture of hydride and *N*-methylpyrrolidine with **12** and a heating period of 50 hr at 60° led to a 78% yield of *cis*-2-methylbuta-1,3-dien-4-yl(trimethyl)silane: bp 40° (28 mm); nmr (CCl_4) 0.10 [s, $(CH_3)_3Si$], 1.79 (s, CH_3), 4.90 (br s), 5.52 (d, 4-CH, J = 15 Hz), and 6.73 (d, 3-CH, J = 15 Hz).

Anql. Calcd for $C_8H_{16}Si$: C, 68.48; H, 11.50. Found: C, 68.57; H, 11.29.

Hydraluminations with Lithium Aluminum Hydride. A. cis-β-Styryl(trimethyl)silane.—A solution of 1.0 g (26 mmol) of lithium aluminum hydride and 4.5 g (26 mmol) of *cis*-β-styryl(trimethyl)silane in 50 ml of anhydrous tetrahydrofuran was heated at reflux for 12 hr and then hydrolyzed. Work-up gave exclusively β-phenylethyl(trimethyl)silane, identified by ir and nmr comparison with an authentic sample.

B. Phenylethynyl(trimethyl)silane.—A similar reduction of this silane gave phenylacetylene as the only product.

Bromodesilylation of *trans*,β-Styryl(trimethyl)silane (17).—A solution of bromine (4.55 g, 28.4 mmol) in 8 ml of carbon tetrachloride was added dropwise to a stirred, cold (−20°) solution of **17** (95% *trans*, 5.0 g, 28.4 g) in 45 ml of the same solvent. The color was discharged promptly and some frothing was noted. After stirring for 15 hr at 20–25°, the solution was worked up by distillation. The β-bromostyrene (4.7 g, 90%) distilled at 106–108° (19 mm) and was shown by vpc analysis to be composed of 88% *trans*- and 12% *cis*-β-bromostyrene. The nmr spectrum confirmed this conclusion.

Registry No.—**5a**, 4250-82-2; **5b**, 2170-06-1; **5c**, 4131-47-9; **5d**, 4131-48-0; **5e**, 1199-95-7; **5f**, 20505-08-2; **5g**, 536-74-3; **5h**, 932-87-6; **6**, 1191-15-7; **10**, 6224-91-5; **11**, 14630-42-3; **12**, 18387-60-5; *trans*-β-styryl(trimethyl)silane, 19372-00-0; *cis*-β-styryl(trimethyl)silane, 19319-11-0; *trans*-β-styryl(triethyl)germane, 19319-12-1; *cis*-β-styryl(trimethyl)germane, 31790-89-3; *cis*-β-styryl(triethyl)germane, 19319-00-7; *cis*-β-*tert*-butylstyrene, 3740-05-4; dimethyl(*cis*-β-styryl)phosphine, 31734-51-7; 1,3-dimethyl-2,4-bis(trimethylsilyl)butadiene, 31734-52-8; *trans*-dimethylbuten-1-yl(trimethyl)silane, 20107-37-3; *cis*-dimethylbut-1-en-1-yl(trimethyl)silane, 26567-95-3; *trans*-2-

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[25] The individual dimers, separated by vpc, had the following nmr absorptions: isomer A, 0.1 (Me_3Si), 0.16 (Me_3Si), 1.77 (d, CH_3, J = 7.5 Hz), 1.82 (s, CH_3), 4.98 (br, 1 H), and 6.03 (q, 1 H, J = 7.5 Hz); and isomer B, −0.04 (Me_3Si), 0.09 (Me_3Si), 1.62 (d, CH_3, J = 7.5 Hz), 1.77 (s, CH_3), 4.9 (br, 1 H), and 5.7 (q, 1 H, J = 7.5 Hz) (G. Gupta, unpublished studies).

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methylbuta-1,3-dien-4-yl(trimethyl)silane, 31734-55-1; *cis*-2-methylbuta-1,3-dien-4-yl(trimethyl)silane, 31734-56-2.

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Mass Spectrometry in Structural and Stereochemical Problems. CCIX.[1] Functional Group Interaction after Electron Impact. Anomalous Ether Cleavage in Bifunctional Benzyloxy Ethers[2]

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In a series of bifunctional benzyloxy ethers, the scope and limitations of the unexpected C–O cleavage at the ether function with charge retention on the benzyloxy moiety (*m/e* 107) has been investigated. Deuterium-labeling experiments indicated that simple C–O ether cleavage alone could not account for the formation of this ion. Its generation was found to be independent of the distance between the two functional groups. From these and other data, it was concluded that the structure of this ion was best represented as protonated benzaldehyde.

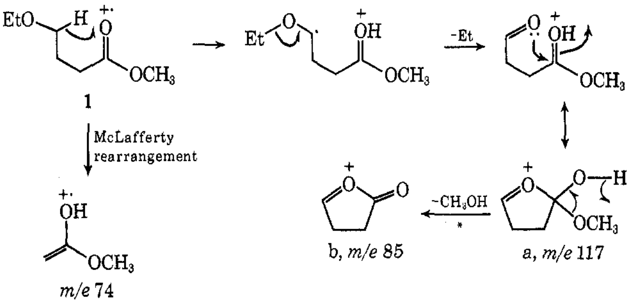
During the last decade the fragmentation patterns of almost every class of monofunctional compounds were thoroughly investigated,[4] and in the last few years the question of whether two functional groups in the same molecule would give rise to fragmentations independent of one another or to unique fragmentations resulting from direct interaction of the two groups has been the subject of several investigations.[5-14] As an extension of work reported earlier,[14] we became interested in pursuing further the nature of the process leading to the intense peaks at *m/e* 117 and 85 in the mass spectrum[15] (Figure 1) of methyl 4-ethoxybutyrate (**1**). With the

$EtO(CH_2)_3CO_2CH_3$
1

$C_6H_5CH_2O(CH_2)_3CO_2CH_3$
2

aid of deuterium-labeling studies, high-resolution measurements, and metastable defocusing experiments,[16] the formation of these ions was rationalized as shown in Scheme I.

SCHEME I



It was reasoned that, if the ethyl ether portion of **1** were replaced with another substituent which would yield a radical more stable than ethyl, the process leading to ions of masses 117 and 85 should be enhanced. To this end methyl 4-benzyloxybutyrate (**2**) was synthesized and its mass spectrum (Figure 2) was recorded. These expectations were only partially fulfilled in that the peaks at *m/e* 117 and 85 were observed in Figure 2, but their intensities were no greater than in the spectrum (Figure 1) of **1**. Instead, a host of additional peaks was observed, most significant and interesting of which being the peak at *m/e* 107 (this peak becomes the base peak at 12 eV). High-resolution measurements indicated the composition of this ion to be C_7H_7O, which corresponds formally to cleavage of the C–O bond of the ether function with charge retention on the benzyloxy fragment. This finding was particularly unusual, since normally cleavage of an ether C–O bond with charge retention on the oxygen-containing fragment is a very unfavorable process[17] (in the spectrum of benzyl *n*-butyl ether, the *m/e* 107 peak is negligible—Σ_{40} 0.1%). Because of the uniqueness of this cleavage, we suspected that the ester function at the other end of the molecule was playing an unexpected role in this process and considered it of interest to determine the scope and limitations of this process.

Results and Discussion

It was felt that the two most obvious parameters which might influence the formation of the "anomalous" *m/e* 107 peak would be (a) the length of the hydrocarbon chain separating the two functions and (b) the nature of the functional group at the end of the chain. As a first step in this investigation, the effect of varying the chain length between the two functions on the relative intensity of the *m/e* 107 peak was probed. To this end

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[1] For paper CCVIII, see J. R. Dias, Y. Sheikh, and C. Djerassi, *J. Amer. Chem. Soc.*, in press.

[2] Financial support from the National Institutes of Health (Grant No. AM 04257) is gratefully acknowledged.

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[15] Mass spectra recorded at nominal voltages of 70 and 12 eV. Unless otherwise stated, only 70-eV spectra are shown.

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[17] Reference 4, p 227.