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Regiochemistry and Stereochemistry in the Hydralumination of **Heterosubstituted Acetylenes.** Interplay of Inductive and Resonance Effects in Electron-Rich Alkynes¹

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The hydralumination of certain electron-rich alkynes with diisobutylaluminum hydride was studied, in order to determine the influence of inductive and resonance factors on the regiochemistry and stereochemistry of the addition. Dimethyl(phenylethynyl)amine underwent an overall trans hydralumination, which placed the RoAl group α to the phenyl group. In addition, one-third of the amine was consumed in a competing reductive dimerization. In additions moderated by N-methylpyrrolidine, no reductive dimerization of the alkyne was observed, but the initial cis adduct was detected by NMR spectroscopy. Ethyl phenylethynyl sulfide gave only the cis hydralumination adduct with the R_2Al attached to the phenyl-substituted vinyl carbon and the thio-substituted vinyl carbon in a 17:83 ratio. 1-Ethoxy-1-hexyne gave principally the cis hydralumination adduct with the R₂Al group exclusively α to the butyl group. In contrast, both phenylethynyllithium and diphenyl(phenylethynyl)aluminum underwent mono- and bishydraluminations to yield adducts having all metallo groups β to the phenyl group. Finally, chloro- and bromo(phenvl)acetylenes were relatively unreactive toward R₂AlH; at higher temperatures, addition did occur but with concurrent loss of halogen. The foregoing observations are interpreted in terms of a mechanism involving (a) electrophilic attack by R2AlH on the triple bond; (b) addition of the Al-H bond, in accord with developing $p_{\pi}-p_{\pi}$ or $p_{\pi}-d_{\pi}$ polarizations, to yield the cis adduct; (c) isomerization to the trans adduct, where feasible; and (d) for those cases where the corresponding 1-alkyne is also formed, the cis elimination of R_2AIE (where E = Br, Cl, SEt, or OEt) from this trans adduct.

The addition of alkylaluminum hydrides to alkynes, with subsequent hydrolysis, constitutes a mild, convenient method for the cis reduction^{2,3} or, in certain cases, the trans reduction⁴ of the C \equiv C group (eq 1). Since the position of the alkylalumino group on the resulting C==C linkage is readily labeled by treatment with D₂O, both the stereochemistry and the regiochemistry of hydralumination can be determined by NMR spectroscopy (eq 2).³⁻⁶



The hydralumination of heterosubstituted acetylenes, considered in the present study, was deemed worth investigating on several counts. First of all, the interplay of inductive and resonance effects for the heterosubstituent E in $R'C \equiv CE$ (where $E = R_2N$, RO, RS, X, or M) could give rise to varying proportions of the four possible aluminum products, adducts 1 and 2 in eq 1 and their two regioisomers. Thus, analysis of these product ratios in terms of electronic effects for group E promised further insight into the nature of the transition state. Secondly, the hydralumination of acetylenic ethers and amines seemed to be a feasible synthetic route to vinylic ethers and enamines, respectively, of defined stereochemistry. Since such hydraluminations occur at or below room temperature and the hydrolytic work-up ensues under mildly basic conditions, these hydrolysis-sensitive olefins were expected to remain intact.

Finally, it was of interest to learn whether the cis or trans stereochemistry of such additions might be subject to kinetic or thermodynamic control. As with the cases of trialkylsilyl- and trialkylgermylacetylenes^{5,6} (eq 3), the prospect of achieving cleanly either a cis or a trans hydralumination of these heterosubstituted acetylenes was most attractive.



Results

As model systems, the following available electron-rich acetylenes were subjected to the action of diisobutylaluminum hydride (3): dimethyl(phenylethynyl)amine (4); 1-ethoxy-1-hexyne (5); ethyl phenylethynyl sulfide (6); phenylethynyllithium (7); and diphenyl(phenylethynyl)aluminum (8). The behavior of chloro(phenyl)acetylene (9) and bromo(phenyl)acetylene (10) was also examined, even though the halogen atom was expected to exert a -I effect on the C=C bond. However, since hydralumination of alkynes is now known to involve electrophilic attack by monomeric R₂AlH,^{6,7} it was of interest to learn whether the halogen would show a +T effect in the transition state.

With the exception of the halo(phenyl)acetylenes, all the heterosubstituted acetylenes, RC=CE, underwent hydraluminations more rapidly than their corresponding 1alkynes. For example, by competitive hydralumination⁸ at 35° the initial reaction rate of dimethyl(phenylethynyl)amine was shown to be ca. 1600 times that of phenylacetylene. In fact, the high reactivity of the acetylenic amine (4), ether (5), and sulfide (6) permitted their smooth hydralumination, even in the presence of 1 equiv of N-methylpyrrolidine. The complex of diisobutylaluminum hydride with the latter amine is a less reactive reagent⁴ but the presence of the amine suppressed competing reactions. Hydraluminations without N-methylpyrrolines led, in certain cases, to (a) isomerization of cis adducts to trans adducts (cf. eq 3); (b) reductive dimerization of RC=CE to yield 1.3-alkadienylaluminum adducts;⁵ and (c) reductive scission of $RC \equiv CE$ to produce $RC \equiv CH$.

The stereochemistry of the olefins obtained by the hydrolysis of the aluminum adducts (cf. eq 1 and 2) was assigned upon the basis of the magnitude of the vinylic proton NMR coupling constants and the characteristic ir C-H bending vibrations. The position of the R₂Al group in the adduct and hence the regiochemistry were determined by the D_2O -labeling technique (eq 2) and an NMR analysis as to which vinylic proton signals were decreased. Crucial to this method was the umambiguous assignment of the observed NMR vinylic proton signals to the protons α and β to the group E in RCH=CHE. By use of tabulated group contributions to the chemical shifts of such protons for both cis and trans 1,2-disubstituted ethylenes,⁹ estimates of the expected chemical shifts for the protons in each geometrical isomer could be obtained. Such calculated values gave good assurance that the observed signals were ascribed to their proper vinylic protons.

Dimethyl(phenylethynyl)amine. By far the most reactive of the heterosubstituted acetylenes examined in this work was dimethyl(phenylethynyl)amine (4). When admixed with the hydride 3 at $0-25^{\circ}$ the reaction is not only rapid but reductive dimerization consumes ca. one-third of the starting amine. The only isolable monoamine proved to be dimethyl[(E)- β -styryl]amine (12), showing that a net trans hydraluminum had resulted. Deuterium labeling showed, furthermore, that the dialkylalumino group was attached exclusively to the vinvlic carbon α to the phenyl group (11). An NMR spectral analysis of the reduced dimer obtained by hydrolysis showed it to be a 1,3-bis(dimethylamino)-2,4-diphenyl-1,3-butadiene (14). Treatment of the aluminum precursor of this butadiene with D₂O led to the disappearance of the vinylic proton at C_4 in 14. Finally, with the assumption that the stereochemistry in 14 and its aluminum precursor 13 will parallel that found for 12 (i.e., trans), the most reasonable stereochemistry of 13 and 14 seems to be Z,Z for 13 and Z,E for 14 (Scheme I).

In order to learn whether the trans adduct 11 was formed directly or by the isomerization of an initial cis adduct, a mixture of the amine 4 and the hydride 3 was monitored at -20° by NMR spectroscopy. Under these conditions only the vinylic signal attributable to 11 was detected; in fact, even after 40% of 4 was consumed, barely any of 13 was ob-



servable. In hopes of trapping any initially formed cis adduct by complexing with an external amine, the NMR spectral monitoring of 3 and 4 at -20° was repeated in the presence of N-methylpyrrolidine. Indeed, a new vinylic proton signal of modest intensity was observed at 6.28 ppm, 0.28 ppm downfield from that of 11. Since there are tertiary amine sites available in 11 and unconsumed 4, it seems unlikely that this new vinyl proton is due to a complex of 11 with a tertiary amine. Such complexation could also have occurred in the former NMR experiment where no N-methylpyrrolidine was present. The new downfield signal at 6.28 ppm is, on the other hand, consistent with the signal expected for the cis adduct 15. From chemical shift parameters a vinyl proton β , cis to a phenyl group would be expected to absorb at lower fields than one that is β , trans.⁹ Although the chemical shift parameter for the free R₂Al or the complexed R₂Al:NR₃ substituent is not known, NMR studies of triphenylaluminum in C₆D₆ and in THF have shown that the ortho protons are markedly deshielded, compared with the meta and para protons.¹⁸ This finding supports the suggestion that the cis proton in 15 would also be deshielded by the R₂Al group. These considerations lead to the suggestion that 4 undergoes intitial cis hydralumination to produce 15 and that, in the absence of an external amine, this adduct isomerizes rapidly to the trans adduct 11 (eq 4). Attempts to obtain evidence for the presence of



15 by means of low-temperature protolysis of the reaction mixture and the isolation of dimethyl[(Z)- β -styryl]amine have thus far failed. Possibly the ready isomerizability of such cis enamines may account for this failure.

Finally, it is noteworthy that 11, which is probably an associated molecule, did not show any tendency to split out i-Bu₂Al-NMe₂ and form phenylacetylene when heated at 100°. As will be seen later on, such cis eliminations are considerably easier with other heteroatoms.

Ethyl Phenylethynyl Sulfide. In contrast with the acetylenic amine, this sulfide (6) underwent smooth and exclusive cis hydralumination, without any sign of reductive dimerization. By deuterium labeling, however, the reaction was shown to be regioselective, rather than regiospecific; the isomeric aluminum compounds, 16 and 17, were formed in a $83:17 \pm 2$ ratio (eq 5).

$$C_{6}H_{5}C = CSC_{2}H_{5} \xrightarrow{3}$$

$$C_{6}H_{5}C = C \xrightarrow{SC_{2}H_{5}} + \underbrace{C_{6}H_{5}}_{i \cdot Bu_{2}Al} \xrightarrow{C = C} \underbrace{SC_{2}H_{5}}_{H} (5)$$

$$16$$

$$17$$

Attempted isomerization of 16 and 17 to their trans adduct by heat, addition of a Lewis acid (*i*-Bu₂AlCl),⁴ or Ni(0)^{10,11} failed; no new vinylic proton signals could be detected by NMR spectroscopy. Prolonged heating at 80–90°, however, did give gradually increasing amounts of phenylacetylene. These results can be explained by proposing a slow isomerization of 17 to its trans adduct (18), followed by a relatively rapid cis elimination of *i*-Bu₂Al-SC₂H₅ (cf. eq 6 and below).



1-Ethoxy-1-hexyne. Hydralumination of this acetylenic ether (5) in the absence of N-methylpyrroldine gives an uncontrolled series of reactions, involving extensive reductive cleavage of the C=C-O linkage.^{12,13} A much cleaner reaction was achieved in the presence of N-methylpyrrolidine, where again the stereochemistry and regiochemistry differ essentially from those of the acetylenic amine or sulfide. Here, the hydralumination is highly stereoselective, with the cis adduct composing >97% of the addition products.¹³ By deuterium labeling, on the other hand, the reaction was shown to be regiospecific, with the alumino group attached exclusively to the vinylic carbon α to the *n*-butyl group (19) (eq 7).



Even in the presence of N-methylpyrrolidine, however, ca. 30% of 5 is cleaved to yield 1-hexyne. Since the amount of 1-hexyne formed is larger in the absence of the amine, the reductive cleavage seems to be due to the isomerization of 19 to its trans adduct 20 and the subsequent cis elimination of i-Bu₂Al-OC₂H₅ (eq 8).



Halo(phenyl)acetylenes. Neither the chloro (9) nor the bromo (10) derivative reacts with hydride 3 in cyclohexane at 25°. This ranks their reactivity toward 3 lower than that of diphenylacetylene, one of the least reactive alkynes.⁸ Heating 9 or 10 with 3 does effect hydralumination, but, thus far, no β -halostyrenes have been detected upon hydrolysis. Instead, varying amounts of styrene and ethylbenzene have been isolated. Interestingly, when mixtures of 10 and 3 are monitored by ir spectroscopy, it can be shown that phenylacetylene is formed during the early stage of reaction.¹³ In light of the pattern emerging for the reductive cleavage of acetylenic sulfides (eq 6) and ethers (eq 8), it is reasonable to suggest a mechanism involving a slow cis addition of 3 to 9 or 10, followed by isomerization to the trans adduct and subsequent elimination (eq 9). Attempts



to detect either of the postulated intermediates, 21 and 22, have thus far been unsuccessful.

Phenylethynylmetallic Derivatives. Both phenylethynyllithium (7) and diphenyl(phenylethynyl)aluminum (8) underwent prompt reaction with hydride 3. In fact, bishydralumination of either 7 or 8 competed seriously with monohydralumination, such that even 1 equiv of 3 led, upon hydrolysis, to mixtures of styrene and ethylbenzene. Although stereochemical information could obviously not result from these reactions, the regiochemistry could be obtained by deuterium labeling. The mono- and bishydraluminations were, in fact, regiospecific: the resulting styrene was exclusively the β , β -dideuterio isomer and the ethylbenzene was the β , β , β -trideuterio compound. Accordingly, for both 7 and 8, the aluminum precursors are of the type 23 and 24 (eq 10).



Discussion

From consideration of relative rates⁸ and the experimental conditions required for hydralumination, the following order of decreasing reactivity can be established for these heterosubstituted alkynes: $C_6H_5C\equiv CNMe_2 \gg$ $C_4H_9C\equiv COC_2H_5 > C_6H_5C\equiv CM [M = Al(C_6H_5)_2 \text{ or Li}] >$ $C_6H_5C\equiv CSC_2H_5 \gg C_6H_5C\equiv CX (X = Cl \text{ or Br})$. Since all except the halo(phenyl)acetylenes are much more reactive than their corresponding 1-alkynes, they may be viewed as "electron-rich" alkynes, whose E group donates electron density to the C \equiv C group in the transition state of hydralumination. Such an interpretation is consonant with the known electrophilic character of R₂AlH attack on alkynes.^{6,7} However, the exact nature of the electron donation by group E should be analyzed, since it clearly exerts a profound influence on the stereochemistry and regiochemistry of the addition.

The only known cases where the hydralumination of alkynes leads principally to the trans adduct are those involving acetylenic silanes,⁴ germanes,⁴ and amines. For the first two types, a recent study has demonstrated that the cis adduct is actually the first-formed product and that the trans product results by isomerization.^{4,6} In the case of dimethyl-(phenylethynyl)amine, the presence of *N*-methylpyrrolidine did permit detection of what appears to be the cis adduct (15). Just as with the acetylenic silanes and germanes, the external amine seems to be able to complex with the cis adduct and thereby slow down its isomerization. Thus, it would appear warranted to conclude that probably all hydraluminations of alkynes are kinetically controlled cis additions.^{6,7,14}

The variation in regiochemistry with the nature of group E is most instructive: (a) the dimethylamino and ethoxy groups direct the dialkylalumino group to their β carbon; (b) the metallo groups give exclusively α attachment of R₂Al groups; and (c) the ethylthio group displays ca. a five-fold preference for α attachment over β . Since all these substituents enhance the reactivity of the C=C group, it is more logical to ascribe the changes in orientation to differing polarizations of the triple bond, rather than to electron donation or withdrawal by E. The operation of p_{π} - p_{π} delocalization in the transition state of reaction with the acetylenic amine or ether (25) would account nicely for the observed regiospecificity; likewise, the polarization fostered



by $d_{\pi}-p_{\pi}$ delocalization in the transition state for the acetylenic sulfide (26) rationalizes the regioselectivity. Finally, the metallo group apparently polarizes its C-M σ bond markedly, enlarging the π cloud at the α carbon (27). Thus, it can be concluded that in the transition state the +T effect dominates with the Me₂N and EtO groups; with EtS, the -T effect is definitely larger and with the M group the +I effect takes precedence.¹⁵

It might be noted that all these acetylenes have potential Lewis basic sites on group E. Consequently, preliminary coordination of the hydride R_2AlH at these sites can be as-



sumed. However, as with other coordination complexes of organoaluminum compounds, such complexes are likely to be in equilibrium with the free acetylenes. Various studies have shown that uncomplexed alkynes and organoaluminum reagents undergo hydralumination and carbalumination more readily.^{3,7}

The isomerization of cis adducts and the loss of R_2AlE from the resulting trans adducts were detected in the case of 1-ethoxy-1-hexyne and were inferred for the cases of ethyl phenylethynyl sulfide and the halo(phenyl)acetylenes (eq 6, 8, and 9). The ease of these cis, trans isomerizations seems to be related to the importance of the same +T effect of group E invoked in explaining the regiospecificity (25). Operation of such electron delocalization in cis adduct 28 should lower the barrier to rotation about the C==C bond (eq 12).¹⁶ Once the trans adduct is formed, direct



coordination of electrons on E with the aluminum is possible (29, or a dimer thereof). Such direct interaction can set the stage for the elimination of R_2Al-E , if energetically favorable. Since various amines and mercaptans add readily to alkynes with metal salt catalysts, elimination of R_2AlNMe_2 or R_2AlSEt from 29 would not be expected to occur readily. On the other hand, eliminations of MOR and MX from various aromatic and olefinic systems are richly precedented. Hence, the large amounts of 1-alkyne obtained from the acetylenic ether and halides seem to be best explained by an addition-isomerization-elimination sequence.

Finally, the preparative possibilities of these hydraluminations should be borne in mind. Vinylic ethers and sulfides of cis configuration can be prepared in good or excellent yields. Enamines of trans configuration are likewise accessible. Trimethylamine can be used in place of Nmethylpyrrolidine for moderating the reaction; the former amine can more readily be removed upon work-up. In addition, the bishydralumination of lithium acetylides provides a convenient route to interesting α, α, α -trimetalloalkanes and the CD₃ group.

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 457. Proton magnetic resonance spectra were measured with Varian spectrometers, either a Model A-60 or a Model HA-100D, the latter being equipped with a Varian variable temperature control, Model V-6040, and a Hewlett-Packard audiofrequency generator, Model HP-205AG, for proton and deuterium spin decoupling. The samples were measured as solutions 10% by weight in pure solvents and tetramethylsilane was added as an internal standard. Such data 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. Gas chromatographic analyses were performed with an F & M instrument, Model 720, equipped with dual columns of 10% silicone gum rubber on 60-80 mesh Chromosorb W (12 ft \times 0.25 in). Elemental analyses were carried out by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

All preparations and reactions involving substances sensitive to moisture and oxygen, such as organometallics and certain of the acetylenic compounds, were conducted under an atmosphere of dry, oxygen-free nitrogen. Appropriate techniques for such manipulations, including the necessary purification of solvents and the measurement of spectra for sensitive substances, have already been described. 6,7

Preparation of Starting Materials. The diisobutylaluminum hydride, as obtained from Texas Alkyls, Inc., was 94% pure. Its purification to a 99% grade and its analysis by a modified isoquino-line titration procedure were done in accordance with published methods.⁷

Chloro(phenyl)acetylene was prepared from phenylethynylsodium and p-toluenesulfonyl chloride, bp 23-24° (0.35 mm).¹⁷ Phenylethynyllithium was prepared as a colorless suspension in cyclohexane by admixing equimolar quantities (18.2 mmol) of freshly distilled phenylacetylene and a 2.2 M hexane solution of *n*-butyllithium in 20 ml of cyclohexane. Diphenvl(phenvlethynvl)aluminum was prepared from triphenylaluminum and phenylacetylene by adherence to a known procedure,¹⁸ mp 142-144°, recrystallized from benzene and cyclopentane. Dimethyl(phenylethynyl)amine was prepared by heating bromo(phenyl)acetylene with trimethylamine for 50 hr at 55° in a sealed tube, bp 45-47° (0.07 mm).¹⁹ Ethyl phenylethynyl sulfide was prepared by allowing sodium thioethoxide to react with bromo(phenyl)acetylene in DMF at lower temperatures,²⁰ bp 75-76° (0.35 mm). Because alkoxy(phenyl)acetylenes are difficult to synthesize in the pure state and are prone to polymerization,²¹ the acetylenic ether chosen for this study was the commercially available 1-ethoxy-1-hexyne (Farchan Chemical Co.), bp 60-61° (0.9 mm).

Reactions of the 1-Substituted Alkynes with Diisobutylaluminum Hydride. General Procedure. The alkyne was dissolved or suspended in an anhydrous saturated hydrocarbon at the chosen temperature. In those cases where anhydrous N-methylpyrrolidine was used, it was admixed with the alkyne before reaction. The reaction vessel was equipped with a reflux condenser surmounted by a nitrogen gas inlet, a neck provided with a rubber septum, and a magnetic stirring bar. The diisobutylaluminum hydride was then added, either dropwise or in one portion, by means of a gas-tight syringe. After spectral monitoring or the hydrolysis of aliquots had shown the reaction to be complete, the chilled reaction mixture was cautiously treated with small amounts of degassed H₂O or D₂O (99.9%), in a dropwise manner, to yield a fine, granular suspension of aluminum hydroxide, which could be filtered off and washed with solvent to give directly a dry organic filtrate. (In some runs, dilute, degassed hydrochloric acid was used for effecting homogeneous hydrolysis. Thereafter, the separated organic layer was dried over anhydrous calcium sulfate.) Removal of solvent on a rotary film evaporator, gas chromatographic analysis, purification by distillation or preparative GLC, and spectral characterization completed the procedure.

Trans Hydralumination of Dimethyl(phenylethynyl)amine (4). A. Without N-Methylpyrrolidine. To 3.3 g (22.8 mmol) of 4 in 10 ml of dry cyclopentane was added 4.0 ml (22.5 mmol) of the hydride in a dropwise manner, while the solution was cooled to 0°. The solution gradually turned yellow but no gas evolution could be observed. After 10 min of stirring at 25° an aliquot was withdrawn for NMR spectral analysis. The spectrum, recorded at 30° after a total reaction time of 35 min, showed that 4 was already consumed and that the trans hydralumination adduct, $C_6H_5(i-Bu_2Al)_2$ -C=C(NMe₂)H (11), and the hydraluminated dimer, $C_6H_5(i-Bu AlC = C(NMe_2)(C_6H_5)C = C(NMe_2)H$ (13) (cf. infra), had been formed in a ratio of 2:1. (Integrated signals for the respective vinylic and NMe₂ signals of 11 and 13 were in agreement with this ratio; the composite phenyl signal area between 6.8 and 7.3 ppm also corresponded to that to be expected.) Spectral data (cyclopentane) for 11: δ 2.8 (d, NMe peaks separated by 2.0 Hz) and 6.08 (s, with shoulder peak of ca. one-third intensity at 6.06). For 13: δ 2.32 (s, NMe₂), 2.52 (s, NMe₂, with a shoulder at 2.48), 2.68 (s, NMe₂), and 6.47 (s). For complexed diisobutylaluminum hydride: δ 3.63 (br, AlH) and 3.78 (sharp, AlH). After a reaction time of 50 hr the NMR spectrum of the mixture recorded at 0° displayed sharp signals without shoulders at δ 2.23, 2.47, 3.09, 3.20, and 3.27 (NMe₂) and at 6.01 and 6.43 (vinylic C--H).

The main reaction solution was slowly treated with water after a total reaction time of 4 hr. The color of the mixture changed from yellow to orange-red upon completion of hydrolysis. Upon extraction with ether the red color was adsorbed by the aluminum hydroxide and the filtered ether solution then became yellow. The NMR spectrum (CDCl₃) of the pale yellow distilled product [3.0 g, bp 50-53° (0.1 mm)] showed it to be dimethyl $[(E)-\beta$ -styryl]am-

ine²² (12): δ 2.5 (s, NMe₂), 5.04 (d, =-CH, J = 14 Hz), 6.58 (d, C=-CH, J = 14 Hz), 6.85–7.25 (m, 5 H); ir (neat) significant bands at 695, 790, 935 (s, trans CH=-CH out-of-plane bending) and 1635 cm⁻¹ (s, C=-C stretch).

The distillation residue consisted of 1.5 g of a viscous brown oil: NMR (CDCl₃) δ 2.58 and 2.62 (s, 6 H each, NMe₂ groups), 5.48 and 6.18 (s, 1 H each, C=CH), and 6.80–7.4 (m, 10 H); ir (neat) 698 (s), 760 (s), 975 (m), 1070 (s), 1090 (s), 1130 (s), 1335 (s), 1380 (s), 1415 (s), 1432 (s), 1480 (s), 1560–1630 (s, broad set of bands), and 2795–3075 cm⁻¹ (s, broad set of bands). This product appeared to be (*Z*,*E*)-1,3-bis(dimethylamino)-2,4-diphenyl-1,3-butadiene (14).

Another run of the hydralumination was carried out and then the reaction mixture (after 4 hr of reaction time) was treated slowly with D₂O (99.9% pure) and the hydrolysate was worked up in the standard manner. The distilled dimethyl[(E)- β -styryl]amine obtained was analyzed spectroscopically: NMR (neat) δ 2.42 (s, NMe₂) 6.56 (t, =CH, J = 2 Hz), 6.82–7.25 (m, 5 H); ir (neat) bands at 790 and 935 cm⁻¹ had essentially disappeared; bands at 695 and 1620 cm⁻¹ were still strong.

Calculations of the chemical shifts for the vinyl protons⁹ result in an estimate of 5.44 ppm for the proton adjacent to the phenyl group (observed, 5.04) and of 6.34 for that adjacent to the NMe₂ group (observed, 6.58). Thus, the signal assignment for these protons should be the reverse of those made in the literature.²² Accordingly, then, the deuterium labeling showed that the aluminum in the hydralumination adduct was attached to the phenyl-substituted vinyl carbon.

Furthermore, the NMR spectrum of the dimeric 14, which was isolated as a distillation residue from the run with a D₂O work-up, had only the vinyl singlet at 6.18 ppm. Since the vinyl singlet at 5.48 ppm had disappeared, the aluminum precursor of 14 must have been of the general structure $C_6H_5(i-Bu_2Al)C=C(NMe_2)-(C_6H_5)C=C(NMe_2)H$.

Another run was conducted with 2.31 g (16 mmol) of 4 and 3.0 ml (17 mmol) of the hydride in 6.0 ml of cyclopentane at -20° and the reaction was followed by NMR spectroscopy. Under these conditions the aminoacetylene was 50% consumed in 40 min and little dimerization took place.

B. With N-Methylpyrrolidine. A solution of 1.15 g (8 mmol) of 4 and 2.0 ml (8 mmol) of anhydrous N-methylpyrrolidine dissolved in 10 ml of dry heptane was cooled in a Dry Ice-acetone bath (-78°) . To this chilled suspension was slowly added 2.1 ml (12 mmol) of the hydride. An aliquot was withdrawn and its NMR spectrum recorded at -23° after different periods of time. At -23° no vinyl proton ascribable to the aluminum precursor of the reduced dimer 13 (=CH at 6.42 ppm with =CH of C₆H₅(*i*-Bu₂-Al)C=C(NMe₂)H taken as 6.0 ppm) was discernible but there was a singlet at 6.28 ppm, which was ca. 15% of the signal of the disobutyl[(Z)- β -dimethylamino- α -styryl]aluminum (11) at 6.0 ppm. The signal at 6.28 ppm might have been due to the (E)- β -dimethylamino- α -styryl isomer (15) of 11.

Finally, the temperature was raised to 30° and under these conditions the reaction was complete in ca. 5 min. Here, only the monomeric product was detectable; no dimeric vinyl protons were present. The usual hydrolytic work-up showed that the resulting product was pure 12.

Heating a sample of the hydralumination adduct in heptane solution for 45 min and working up in the usual manner gave only 12, with no detectable amount of phenylacetylene.

Cis Hydralumination of Ethyl Phenylethynyl Sulfide (6). A. Hydrolytic Work-up. Stirring a solution of 1.82 g (11.2 mmol) of 6 and 2.0 ml (11.2 mmol) of the hydride in 10 ml of dry cyclopentane at 25° for 12 hr and hydrolytic work-up gave almost a quantitative yield of ethyl cis- β -styryl sulfide.^{23,24} By GLC analysis on a 12-ft column packed with silicone gum rubber only ca. 0.1% of phenylacetylene was detected. Spectral data for ethyl cis- β -styryl sulfide: NMR (CDCl₃) δ 1.30 (t, CH₃, J = 7.0 Hz), 2.72 (q, CH₂, J= 7.0 Hz), 6.20 (d, =CH, J = 11 Hz), 6.46 (d, =CH, J = 11 Hz), 6.97-7.70 (m, 5 H); ir (neat) 698 (s), 725 (m), 770 (s), 850 (s), 910 (m), 970 (m), 1030 (m), 1055 (m), 1070 (m), 1265 (s), 1365 (s), 1445 (s), 1490 (s), 1565 (m), 1595 (s), 2870 (m), 2925 (s), 2970 (s), 3020 (m), and 3050 cm⁻¹ (m).

Calculation of the chemical shifts for the vinyl protons,⁹ whose coupling constant showed them to be cis,²⁵ yielded values of 6.59 and 6.18 ppm for the hydrogens α and β , respectively, to the phenyl group. These estimates compare fairly well with the observed values of 6.46 and 6.20 ppm and they help to secure the attribution of the signals to the proper vinylic proton. In addition, infrared correlations²⁶ for 1-alkylthio-1-alkenes lead one to expect a strong out-of-plane bending vibration at 935 cm⁻¹ for a trans CH=CH group or a strong in-plane bending vibration at 1330-1350 cm⁻¹ for a cis CH=CH group. The absence of the former band and the presence of a strong band at 1365 cm^{-1} confirmed the assignment of the cis configuration.

B. Work-up with Deuterium Oxide. The foregoing hydralumination was repeated: in one case, with 2 equiv of the hydride in cyclopentane at 25° for 5 hr; and, in the other case, neat, with 3 equiv of the hydride. Addition of D₂O and usual work-up yielded ethyl $trans-\beta$ -styryl sulfide, which was examined by NMR spectroscopy (neat): both vinylic doublets had disappeared and now two broad singlets (with hint of triplet character, $J_{\rm HD} \simeq 2.0$ Hz) appeared at 6.08 and 6.33 ppm in an intensity ratio of (a) 82:19, for the run with 2 equiv of hydride; and (b) 85:15, for that with 3 equiv. These results showed that $C_6H_5CH=C(SEt)Al-i-Bu_2$ was the principal regioisomer and $C_6H_5(Al-i-Bu_2)C=C(SEt)H$ the minor.

C. Attempted Isomerization. When 1.82 g (11.2 mmol) of 6 and 6.0 ml (33 mmol) of the hydride were heated in 15 ml of dry cyclohexane for 5 hr, ca. 1-2% of phenylacetylene was detected upon hydrolytic work-up, but the sulfide isolated had not isomerized to the trans configuration. Also, neither the addition of diisobutylaluminum chloride to such a hydralumination reaction, followed by heating, nor the addition of a small amount of bis(1,5-cyclooctadiene)nickel $(0)^{10}$ caused any isomerization.

Cis Hydralumination of 1-Ethoxy-1-hexyne (5) in the Presence of N-Methylpyrrolidine. A solution of 3.50 g (28 mmol) of freshly distilled 5 and 2.4 g (28 mmol) of anhydrous N-methylpyrrolidine in 20 ml of dry pentane was cooled to -78° and then slowly treated with 5.6 ml (31 mmol) of the hydride. The temperature of reaction mixture was gradually allowed to come to room temperature and to remain there for 10 hr. One-half of the resulting mixture was worked up in the usual manner with water, the other half with D₂O.

The organic layer from the hydrolysis was shown by GLC to contain 1-hexyne (ca. 30%) and 1-ethoxy-1-hexene; the latter was chiefly (>97%) the cis isomer, bp 65-66° (0.9 mm). Spectral data: NMR (neat) δ 0.75-1.5 (m, OCCH₃, n-C₃H₇), 2.07 (br q, CH₂C=, J = 7.0 Hz), 3.69 (q, OCH₂, J = 7.0 Hz), 4.27 (ca. q, =CH, $J \simeq 6.5$ -8.0 Hz), 5.86 (d of t, =CH, J = 6.5 and 1.2 Hz); ir (neat) 600-1100 clear, 1115 (s), 1660 cm⁻¹ (s). By the magnitude of the coupling constant for the vinyl protons, it is clear that the double bond had the cis configuration. Calculation of the expected chemical shifts for the vinyl protons gave a value of 4.44 ppm for the proton α to the *n*-butyl group and 6.17 ppm for that β to this group. These agree reasonably well with the observed values of 4.27 and 5.86 ppm.

Similar work-up of the other portion of the reaction mixture with D₂O gave a deuterated cis-1-ethoxy-1-hexene with these spectral properties: NMR (neat) the quartet centered at 4.27 had almost disappeared and the doublet of triplets at 5.86 had collapsed to a broad singlet. Hence, the aluminum precursor was preponderantly $(n-Bu)(i-Bu_2Al)C=C(OEt)H$.

Anal. Calcd for C₈H₁₆O: C, 74.94; H, 12.59. Found: C, 74.73; H, 12.64.

Attempted Hydralumination of Halo(phenylethynyl)acetylenes [Cl (9) and Br (10)]. A solution of 1.40 g (10.2 mmol) and 9 and 1.85 ml (10.5 mmol) of the hydride in 20 ml of dry cyclo-hexane was allowed to stand at 25° for 4 hr. Usual work-up revealed the presence of the starting chloro(phenyl)acetylene and ca. 3% of phenylacetylene.

A solution of 3.0 g (16.5 mmol) of 10 and 8.25 ml (49.5 mmol) of the hydride in 80 ml of dry cyclohexane was allowed to stand at room temperature for 5 days and then worked up with water. A GLC analysis on a 12-ft column packed with silicone SE-30 on firebrick showed the presence of styrene (59%), ethylbenzene (22%), and phenylacetylene (19%); this analysis was confirmed by NMR spectroscopy.

Hydralumination of Phenylethynyllithium (7). Phenylacetylene (930 mg, 9.1 mmol) in 20 ml of dry heptane was treated with 4.2 ml of n-butyllithium in hexane (2.21 M, 9.3 mmol) to yield a colorless suspension of 7. Then 3.25 ml (18.2 mmol) of the hydride was added with stirring, after which the precipitate dissolved within 30 min. After a further 90 min at room temperature, the usual hydrolytic work-up led only to phenylacetylene; no styrene or ethylbenzene could be detected.

When another run with the foregoing proportions of reagents was heated at 80° for 60 min before hydrolysis, subsequent workup yielded an oil and a solid (2:1). A NMR spectral analysis of the former revealed the presence of phenylacetylene and ethylbenzene in a ratio of 2:3, with only traces of styrene. The solid appeared to be polystyrene, based upon its solubility in acetone and its ir and NMR spectra.

When 18.2 mmol of 7 was heated with 73 mmol of the hydride in 20 ml of dry cyclohexane for 24 hr at 80°, subsequent work-up with D_2O and GLC analysis showed the presence of only ethylbenzene. A NMR spectrum of this hydrocarbon in CDCl₃ displayed broad singlets at 2.62 and 7.2 ppm, but essentially no absorption at 1.0 ppm. Thus, the product was preponderantly β,β,β -trideuterioethylbenzene.

Hydralumination of Diphenyl(phenylethynyl)aluminum (8). A solution of 1.27 g (4.5 mmol) of 8 and 0.80 ml (4.5 mmol) of the hydride in 10 ml of dry benzene was maintained at 20° for 0.5 hr and then at 40° for 22 hr. Work-up with D₂O and GLC analysis showed the products to be phenylacetylene (55%), styrene (18%), and ethylbenzene (27%). A NMR spectral examination showed that the products to be deuterated thus: $C_6H_5C \equiv CD$ (absence of absorption at 2.75 ppm); C₆H₅CH=CD₂ (broad singlet at 6.6 and absence of absorptions in the region 5.0-5.8 ppm); and C₆H₅CH₂CD₃ (broad singlet at 2.62 ppm and absence of absorptions in the region 0.95-1.25 ppm).

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Registry No.-3, 1191-15-7; 4, 4604-65-3; 5, 2806-51-1; 6, 14476-62-1; 7, 4440-01-1; 8, 1157-32-0; 9, 1483-82-5; 10, 932-87-6; 11, 55133-72-7; 12, 14846-39-0; 13, 55133-73-8; 14, 55133-74-9; phenylethynylsodium, 1004-22-4; p-toluenesulfonyl chloride, 98-59-9; phenylacetylene, 536-74-3; n-butyllithium, 109-72-8; Nmethylpyrrolidine, 120-94-5; ethyl $cis-\beta$ -styryl sulfide, 20890-79-3; ethyl trans-β-styryl sulfide, 20890-80-6; cis-1-ethoxy-1-hexene, 50849-04-2.

References and Notes

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