Anal. Calcd for $C_{23}H_{33}IO$: C, 61.04; H, 7.34; I, 28.05. Found: C, 60.95; H, 7.15; I, 27.73.

17α-Hydroxy-20-methylenepregn-4-en-3-one (**10**).—The ketone **9** (2 g) was converted by procedure B into **10**: yield 1.84 g (93%); mp 239–241°; $[\alpha]_D$ −113° ($CHCl_3$); uv max 240 nm (ε 16,700); nmr ($CDCl_3$) δ 4.92 (d, $C{=}CH_2$). *Anal.* Calcd for $C_{22}H_{32}O_2$: C, 80.44; H, 9.83. Found: C, 80.06; H, 9.85.

Methyl 3β-Acetoxy-5α-hydroxy-6-methylenebisnorcholan-21-oate (**14**).—The general method B converted the ketone **13** (2.0 g) into **14**: yield 1.9 g (96%) mp 103–105°; $[\alpha]_D$ −59° ($CHCl_3$); nmr ($CDCl_3$) δ 4.77 and 4.63 ($C{=}CH_2$). *Anal.* Calcd for $C_{26}H_{40}O_5$: C, 72.19; H, 9.32. Found: C, 72.10; H. 8.95.

1-Hydroxymethyl-1-(6′-methoxy-2′-naphthyl)cyclopropane (**16**).—The ketone **15** (2.5 g) was converted by the general method A into **16**: yield 2.0 g (76%); mp 79–80°; nmr ($CDCl_3$) δ 0.86 (m, cyclopropyl) and 3.66 (s, CH_2); mass spectrum *m/e* (rel intensity) 228 (47) and 197 (100).

1-Hydroxymethyl-1-phenylcyclopropane (**17**).—Method A converted ω-hydroxyacetophenone (0.4 g) into the known[8] **17**: yield 0.215 g (49%); nmr ($CDCl_3$) δ 0.78 (s, cyclopropyl), 2.06 (s, OH), 3.55 (s, CH_2), 7.1–7.3 (m, aromatic).

Reaction of Androstan-3-one (4) with the Zinc–Methylene Iodide Reagent.—The general procedure A, modified by the use of tetrahydrofuran as solvent, converted the ketone **4** into a mixture from which was isolated a low yield of the known[9] 3,3-ethano derivative **6**: mp 76–77°; $[\alpha]_D$ +6° ($CHCl_3$); nmr ($CDCl_3$) δ 0.19 (cyclopropyl). The methylene derivative **5** was also isolated: mp 89–90°; $[\alpha]_D$ −9° ($CHCl_3$); nmr ($CDCl_3$) δ 4.63 ($C{=}CH_2$). *Anal.* Calcd for $C_{20}H_{32}$: C, 88.16; H, 11.84. Found: C, 88.12; H, 11.49.

Reaction of 17β-Acetoxyandrosta-4,6-dien-3-one (7) with the Zinc–Methylene Iodide Reagents.—The process A, modified by the use of tetrahydrofuran as solvent, converted the ketone **7** (100 mg) into the known derivatives **8a**, yield 19 mg (18%), nmr ($CDCl_3$) δ 6.00 (s, 4 H), and the isomer **8b**, yield 12 mg (12%), nmr ($CDCl_3$) δ 5.94 (s, 4 H). Identification was confirmed by comparison of infrared spectra and gas chromatographic retention times with those of authentic samples.[10]

Reaction of 17β-Acetoxy-19-norandrost-5(10)-en-3-one (18) with the Zinc–Methylene Iodide Reagent.—The general procedure A converted the ketone **18** (0.5 g) into a mixture, ir (film) 3450 cm^{-1}. Column chromatography on silica gel or standing in methylene chloride solution converted the two major components into new compounds of different tlc polarity. The products isolated by column chromatography are considered to be the 2 (or 4) ξ-methyl ketone **19**, yield 110 mg (10%), nmr ($CDCl_3$) δ 0.8 (m, cyclopropyl), 1.15 (d, J = 7 Hz, CH_3), mass spectrum *m/e* 344 (M^+), and the 4 (or 2) ξ isomer **20**, 110 mg (10%), nmr ($CDCl_3$) δ 0.48 (m, cyclopropyl), 1.14 (d, J = 7 Hz, CH_3), mass spectrum *m/e* 344 (M^+).

Registry No.—**4**, 1224-95-9; **5**, 28113-74-8; **6**, 21152-61-4; **7**, 2352-19-4; **10**, 25596-88-7; **11**, 31729-63-2; **12**, 31790-94-0; **14**, 31729-64-3; **16**, 31729-65-4; **17**, 31729-66-5; **18**, 19906-32-2; **19**, 31729-68-7; **20**, 31729-69-8; zinc–methylene iodide, 31729-70-1.

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(8) H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **41**, 2429 (1963).

(9) N. S. Bhacca, M. E. Wolff, and W. Ho, *Tetrahedron Lett.*, 5427 (1968).

(10) G. Tarzia, N. H. Dyson, I. T. Harrison, J. A. Edwards, and J. H. Fried, *Steroids*, **9**, 387 (1967). Authentic samples were kindly supplied by Dr. N. H. Dyson.

Dechlorination of Benzotrichloride and Tolane Tetrachloride by Metals

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The reductions of benzotrichloride and tolane tetrachloride to *cis*- and *trans*-α,α′-dichlorostilbene by iron, copper, and zinc are often quantitatively irreproducible owing to their heterogeneity. Only zinc caused any complete dechlorination to diphenylacetylene, while only copper preferentially converted tolane tetrachloride to the trans isomer. An authentic pure sample of *cis*-α,α′-dichlorostilbene was obtained by preparative gas chromatography, and the literature melting point was shown to be incorrect. The ir and Raman spectra of the cis and trans isomers are compared.

During a study of the oxidizing ability of organic polyhalides, it became apparent that there are discrepancies in the literature regarding the dechlorination of benzotrichloride and of tolane tetrachloride. Consequently, we have used improved analytical techniques to determine the products of dechlorination of benzotrichloride and tolane tetrachloride by iron, copper, and zinc and have found that these heterogeneous reactions are often hard to reproduce.

Results

Reduction of Benzotrichloride by Iron and Copper.—Iron powder in boiling aqueous suspension is reported[1] to reduce benzotrichloride to *trans*-α,α′-dichlorostilbene, *via* the intermediacy of tolane tetrachloride.[2] We confirmed that reduction for 1 hr gave tolane tetrachloride; however, after 24 hr we obtained 72% *cis*-α,α′-dichlorostilbene and only 28% of the trans isomer. Reduction with active copper powder[3] in pyridine at 65° for 2 hr gave only tolane tetrachloride.[4] Thus, both methods are suitable for the convenient synthesis of tolane tetrachloride.

In contrast, neat dry benzotrichloride shaken with iron powder for 1 day at 20° gave no coupled products, although a dark red solution was formed.

Reduction of Tolane Tetrachloride by Iron.—Reduction of tolane tetrachloride with iron powder for 4 hr in boiling aqueous suspension is reported to yield 64% of *trans*-α,α′-dichlorostilbene.[2] However, even after 1 day, we obtained 68% unchanged tolane tetrachloride, 23% *cis*-α,α′-dichlorostilbene, and only 9% of the trans isomer. The cis/trans ratio, 2.6, is identical with that which we obtained on reduction of benzotrichloride with iron powder. This is therefore consistent with the intermediate formation of tolane tetrachloride in this latter reaction.

Reduction of Tolane Tetrachloride by Copper.—Freshly prepared active copper powder[3] suspended in dimethylformamide at 140° completely dechlorinated tolane tetrachloride to 28% *cis*- and 72% *trans*-α,α′-dichlorostilbene in only 30 min. Reduction in pyridine

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(1) Y. Ogata and R. Oda, *Bull. Inst. Phys. Chem. Res. (Tokyo)*, **21**, 616 (1942); *Chem. Abstr.*, **43**, 2194*d* (1949).

(2) Y. Ogata and H. Nakamura, *J. Org. Chem.*, **21**, 1170 (1956).

(3) A. H. Blatt, Ed., "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1953, p 446.

(4) Compare U. Hanhart, *Ber.*, **15**, 898 (1882).

at 65° was much slower;[5] after 3 hr there remained 54% unchanged tolane tetrachloride together with 38% *trans*-α,α'-dichlorostilbene and only 8% of the cis isomer. In each case the cis/trans ratio is much smaller than that for reduction by iron, and copper was the only reducing agent which produced the trans isomer preferentially.

In contrast, copper is said[6] to reduce 4,4'-dichlorotolane tetrachloride in pyridine to 72% *cis*-α,α'-dichloro-4,4'-dichlorostilbene and only 28% of the trans isomer.

Reduction of Tolane Tetrachloride by Zinc.—Blank[7] and Taylor and Murray[8] reported that zinc powder reduces tolane tetrachloride to a mixture of *cis*- and *trans*-α,α'-dichlorostilbene which can be separated with cold ethanol. However, Weis[1] claimed that reduction by zinc in dimethylformamide for 30 min at 140° gave only the cis isomer, which is not further dechlorinated to diphenylacetylene.

We have performed a number of reductions of tolane tetrachloride by zinc in dimethylformamide. A different product distribution was obtained in each case (Table I), and there was no unchanged starting material. It is apparent that the extent of dechlorination to diphenylacetylene is highly variable. Measurements at various reaction times for reaction 7 showed that the cis isomer must be initially produced in preference to the trans. However, the trans isomer is rapidly reduced to diphenylacetylene, while the cis form undergoes such further reduction only to a much smaller extent. From only two reactions, 1 and 7, did we obtain, after recrystallization from methanol, the white crystals melting sharply at 68° which were identified by Weis[6] as *cis*-α,α'-dichlorostilbene. However, we found, by vpc, that these crystals comprised two components in a 1:2 ratio, and after isolation by preparative gas chromatography these were identified as diphenylacetylene, mp 61°, and authentic *cis*-α,α'-dichlorostilbene, mp 58°, respectively (see Experimental Section). The mixture melted sharply, and at higher temperature than either component, suggesting the formation of a molecular complex. Bergmann[9] has noted such a 1:2 complex, mp 67–69°, from the chlorination of diphenylacetylene, and Iwai, *et al.*,[10] from the reaction of diphenylacetylene with nitryl chloride.

TABLE I
REDUCTION OF TOLANE TETRACHLORIDE BY ZINC DUST IN DIMETHYLFORMAMIDE AT 140°

Reaction	Reaction time, min	Product distribution by vpc, % c-PhCCl=CClPh	 t-PhCCl=CClPh	 PhC≡CPh
1	30	67[a]	0	33[a]
2	30	27	0	73
3	30	53	33	14
4	30	50	24	26
5	30	42	42	16
6	30	52	18	30
7	60	58	26	16
7	90	54	13	33
7	120	50	6	44
7	150	48	Trace	52
7	180	46	0	54
7	180	67[a]	0	33[a]

[a] After recrystallization from methanol.

The ir and Raman spectra of *cis*- and *trans*-α,α'-dichlorostilbene are compared in Table II.

Discussion

The reductions of benzotrichloride and tolane tetrachloride described above are summarized in Table III. They are often irreproducible and there are many discrepancies in the published literature. This is probably due to the complete heterogeneity of the reactions, where neither the metal powder nor, in some cases, the organic substrate is soluble in the medium used. In addition the precise condition of the metal surface and the efficiency of stirring[1] are important. Another variable lies in the precautions taken against light, since we found that sunlight, even through glass, isomerizes *cis*-α,α'-dichlorostilbene in solution to the trans form within a week, although the reverse process did not occur. Our procedure of product analysis by direct gas chromatography rather than by reliance on product isolation as previous authors had done is also probably responsible for some of the differences between our results and theirs.

Comparison of the reductions of benzotrichloride and tolane tetrachloride by iron described above shows that the latter compound is more rapidly reduced when produced *in situ* from benzotrichloride than when it was used as the starting material. This may be due to more intimate contact between tolane tetrachloride formed as an intermediate and the metal, since it is partly soluble in the reaction mixture containing benzotrichloride. In contrast, when the tolane tetrachloride is the initial substrate it is insoluble in the wholly aqueous medium employed. In support of this, the converse situation prevails in the corresponding reductions with copper, when the tolane tetrachloride is completely soluble in the pyridine or dimethylformamide medium employed.

Our preparation of *cis*-α,α'-dichlorostilbene with mp 58°, lower than that reported previously, deserves comment. The compound was isolated by preparative gas chromatography and was shown by gas chromatography to be free from the trans isomer. In contrast, literature preparations of supposedly pure *cis*-α,α'-dichlorostilbene have relied on purification by solvent extraction and recrystallization. However, we found that recrystallization did not completely separate all trans isomer from the cis compound, because the latter is more soluble. Hence recrystallization is an ineffective method for the purification of *cis*-α,α'-dichlorostilbene, although the trans isomer can be obtained pure in this way. It appears that, while the "α-dichlorostilbene" of the literature[11] is the pure trans-α,α'-dichlorostilbene, the so-called "β-dichlorostilbene," with reported melting points of 61–64°,

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[5] Compare L. V. Johnson, F. Smith, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 4710 (1952).

[6] C. D. Weis, *Helv. Chim. Acta*, **49**, 234 (1966).

[7] A. Blank, *Justus Liebigs Ann. Chem.*, **248**, 17 (1888).

[8] T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938).

[9] E. Bergmann, *ibid.*, 402 (1936).

[10] I. Iwai, K. Tomita, and J. Ide, *Chem. Pharm. Bull.*, **13**, 118 (1965). These authors erroneously identify the complex as 2:1 diphenylacetylene–*cis*-α,α'-dichlorostilbene, but their analytical results actually support a 1:2 complex.

[11] J. Heilbron, Ed., "Dictionary of Organic Compounds," 4th ed, Oxford University Press, New York, N. Y., 1965, and references cited therein.

TABLE II

IR AND RAMAN SPECTRA OF *cis*- AND *trans*-DICHLOROSTILBENES

Isomer	Ir C=C, aromatic, 1600 cm^{-1}	Ir C—Cl, 700 cm^{-1}	Raman C=C, aromatic, 1600 cm^{-1}	Raman C—Cl, 700 cm^{-1}
Cis	1570 (w), 1590 (w), 1610 (w)	760 (m)	1575 (s), 1600 (s), 1605 (s), 1620 (s)	775 (w)
Trans		730 (s)[a]	1575 (w), 1600 (s), 1620 (w), 1650 (s)	760 (w)

[a] Aromatic C–H deformation probably overlaps with this band.

TABLE III

DECHLORINATION OF BENZOTRICHLORIDE AND TOLANE TETRACHLORIDE BY IRON, COPPER, AND ZINC

Reductant	Conditions	Product
	Benzotrichloride	
Fe	Aqueous suspension, 100°, 1 hr	$PhCCl_2CCl_2Ph$
	Aqueous suspension, 100°, 24 hr	72% *cis*-, 28% *trans*-$PhCCl{=}CClPh$
Active Cu	Pyridine suspension, 65°, 2 hr	$PhCCl_2CCl_2Ph$
	Tolane Tetrachloride	
Fe	Aqueous suspension, 100°, 24 hr	23% *cis*-, 9% *trans*-$PhCCl{=}CClPh$ 68% unchanged $PhCCl_2CCl_2Ph$
Active Cu	Dimethylformamide suspension, 140°, 30 min	28% *cis*-, 72% *trans*-$PhCCl{=}CClPh$
Active Cu	Pyridine suspension, 65°, 3 hr	38% *trans*-, 8% *cis*-$PhCCl{=}CClPh$ 54% unchanged $PhCCl_2CCl_2Ph$
Zn	Dimethylformamide suspension, 140°	Mixture of *cis*- and *trans*-$PhCCl{=}CClPh$ and $PhC{\equiv}CPh$; distribution varies with reaction time (see Table I)

is not the pure cis isomer but is probably contaminated with small amounts of the trans compound.[4,7–9,12,13]

Table II shows that our *cis*- and *trans*-α,α′-dichlorostilbenes exhibit characteristic ir and Raman spectra which are in agreement with the proposed assignment. There is no C=C stretching band in the ir of the trans isomer. The C—Cl stretching for the cis isomer is higher than that for the trans isomer (ir, cis 760 cm^{-1}, trans 730 cm^{-1}; Raman, cis 775 cm^{-1}, trans 760 cm^{-1}). This trend is also true for the analogous case of *cis*- and *trans*-dichloro-2-butene,[14] where the cis isomer showed a C—Cl stretch at 755 cm^{-1} *vs.* 730 cm^{-1} for the trans isomer. This suggests a greater single bond character in the cis isomer and agrees with the observation that the C=C stretch is at 1620 cm^{-1} for the cis isomer but at 1650 cm^{-1} for the trans isomer. A similar shift is noted in dichloroethylene, where the C=C stretch is at 1590 cm^{-1} for the cis isomer but at 1653 cm^{-1} for the trans isomer.[15]

Experimental Section

Gas Chromatographic Analysis.—Vpc analyses of reaction products and of the purity of compounds isolated were made on 6 ft of 10% OV-1 silicone gum rubber on 80–100 Supelcoport, using an all-glass system to avoid the decomposition of benzotrichloride and tolane tetrachloride which often occurs on stainless steel columns. Peaks were identified by spiking with authentic samples, by mass spectrometry, and in some cases by collection. Despite reports that *cis*- and *trans*-α,α′-dichlorostilbenes interconvert above 200°,[8] this did not occur in our system since it was possible to chromatograph pure samples of both isomers without isomerization.

Purification of Benzotrichloride.—Benzotrichloride filtered through alumina and fractionated under nitrogen at reduced pressure still contains small amounts of tolane tetrachloride and the α,α′-dichlorostilbenes. When necessary these were removed by recrystallization twice from hexane at −10°, the feathery white crystals then being remelted and purged with nitrogen to remove all residual hexane.

Preparative Methods.—Reactions were generally carried out, in subdued light, as described in the literature cited in the Results section. Vpc analyses of product distribution were performed on the reaction solutions directly after removal of the spent metal.

Tolane tetrachloride was prepared by reduction of benzotrichloride with iron[2,3] or copper[5] as previously described. It was recrystallized with activated charcoal from benzene–methanol as white, chunky crystals, mp 162°.

Anal. Calcd for $C_{14}H_{10}Cl_4$: C, 52.5; H, 3.2; Cl, 44.3. Found: C, 52.6; H, 3.2; Cl, 44.3.

***trans*-α,α′-Dichlorostilbene** was prepared by reducing benzotrichloride with iron powder in boiling aqueous suspension for 24 hr.[2] It was finally recrystallized with activated charcoal from benzene–methanol to give white crystals, mp 140° (lit.[11] mp 140–142°). The mass spectrum showed a molecular ion peak at mass number 248, together with isotopic chlorine peaks, and vpc showed that it contained none of the cis isomer. The ir spectrum was identical with that published for the trans isomer, and the ir and Raman spectra have been discussed above.

Anal. Calcd for $C_{14}H_{10}Cl_2$: C, 67.5; H, 4.1; Cl, 28.4. Found: C, 67.5; H, 4.0; Cl, 28.5.

***cis*-α,α′-Dichlorostilbene.**—Tolane tetrachloride was reduced with zinc in dimethylformamide as described by Weis[6] to obtain, in two instances, the white crystals, mp 67–68°, identified by him as *cis*-α,α′-dichlorostilbene. Vpc showed these crystals to contain two components which were separated by preparative gas chromatography on 2 ft of 25% Dow-Corning silicone 200 oil on Gas-Chrom Z at 170°.

The more volatile component melted at 61° and was identified as diphenylacetylene (lit.[11] mp 62°), since both its mass spectrum (large molecular ion peak at mass number 178) and infrared spectrum were identical with those for an authentic sample.

The second component was recrystallized from methanol to give white, feathery crystals, mp 58°. It had a mass spectrum with a molecular ion peak at mass number 248, together with satellite peaks characteristic of chlorine isotopes, and exhibited a splitting pattern almost identical with that for *trans*-α,α′-dichlorostilbene. Vpc showed that it contained none of the trans isomer. The ir and Raman spectra have already been discussed above.

Anal. Calcd for $C_{14}H_{10}Cl_2$: C, 67.5; H, 4.1; Cl, 28.4. Found: C, 67.7; H, 4.0 Cl, 28.3.

The complex of *cis*-α,α′-dichlorostilbene with diphenylacetylene had an analysis in agreement with the 2:1 proportions shown by vpc.

Anal. Calcd for $C_{42}H_{30}Cl_4$: C, 74.5; H, 4.5; Cl, 21.0. Found: C, 74.7; H, 4.3; Cl, 21.0.

Registry No.—Benzotrichloride, 98-07-7; tolane tetrachloride, 13700-81-7; *cis*-α,α′-dichlorostilbene,

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[12] H. Staudinger, *Ber.*, **49**, 1971 (1916).

[13] W. Löb, *Z. Elektrochem.*, **9**, 906 (1903).

[14] L. F. Hatch and J. J. D'Amico, *J. Amer. Chem. Soc.*, **73**, 4393 (1951).

[15] L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen, London, 1968, p 32.

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

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

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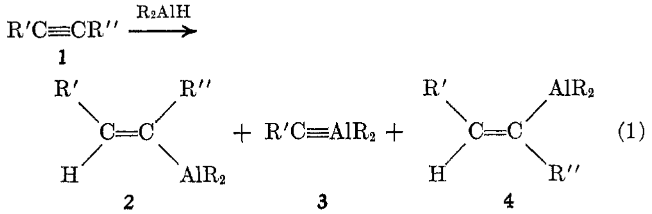
The regiospecificity and stereochemistry for the addition of aluminum–hydrogen bonds to unsymmetrical acetylenes were examined in order to evaluate the steric and electronic factors of this important reaction. Phenylethynyl derivatives of the type $C_6H_5C{\equiv}CE$ (5), where E = CMe_3, $SiMe_3$, $GeMe_3$, $GeEt_3$, $SnMe_3$, 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.



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

(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]