Stereochemistry and Orientation in the Reactions of 1-Phenylpropyne with Diisobutylaluminum Hydride[1]

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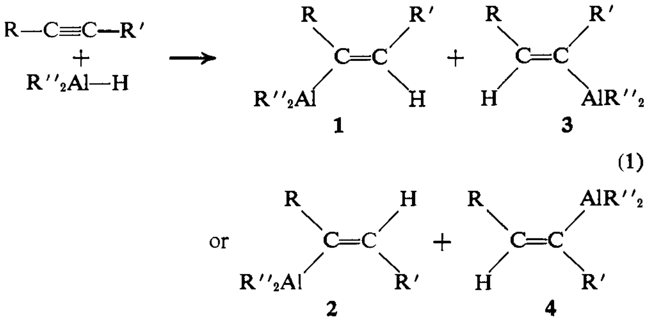
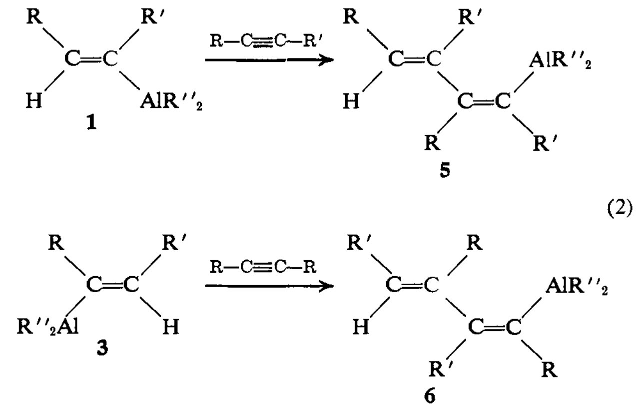
Abstract: The reactions of 1-phenylpropyne with diisobutylaluminum hydride were examined as to the stoichiometry, stereochemistry, and orientation of addition. Depending upon experimental conditions, hydrolytic work-up of the reaction mixture yielded *cis*- or *trans*-1-phenylpropene (monoaddition of Al–H), *n*-propylbenzene (diaddition of Al–H), *cis,cis*-2,3-dimethyl-1,4-diphenyl-1,3-butadiene and *cis,cis*-1,3-dimethyl-2,4-diphenyl-1,3-butadiene (addition of phenylpropenyl–aluminum bonds), and finally, principally 1,2,4-trimethyl-3,5,6-triphenylbenzene (trimerization of 1-phenylpropyne). Treatment of the reaction mixtures with D_2O and the identification of the deuterated hydrocarbons by nmr spectroscopy established the greater importance of polar factors, compared with steric effects, in determining the orientation of additions of Al–H and Al–C bonds to alkynes. The diisobutylaluminum preferred to position itself on the carbon adjacent to the phenyl group in 1-phenylpropyne. The possible mechanisms for the isomerization of *cis*-vinylaluminum systems to the *trans* configuration were compared with the behavior of 1-phenylpropyne, diphenylacetylene, and 1,3,3,3-tetraphenylpropyne toward diisobutylaluminum hydride. The reversal of hydride addition to these alkynes, the detection of bisalumino adducts, and the novel carbon–carbon bond cleavage with the tetraphenylpropyne were brought forward as evidence favoring a diaddition–elimination of R'_2AlH for the isomerization mechanism.

The interaction of group III metal alkyls or hydrides with alkynes presents a most fruitful approach to the evaluation of stereochemical and electronic factors in organometallic reactions. As portrayed in eq 1, metal–hydrogen bonds could add to the carbon–carbon triple bond in a *cis* (**1**) or *trans* (**2**) fashion. Moreover, with unsymmetrically substituted acetylenes the realization of two additional modes of orientation are possible (*e.g.*, **1** and **3**) which might be a result of polar or steric factors.



In a pioneering study Wilke and Müller demonstrated that dialkylaluminum hydrides can add to alkynes in a stereospecific *cis* fashion.[3] Subsequently, the present workers were able to show that *trans* addition can be achieved by use of an excess of dialkylaluminum hydride with extended reaction times. Evidence was put forward favoring a diaddition–elimination pathway for the *cis–trans* isomerization.[4] In a similar manner, hydroboration has been found to effect the *cis* reduction of alkynes in a highly feasible manner.[5]

However, since metal–carbon bonds also can add to the acetylenic linkage,[6] the vinylaluminum adducts resulting from the reaction of alkynes and dialkylaluminum hydrides (structures **1–4** in eq 1) can themselves add to alkynes (oligomerization). With the isomeric vinylaluminum systems, **1** and **3**, the mode of further reaction with alkyne should again depend upon steric and polar influences. One such possibility is depicted in eq 2. Therefore, it is clear that insight into the electronic influences governing the addition of Al–H and of Al–C bonds to alkynes could be revealed by the ratios of adducts **1** and **3** and of **5** and **6** formed from unsymmetrical alkynes.



Previous research on the reduction and oligomerization of alkynes has concerned itself principally with symmetrical acetylenes.[6a] Hence, no information could be obtained concerning the nature of the electronic

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[1] Part V of the series, Organometallic Compounds of Group III. Previous papers: J. J. Eisch, *et al.*, *J. Am. Chem. Soc.*, **86**, 4221 (1964); **85**, 2165 (1963); **84**, 3605, 3830 (1962); *J. Organometal. Chem.*, **2**, 184 (1964).

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[3] G. Wilke and H. Müller, *Chem. Ber.*, **89**, 444 (1956); *Ann.*, **618**, 267 (1958).

[4] A preliminary report on the isomerization of vinylaluminum compounds by agency of $R_2Al–H$ has been published: J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **85**, 2165 (1963).

[5] (a) H. C. Brown and G. Zweifel, *ibid.*, **81**, 1512 (1959); **83**, 3834 (1961); (b) *cf.* D. J. Pasto, *ibid.*, **86**, 3039 (1964), for interpretations of the anomalous oxidation products from such hydroborations.

[6] (a) G. Wilke and H. Müller, *Ann.*, **629**, 222 (1960); (b) *Cf.* J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **84**, 1501 (1962), for the addition of phenyllithium and of triphenylaluminum to the triple bond of tolane.

Table I. Hydrolysis Products from the Reactions of Alkynes with $(i\text{-}C_4H_9)_2AlH$

Expt	Alkyne	Molar ratio of alkyne: R_2AlH	Temp, °C	Time, hr	Hydrolysis products (molar ratio)
1	1-Phenylpropyne	1:1	50	8	*cis*-1-Phenylpropene (**25**), *n*-propylbenzene (**1**), and *cis,cis*-2,3-dimethyl-1,4-diphenyl-1,3-butadiene (1)
2	1-Phenylpropyne	2:1	80	60	*cis,cis*-2,3-Dimethyl-1,4-diphenyl-1,3-butadiene (**10**) and *cis,cis*-1,3-dimethyl-2,4-diphenyl-1,3-butadiene (**1**)
3	1-Phenylpropyne	16:1	150	72	1,2,4-Trimethyl-3,5,6-triphenylbenzene (principally)
4	1-Phenylpropyne	1:1	50	8	*cis*-1-Deuterio-1-phenylpropene (4.6), *cis*-2-deuterio-1-phenylpropene (1.0), and *cis,cis*-1-deuterio-2,3-dimethyl-1,4-diphenyl-1,3-butadiene[a]
5	1-Phenylpropyne	1.1:1	50	26 26[b]	*cis*-1-Phenylpropene (only traces of *n*-propylbenzene and *cis,cis*-2,3-dimethyl-1,4-diphenyl-1,3-butadiene)
6	1-Phenylpropyne	1.1:1	50 75–100	26 26[b] 48[b]	*cis*-1-Phenylpropene (3.8), *n*-propylbenzene (4.0), *trans*-1-phenylpropene (2.9), and *cis,cis*-2,3-dimethyl-1,4-diphenyl-1,3-butadiene (1.0)
7	Diphenylacetylene	1:1[c]	50	48	*cis*-Stilbene (15.5), *trans*-stilbene (1.0), and *cis,cis*-1,2,3,4-tetraphenyl-1,3-butadiene
			90	48	Trace of bibenzyl, in addition to foregoing stilbenes (*cis:trans* 1.0:4.4)
8	Tetraphenylpropyne	0.84:1.0[d]	110	36	Triphenylmethane (1.6), *cis*-1,3,3,3-tetraphenylpropene (1.0), and ethylbenzene
9	Tetraphenylpropyne		90 90	48 48	1-Deuteriotriphenylmethane (3.5), *cis*-1-deuterio-1,3,3,3-tetraphenylpropene (1.3), *cis*-2-deuterio-1,3,3,3-tetra-phenylpropene (1.0), and ethylbenzene[a]

[a] Reaction mixture treated with D_2O. [b] Volatile products removed during heating period by reduced pressure of 0.1 mm; mainly $(i\text{-}C_4H_9)_3A$ caught in trap at −78°. [c] Heptane as reaction medium. [d] Toluene as reaction medium.

influences considered in eq 1 and 2. Therefore, in order to assess the polar nature of such organometallic additions to unsymmetrical alkynes, a detailed study of the behavior of 1-phenylpropyne, $CH_3—C≡C—C_6H_5$, toward diisobutylaluminum hydride, $(i\text{-}C_4H_9)_2Al—H$, was undertaken. In addition, a more precise understanding was sought of the stereochemistry and possible reversibility of the hydride addition, the factors promoting the isomerization of *cis*-vinylaluminum adducts to the *trans* configuration and the possible mechanisms for the stereospecific oligomerization of alkynes by dialkylaluminum hydrides.

Results and Discussion

In order to dissect the reactions of addition (**1** and **3** in eq 1), isomerization (**1** → **2** and **3** → **4**), and oligomerization (eq 2) from each other, various ratios of 1-phenylpropyne and diisobutylaluminum hydride were interacted at temperatures of 50–100° in the absence of solvent. At 50° a 1:1 ratio of reactants formed the vinylaluminum adducts in a kinetically controlled process. The use of 2:1 or >3:1 ratios of 1-phenylpropyne and diisobutylaluminum hydride led to the reductive dimerization or trimerization of the alkyne. To establish the sites of the carbon–aluminum bonds in the foregoing reaction products, the reaction mixtures were treated with deuterium oxide. Analysis of the resulting deuterated hydrocarbons by nuclear magnetic resonance spectroscopy permitted both the sites of the C–D bonds and the *cis–trans* character of the olefin or diene to be specified. Finally, evidence for the tendency of vinylaluminum systems to undergo *cis–trans* isomerization was obtained by an examination of the hydrocarbons resulting from alkyne–dialkylaluminum hydride interactions at various temperatures. The behavior of diphenylacetylene, 1-phenylpropyne, and 1,3,3,3-tetraphenylpropyne under these conditions proved especially informative. The nature and proportion of the hydrolysis products obtained from these alkynes and diisobutylaluminum hydride are summarized in Table I.

The interaction of 1-phenylpropyne with diisobutylaluminum hydride in a 1:1 ratio[7] exhibited several features of interest relative to possible mechanisms. Firstly, the hydride added to 1-phenylpropyne (**7**) at 50° to yield exclusively the *cis*-1-phenylpropene (**8**) upon hydrolysis. No *trans*-1-phenylpropene (**9**) was formed, although small amounts of *n*-propylbenzene (**10**) and *cis,cis*-2,3-dimethyl-1,4-diphenyl-1,3-butadiene (**11**) were detected. At this temperature the adduction appears to be kinetically controlled, since no fast reversal to **7** could be detected under 100°. Secondly, the treatment of the *cis*-vinylaluminum adducts (**12** and **13**) with D_2O produced the deuterated *cis*-1-phenylpropenes (**8a** and **8b**) in a 4.6:1.0 ratio. Thirdly, when the vinylaluminum adducts (**12** and **13**) were heated at 100° under reduced pressure, 1-phenylpropyne could be recovered from the reaction mixture. This demonstrates that the reverse reaction can be achieved at elevated temperatures. Fourthly, the disproportionation of the (*cis*-phenylpropenyl)diisobutylaluminum adducts (**12** and **13**) to yield triisobutylaluminum (**14**),

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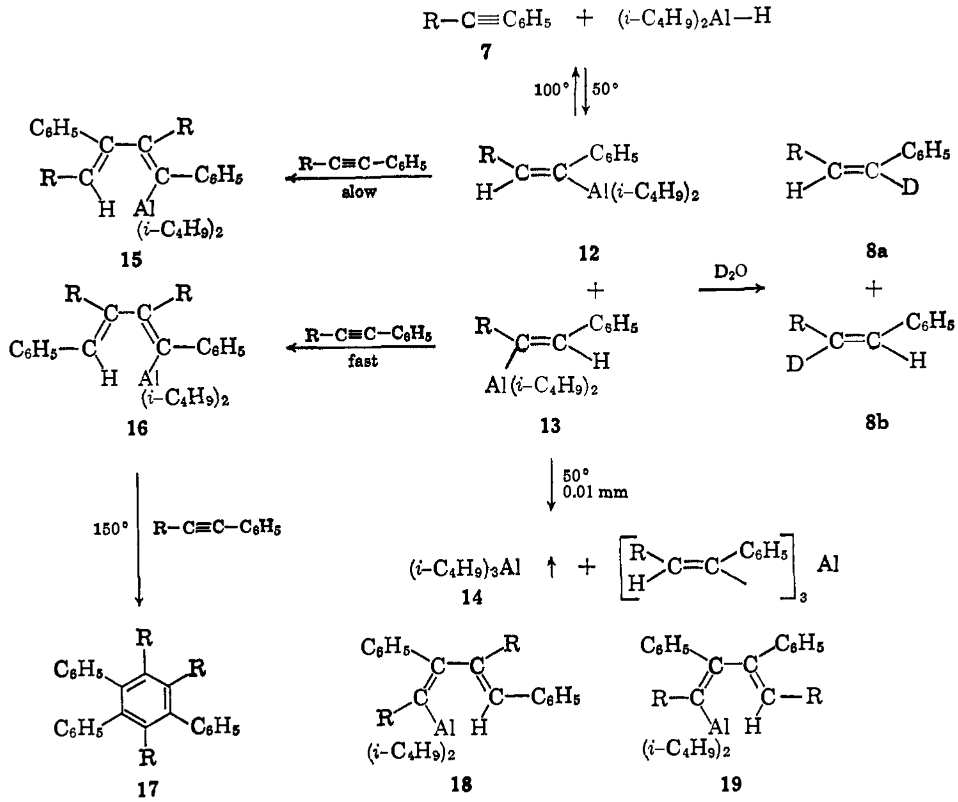
[7] In the succeeding discussion the associated character of alkylaluminum and vinylaluminum compounds is ignored, for lack of data on the equilibrium point between the associated and the monomeric species. For example, diisobutylaluminum hydride is largely trimeric in benzene: E. G. Hoffmann, *Ann.*, **629**, 104 (1960).

Chart I



could be achieved without isomerization of the substituted vinyl moiety. Only *cis*-1-phenylpropene was obtained upon hydrolysis. These transformations are presented in Chart I (R = CH_3). The conditions under which *cis–trans* isomerization was observed and the significance of the *n*-propylbenzene in this connection will be discussed later.

The interaction of the 1-phenylpropyne (**7**) and the metal hydride in other proportions further points up the high stereochemical and polar selectivity of such reactions. As with the addition of Al—H bonds, the vinyl–aluminum linkage added to the C≡C bond in a clean *cis* fashion. Also, not only is the minor vinylaluminum adduct **13** far more reactive than **12**, but **13** reacts with additional 1-phenylpropyne to form exclusively **16**. Under prolonged reaction conditions **12** gave a small amount of **15**. In the sequence **13** → **16**, the absence of the alternative isomer of **16**, structure **18**, was established by deuterolysis experiments. No *cis*,-*cis*-1-deuterio-1,3-dimethyl-2,4-diphenylbutadiene, expected from the deuterolysis of any **18**, was found. Likewise, the addition of 1-phenylpropyne to **12** to form **19** was ruled out by the failure to detect *cis*,*cis*-1,4-dimethyl-2,3-diphenyl-1,3-butadiene. Clearly the butadienylaluminum adducts **15** and **16** are the intermediates responsible for trimerization.[6a] Treatment of 1-phenylpropyne with a small amount of the hydride at 150° led to a high yield of 1,2,4-trimethyl-3,5,6-triphenylbenzene as the principal isomer. In another experiment involving an extended reaction of 2:1 mixture of **7** and hydride, a small amount of 1,3,5-trimethyl-2,4,6-triphenylbenzene was isolated. The preponderance of the unsymmetrical benzene **17** suggests that **16** is its key precursor.

In view of the exclusive *cis* additions observed in expt 1–5 of Table I, it is important to note the results in expt 6–9 where *trans* Al—H additions or C—C bond cleavage was observed. Although R—C≡C—R systems were felt not to add 2 moles of R'_2AlH,[8] the detection of *n*-propylbenzene from **7** and hydride and of bibenzyl from diphenylacetylene clearly support the formation of a bisalumino precursor, such as **20** (Chart II). In the case of tetraphenylpropyne, it is noteworthy that neither *trans*-1,3,3,3-tetraphenylpropene nor 1,1,1,3-tetraphenylpropane were detected, even under stringent reaction conditions. This eliminates the persistence of any *stable* diadduct (such as **20**) or any *trans* isomer. Only *cis* addition of Al-H to the alkyne and the elimination of a tritylaluminum fragment (**21**, R = C_6H_5) were observed. The presence of **21** was proven by the formation of $(C_6H_5)_3CD$ (**22**, R = C_6H_5), when the reaction mixture was treated with D_2O. The deuterated *cis*-1,3,3,3-tetraphenylpropene (**8**, R = $(C_6H_5)_3C$) formed in this experiment was a 1.3:1.0 mixture of **8a** and **b**. These observations are most valuable in understanding the *cis–trans* isomerization of vinylaluminum systems.

Two possible pathways for this isomerization are indicated in Chart II. First, the electronic character shown in **24** (R = C_6H_5) could promote isomerization of **23** into **25**, either intramolecularly by p_π–p_π overlap or intermolecularly as shown in **25**. On the other hand, if diadducts such as **20** were formed, isomerization could ensure by an R_2AlH addition–elimination pathway (**23** → **20** → **26**). With the *cis*-vinylaluminum adducts of 1-phenylpropyne (**12** and **13**) their configurational stability was demonstrated by prolonged heating at 50° without isomerization (expt 5). Indeed, these adducts disproportionated to $(i\text{-}C_4H_9)_3Al$ without change of

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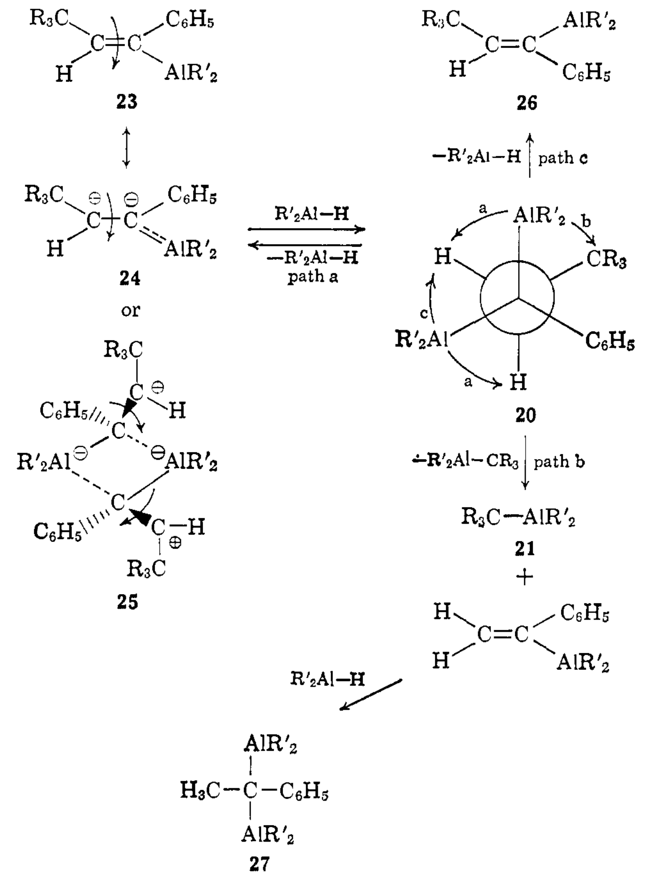
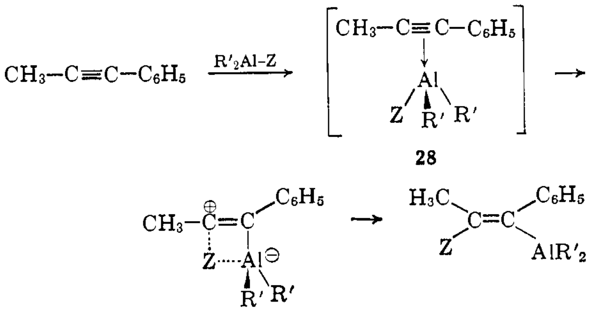
[8] G. Wilke and H. Müller, *Ann.*, **629**, 231 (1960), established that terminal alkynes form geminal bisalumino adducts by deuteration studies.

Chart II



configuration (**12** and **13** → **14**). However, under conditions (100°) where these adducts reverted to 1-phenylpropyne and $(i\text{-}C_4H_9)_2AlH$, isomerization to *trans*-vinylaluminum adducts occurred readily (**24** → **26**, where R = H). Similar isomerization of the adduct derived from diphenylacetylene also was observed (expt 7). In both cases, significant amounts of diadducts (*e.g.*, **20**) were detectable under isomerization conditions. These findings strongly suggest that *cis–trans* isomerization ensues through the formation and decomposition of the bisalumino adduct (**23** or **24** → **20** → **26**). Since diisobutylaluminum hydride can be eliminated from **12** or **13** at 100° (Chart I) to regenerate 1-phenylpropyne, it is altogether reasonable that **20** can eliminate hydride at this temperature and hence be responsible for the observed isomerization. Moreover, the failure of tetraphenylpropyne to undergo *cis–trans* isomerization at 110°, but rather carbon–carbon bond scission, offers unique support for an addition–elimination pathway to isomerization. Because of the bulky trityl group, the postulated diadduct **20** (R = C_6H_5) should be most unstable. Reversion to the *cis*-vinylaluminum adduct (**23** or **24**, R = C_6H_5) by loss of R'_2AlH (path a) should be most favored. Formation of the *trans*-vinylaluminum (path c) demands eclipsing of the bulky $(i\text{-}C_4H_9)_2Al$ and $(C_6H_5)_3C$ groups and hence is disfavored. Any such rotation leads instead to the elimination of diisobutyltritylaluminum (path b, **21**). Hence, the *trans* adduct is prevented from forming and isomerization is not observed. Therefore, it appears that dipolar forms **24** and **25** are not important for the principal isomerization pathway of vinylaluminum adducts. On the other hand, bridging associations such as **25** present a most appealing explanation for the facile disproportionation of these systems (**12** or **13** → **14**) without loss of configuration.

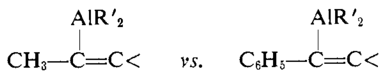
After the foregoing discussion of isomerization mechanism, some comment is appropriate on the stereochemical and polar factors of the addition reactions themselves. From the observed orientation in the addition of Al–H and Al–C bonds to 1-phenylpropyne, polar factors seem more important than steric factors. In the preferred formation of **12** over **13** and of **15** and **16** over **18** and **19**, the bulky diisobutylaluminum group is positioned at the carbon adjacent to the bulky phenyl, rather than the smaller methyl group. Taken together with the stereospecific *cis* addition, these facts are consistent with a four-center transition state where the aluminum center is initiating electrophilic attack on the triple bond (**28**, Z = H or (R')C=C(R)H). The carbon atom of the alkyne better able to sustain the electron deficiency then receives the Z group to complete the addition (eq 3).



(3)

Attempts were made to obtain evidence for the existence of the postulated π complex **28**, but unequivocal proof has thus far eluded experimentation (*cf.* part E in the Experimental Section). On the other hand, the postulated bridging of group Z in **29** helps explain the observed order of group reactivity: Z = H > substituted vinyl >> isobutyl. The better the bridging of group Z in $(R_2AlZ)_x$, the better able it might be to bridge between carbon and aluminum in **29**.[9]

Finally, two aspects of the oligomerization of 1-phenylpropyne are not completely understood. Although steric hindrance seems not important in determining the orientation of triple bond additions, the greater reactivity of vinyl adduct **12** over that of **13** (R = CH_3) may be due to the greater steric accessibility of the carbon–aluminum bond in the former



$$CH_3\text{—}\overset{\displaystyle AlR'_2}{\overset{|}{C}}\text{=}C< \quad \textit{vs.} \quad C_6H_5\text{—}\overset{\displaystyle AlR'_2}{\overset{|}{C}}\text{=}C<$$

However, electronic influences cannot as yet be dismissed. In addition, the reaction of butadienylaluminum adducts (**15** and **16**) with 1-phenylpropyne to form the benzene system (**17**) might occur by means of a simple Diels–Alder addition, with subsequent loss of R'_2AlH, as suggested by Wilke and Müller for symmetrical alkynes.[6a] But the inspection of a Stuart–Briegleb model of **16** (R = CH_3) gives an impression of a most encumbered diene, seemingly little suited for a 1,4 addition to its cisoid form. This raises the possi-

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[9] J. J. Eisch, *J. Am. Chem. Soc.*, **84**, 3834 (1962).

bility that **16** may undergo a 1,4-thermal elimination of R'_2AlH to form 1,2-dimethyl-3,4-diphenylcyclobutadiene. The latter reactive intermediate could easily yield **17** *via* Diels–Alder reactions with 1-phenylpropyne in various orientations.[10] These aspects are receiving further study.

Experimental Section

Manipulation of Organoaluminum Compounds. Because of their sensitivity to oxygen and to protic solvents, organoaluminum reagents were transferred and allowed to react under an atmosphere of dry, oxygen-free nitrogen. Prepurified nitrogen (Matheson, 99.996% min) was passed over shiny copper gauze heated at 400–480° and then passed through two drying towers containing Linde molecular sieves, Type 4-A, and phosphorus pentoxide on glass beads, respectively. The resulting nitrogen gas was distributed to places of use *via* short, butyl rubber connections.

All glassware involved in the transfer and the reactions of organoaluminum compounds was oven dried at 150° and assembled while warm. Alternate evacuation of apparatus and refilling with pure nitrogen were performed repeatedly before use with aluminum alkyls. Transfers of solids and liquids, especially for spectral measurements, were undertaken in a Plexiglas inert atmosphere chamber with antechamber (Manostat). With liquid diisobutylaluminum hydride and organoaluminum reaction products, the use of nitrogen-pressured siphoning or of nitrogen-flushed syringe pipets permitted smooth transfers.

The storage, distillation, filtration, and reactions of aluminum alkyls all were undertaken in a series of two- or three-necked, conical or round-bottomed flasks. These vessels were readily fashioned from commerical one-necked flasks by affixing glass joints at a 45° angle to the original neck. Typically, one neck of each vessel was provided with an inner joint surmounted by a three-way stopcock. Such an arrangement provided ingress of pure nitrogen into the vessel while the other neck(s) was (were) being opened for sampling or being attached to distillation columns, sintered-glass filters, or other flasks bearing reagents (whose joint was of the inner type). Furthermore, the union of a two- or three-necked reaction vessel (A) and an empty two-necked flask (B) served as a simple setup for the removal of volatile components from a reaction mixture. The simultaneous warming of flask A under the reduced pressure of an oil pump allowed the volatile material to be collected in flask B (immersed in a Dry Ice–acetone slush). Similarly, the union of two such flasks by means of a sintered-glass filter provided a convenient means of filtration. An excess pressure of nitrogen in flask A and a partial vacuum in flask B was usually sufficient to filter most solutions.

Small amounts of organoaluminum compounds could be disposed of safely by the dropwise dilution with ethyl ether or hexane, followed by the cautious pouring of the solution into a large amount of water or dilute ethanol.[11]

Preparation and Purification of Reagents. A. Starting Materials. Diisobutylaluminum hydride was prepared by the thermal elimination of isobutylene from the commercially available triisobutylaluminum (Ethyl Corp.) in accordance with the general procedure of Ziegler and co-workers.[12] A convenient distillation apparatus proved to be a 500-ml, round-bottomed flask bearing one stoppered neck and one neck fused to a Vigreux column. The distillation column, in turn, bore a thermometer joint at its top and was itself fused to a one-piece condenser and fraction distributor. Two-necked flasks, each bearing a three-way stopcock, were connected to the four-way fraction collector to receive the distillate. The condenser was cooled with kerosene which was circulated through copper coils immersed in a cold bath. Since aluminum alkyls can ignite spontaneously in air and can also hydrolyze explosively, this method of cooling is advised to prevent serious accident in the event the condenser would break.

In a typical run 250 ml of triisobutylaluminum was placed in the distillation flask, and the liquid was slowly heated under 1 atm of nitrogen in an oil bath to 160–180°. Magnetic stirring of the oil bath permitted a smooth evolution of gas. The isobutylene evolution was monitored by means of a mineral bubbler inserted in the nitrogen line and the olefin could be condensed by passing the evolving gas stream through a Dry Ice–acetone trap. After 12 hr the gas evolution became very slow and hence the slightly turbid liquid was cooled. The system was placed under a reduced pressure of 0.03 mm and gradually heated. From 46–96° about 50 ml of triisobutylaluminum was collected, while between 96–107° (0.1 mm) the diisobutylaluminum hydride distilled over (bath temperature of 125–130°). Redistillation gave bp 112–114° (0.3 mm). The main fraction of about 100 ml had a pycnometrically determined density, d_4^{28} $0.79\bar{3}$. Although the deposition of aluminum and further gas evolution (increase in pressure to 0.1–0.3 mm) signaled some decomposition, satisfactory distillation occurred if the bath temperature was kept below 130°.

Anal.[13] Calcd for $C_8H_{19}Al$: Al, 18.97. Found: Al, 19.08.

1-Phenylpropyne (methylphenylacetylene) was prepared from phenylpropanone *via* conversion to 1-chloro-1-phenylpropene and the dehydrohalogenation of the latter.[14] Thus, 372 g (1.78 moles) of powdered phosphorus pentoxide was placed in a 1-l. round-bottomed flask equipped with a reflux condenser bearing a gas trap. Over a 1-hr period 1.96 g (1.46 moles, bp 62–63° (6 mm)) of phenylpropanone was introduced with intermittent shaking and cooling to moderate the reaction. The solution was heated just below reflux for 4 hr and then the generated phosphorus oxychloride was distilled off, bp 28–35° (19 mm). Subsequently, the isomeric chloroalkenes were collected between 78 and 108° (4 mm) (108 g of colorless liquid, 81%).

Over a period of 2 hr the chloroalkenes were added carefully to a refluxing mixture of 136 g of potassium hydroxide in 300 ml of absolute ethanol. An immediate precipitation of potassium chloride and the appearance of a deep orange color were signs of a positive reaction. After an additional 7 hr at reflux the reaction mixture was hydrolyzed and was extracted with eight 100-ml portions of benzene. Removal of solvents from the dried extracts and distillation gave 100 g (80%) of 1-phenylpropyne, bp 80–82° (17 mm). Redistillation through a 60-cm, helices-filled column provided a colorless liquid, bp 59–61° (4.5 mm) which did not contain halogen. Moreover, a glc analysis on a 6-ft, 30% silicone oil-on-firebrick column at a column temperature of 155° displayed only one peak. Unless kept under nitrogen, 1-phenylpropyne slowly turned yellow. Hence, it was redistilled before each reaction.

Tetraphenylpropyne (phenyltriphenylmethylacetylene) was prepared according to a published procedure in 70% yield, mp 142–142.5°, from ethyl acetate (lit.[15] mp 139°). An infrared spectrum in mineral oil showed no $C{\equiv}C$ stretch absorption.[15]

The **aprotic organic solvents** used as reaction media were all of reagent grade. Liquid alkanes were treated with potassium permanganate and with concentrated sulfuric acid to ensure the absence of unsaturates. Routinely the solvents were refluxed over sodium for 1 day, then distilled and finally redistilled from lithium aluminum hydride directly into the reaction vessel.

B. Authentic Samples of Reaction Products. Pure samples of *cis*-β-methylstyrene and *trans*-β-methylstyrene were available.[16] Commercial samples of reagent grade *trans*-stilbene, *cis*-stilbene, *n*-propylbenzene, and bibenzyl were purified by recrystallization or distillation before use. Their purity by glpc analysis was >98%.

cis,cis-1,2,3,4-Tetraphenylbutadiene was prepared by the lithium metal, reductive dimerization of tolane in ethyl ether, mp 182–183°.[17] In an analogous manner, the treatment of 1-phenylpropyne in ether with lithium metal yielded *cis,cis*-2,3-dimethyl-1,4-diphenyl-1,3-butadiene. Although the structure of this compound does not follow unambiguously from this synthesis, this route does provide an independent, rational support for the structure.[18]

1,1,1,3-Tetraphenylpropane was prepared by treating 500 mg with 50 mg of 5% palladium on carbon, 25 ml of glacial acetic acid, and hydrogen for 10 hr, mp 127–128°.

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(10) In a similar system H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2195 (1961), has found that *cis,cis*-4-bromo-1-bromodimethyltin-1,2,3,4-tetraphenylbutadiene extrudes dimethyltin dibromide at 150° to form the reactive cyclobutadiene.

(11) Further details and illustrations of procedures and apparatus used in this research can be found in the doctoral dissertation of W. C. Kaska, University of Michigan, 1963.

(12) K. Ziegler, H. G. Gellert, H. Lehmkuhl, W. Pfohl, and K. Zosel, *Ann.*, **629**, 11 (1960).

(13) H. L. Watts, *Anal. Chem.*, **30**, 967 (1958).

(14) C. D. Hurd and A. Tockman, *J. Org. Chem.*, **23**, 1087 (1958).

(15) H. Wieland and H. Kloss, *Ann.*, 470, 201 (1929).

(16) The kindness of Professor R. M. Stiles in providing these samples is gratefully acknowledged.

(17) L. I. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, **63**, 1184 (1941).

(18) Unpublished study of A. M. Polikoff, National Science Foundation Undergraduate Research Participant, University of Michigan, 1962–1963.

Instrumentation. Melting points were determined in a Hershberg apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer recording spectrophotometer, Model 21. Ultraviolet spectra were recorded on a Cary spectrophotometer, Model 11. The nmr spectra were recorded for carbon tetrachloride solutions of the compounds containing tetramethylsilane as an internal standard. A Varian spectrometer, Model A-60, was used in all cases; hence, the chemical shifts are given on the δ scale (ppm). Most analyses were performed with Barber-Colman gas chromatograph, Model 10, which has a strontium-90 ionization source.

Reactions of 1-Phenylpropyne with Diisobutylaluminum Hydride. A. General Procedure. A 125-ml, three-necked conical flask (A) was provided with a stopper, nitrogen lead, and connection to a second flask. The latter two-necked flask (B) could be charged with diluting solvent and or hydrolyzing agent at the time of work-up. The reagents were placed in flask A and allowed to react with magnetic stirring and oil bath heating. Just before work-up, flask B was charged with solvent (pentane). Deuterium oxide or ordinary water was added to the pentane by introducing the water vial into flask B and pulling off the cracked vial tip with a wire loop. Hydrolysis was effected by slowly mixing contents of flasks A and B.

In the event of volatile component removal the empty flask B was cooled, while flask A was warmed under vacuum.

B. 1:1 Ratio of Reactants with Hydrolytic Work-up. Diisobutylaluminum hydride (7.93 g, 10.0 ml, 0.0556 mole) was added to 6.47 g (0.0556 mole) of 1-phenylpropyne at 50 ± 1°. The reaction solution became pink after 2 min and gradually turned red-orange over the 8-hr reaction period. Thereupon a vacuum of 0.01 mm was used to remove the acetylene. The cooled reaction mixture was poured cautiously into a cold, stirred mixture of pentane and water. After the resulting slurry was filtered to remove the hydrous aluminum oxide and the collected solid was washed with portions of ethyl ether, the combined organic extracts were dried over anhydrous calcium sulfate. A glpc analysis of the concentrated extract on a 6-ft, 30% silicone oil-on-firebrick column (column temperature at 155°) indicated the presence of *cis*-β-methylstyrene, methylphenylacetylene, and *n*-propylbenzene in a ratio of 24.5:3.3:1.0. The *cis,cis*-2,3-dimethyl-1,4-diphenyl-1,3-butadiene was detected on a 3-ft, 5% silicone gum rubber-on-firebrick column at a column temperature of 100° (ratio of diene to *n*-propylbenzene was 1.3:1.0). All components were identified by injection of authentic samples into the gas-liquid chromatograms and by collection of individual samples for infrared analysis.

The previously unreported *cis,cis*-2,3-dimethyl-1,4-diphenyl-1,3-butadiene was isolated by removing the more volatile components from the reaction mixture and by recrystallizing the residue from absolute ethanol as white leaflets, mp 132.5–133°.

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74; mol wt, 234. Found: C, 92.21; H, 7.71; mol wt (Rast), 245.

The ultraviolet spectrum in cyclohexane displayed one maximum at 290 mμ (log ϵ 4.65). The infrared spectrum showed prominent absorptions at 698, 740, 840, 920, 1025, 1175, 1580 (C=C conjugated with phenyl), and 1615 cm^{-1}. The nmr spectrum consisted of resonances (intensity) due to C_6H_5 at 7.32 (10), to vinyl H at 6.79 (2.06), and to the methyl group at 2.11 (6.2) ppm. The phenyl and methyl signals were a sharp singlet and doublet, respectively, but the vinyl H signal was a poorly resolved quartet. Extending the sweep width increased the resolution of the vinyl quartet and the methyl doublet ($J_{H_1CH_3}$ = 1.1 cps).

C. 2:1 Ratio of 1-Phenylpropyne and Diisobutylaluminum Hydride. A mixture of 7.93 g (0.0556 mole) of diisobutylaluminum hydride and 12.9 g (0.0111 mole) of 1-phenylpropyne was heated at 50–80° for 60 hr. After removal of residual acetylene by heating to 80° under reduced pressure, the residue was hydrolyzed with a pentane–water slurry. A glpc analysis of the isolated crude organic layer using a 5% silicone gum rubber column at 155° revealed two peaks, the first being *cis,cis*-1,3-dimethyl-2,4-diphenyl-1,3-butadiene and the second being the aforementioned symmetrical diene. The predominant product was the latter diene. The majority of the latter diene was removed by fractional crystallization from ethanol, mp 133–133.5°. Further crops of solid melting at 55–58° were combined and distilled, bp 130–132° (0.8 mm). Several recrystallizations of the distillate from *n*-heptane gave white, cubic crystals of the unsymmetrical diene, mp 62.5–64°. Upon prolonged standing in a closed vial the compound changed to a yellow oil.

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74; mol wt, 234. Found: C, 91.91; H, 8.01; mol wt (Rast), 240.

The ultraviolet spectrum of *cis,cis*-1,3-dimethyl-2,4-diphenyl-1,3-butadiene in cyclohexane displayed one maximum at 247 mμ. The infrared spectrum showed prominent bands at 697, 720, 755, 770, 820, 920, 1015, 1025, 1075, 1370, 1585 (C=C conjugated with phenyl), 1610, and 1620 cm^{-1}. The nmr spectrum consisted of a multiplet due to C_6H_5 between 7.06 and 7.42 (intensity of 10.0), a quartet centered at 6.0 due to terminal C_1 vinyl hydrogen ($J_{H_1CH_{3(1)}}$ = 7.0 cps, intensity of *ca.* 1.0), a broad vinyl singlet at 6.12 (intensity of *ca.* 1.1), a methyl doublet at 2.08 ($J_{CH_{3(3)}H_4}$ = 1.1 cps, intensity of 3.0), and another methyl doublet at 1.6 ppm ($J_{CH_{3(1)}H_1}$ = 7.0 cps, intensity of 3.0).

Recrystallization of the residue from the distillation of the unsymmetrical diene from a benzene–ethanol pair provided white needles. After sublimation this solid melted at 324–325°. Isolated in a small amount this compound proved very difficult to analyze in a reproducible manner. However, the nmr spectrum in $CDCl_3$ exhibited a phenyl multiplet centered at 7.38 and a sharp singlet at 1.73 ppm. The absence of vinyl peaks and the following marginal analytical data suggest this compound is 1,3,5-trimethyl-2,4,6-triphenylbenzene.

Anal. Calcd for $C_{27}H_{24}$: C, 93.06; H, 6.94. Found: C, 92.53; H, 7.35.

D. Trimerization of 1-Phenylpropyne by Diisobutylaluminum Hydride. To a solution of 0.80 g (0.0056 mole) of the hydride in 30 ml of xylene (distilled from sodium) was added 10 g (0.087 mole) of 1-phenylpropyne. During the 72-hr heating period at 140–150° a deep orange color developed. After hydrolysis in a pentane–benzene medium and usual work-up, 9.5 g of a yellowish solid were obtained, mp range 180–200°. Recrystallization from acetic acid yielded colorless needles, mp 220–222°. The mother liquors contained some of the symmetrical trimer, 1,3,5-trimethyl-2,4,6-triphenylbenzene.

Anal. Calcd for $C_{27}H_{24}$: C, 93.06; H, 6.94; mol wt, 348.5. Found. C, 92.83; H, 7.04; mol wt (Rast), 350.

The nmr spectrum in carbon disulfide displayed phenyl multiplets between 7.1 and 7.4 (intensity of 15.0), a methyl singlet at 2.05 (6.0), and a second methyl singlet at 1.72 ppm (3.0).

E. Possible Complexation between 1-Phenylpropyne and Diisobutylaluminum Hydride. A 1:1 mixture of the acetylene and the hydride was placed in a 0.05-cm fixed-thickness infrared liquid cell and the twin C≡C bands of the propyne at 2220 and 2250 cm^{-1} monitored over 12 hr. Initially, the bands appeared at 2230 ± 10 and 2260 ± 10 cm^{-1} and did not change their position with time. No new bands (possibly shifted C≡C bands) occurred in the 2100–2230-cm^{-1} range.

In another attempt to detect complexation, a mixture of 6.47 g of 1-phenylpropyne and 7.93 g of diisobutylaluminum hydride was prepared and allowed to stand for 5 min. The colorless solution was cooled and the acetylene was removed at 0.01 mm over a 1-hr period. In this manner 99.4% of the acetylene could be collected in a cold trap. Readdition of the acetylene to the metal hydride caused the immediate formation of an orange-red mixture. The color of the reaction mixture deepened during a 4-hr stirring period at room temperature. Subjecting the mixture to a 6-hr period at 0.01 mm now permitted the recovery of only 77% of the acetylene. Infrared examination of the reaction residue clearly showed that 1-phenylpropyne was still present. Moreover, hydrolysis of a reaction mixture aliquot and glpc analysis revealed the presence of only *n*-propylbenzene, 1-phenylpropyne, and *cis*-β-methylstyrene in a ratio of 1:6:15. After the residual red reaction mixture was allowed to stand for another 6 hr at room temperature, and 0.01 mm, hydrolytic work-up uncovered only *n*-propylbenzene and *cis*-β-methylstyrene in a 1:9 ratio. No liquid passed into the cold trap during this period.

F. Dissociation of the Vinylaluminum Adducts from 1-Phenylpropyne and Diisobutylaluminum Hydride. 1-Phenylpropyne (12.9 g, 0.111 mole) was added dropwise to 15.9 g (0.111 mole) of diisobutylaluminum hydride held at 50° over a 5-hr period. After 20 hr at 50° a hydrolyzed aliquot of the reaction mixture showed upon glpc analysis the presence of *cis*-β-methylstyrene, 1-phenylpropyne, and *cis,cis*-2,3-dimethyl-1,4-diphenyl-1,3-butadiene in a 27:10:1 ratio. Another aliquot taken after 24 hr at 60° revealed only *cis*-β-methylstyrene and the diene.

The reaction mixture was now heated between 50 and 100° under a pressure of 0.01 mm. Approximately 25–30 ml of a colorless fuming liquid was caught in the cold trap. Hydrolysis of this liquid and glpc analysis showed the presence of *cis*-β-methylstyrene, 1-phenylpropyne, and *trans*-β-methylstyrene in a 12.6:3.1:1.0 ratio.

G. Disproportionation of the Vinylaluminum Adducts. Diisobutylaluminum hydride (7.93 g, 0.0556 mole) and 1-phenylpropyne (7.11 g, 0.612 mole) were mixed at 50° and allowed to react for 26 hr. The red reaction mixture was heated at 50° under a reduced pressure of 0.1 mm for 26 hr. A large amount of fuming liquid was collected in the cold trap. Infrared examination of the latter liquid proved it to be chiefly triisobutylaluminum admixed with a little 1-phenylpropyne. The infrared spectrum of the residual reaction mixture showed the absence of C≡C and Al—H absorptions. Hydrolysis of a reaction mixture aliquot and glpc analysis revealed the presence of *cis*-β-methylstyrene, a trace of *n*-propylbenzene, and the symmetrical diene. The absence of *trans*-β-methylstyrene is noteworthy.

H. Isomerization of the Vinylaluminum Adducts. As in part G the acetylene and hydride were heated at 50° for 26 hr. Then under a pressure of 0.1 mm the mixture was heated at 50° for an additional 44 hr. A total of 5.4 g of colorless liquid, chiefly triisobutylaluminum, was collected in the cold trap. The calculated amount of $(C_4H_9)_3Al$ expected to result from disproportionation to $(C_4H_9)Al(C_6H_5C{=}CHCH_3)_2$ is 5.5 g.

The residual red oil was heated for 44 hr at 75° and for 4 hr at 100°, while the pressure was held at 0.01 mm. In this way an additional 2.6 g of liquid, chiefly $(C_4H_9)_3Al$, was collected in the cold trap. (Expected $(C_4H_9)_3Al$, 1.8 g.) Hydrolysis of this trap liquid gave 0.3 g of organic liquid (containing β-methylstyrenes). Hydrolysis of the residual red oil and glpc analysis demonstrated the presence of *n*-propylbenzene, *cis*-β-methylstyrene, *trans*-β-methylstyrene, and *cis,cis*-2,3-dimethyl-1,4-diphenyl-1,3-butadiene in a 4.0:3.8:2.9:1.0 ratio.

I. Deuteriolysis of the Reaction Mixture from a 1:1 Interaction of 1-Phenylpropyne and Diisobutylaluminum Hydride. In view of the tenacity with which water is adsorbed on a glass surface, the following precautions were taken in deuteriolysis experiments. All glassware used in the reaction and especially the equipment used for deuteriolysis was baked in an oven at 250° for several days. Thereupon the flasks were rinsed with 99% deuterium oxide and flamed out under high vacuum for several hours.[19]

A sample of the vinylaluminum adducts then was prepared as in part B. With efficient stirring the organoaluminum adducts were poured into a slurry of 250 ml of dry hexane and 18.0 g of >99.5% deuterium oxide. The suspension was stirred under nitrogen for 7 hr, filtered, and washed with dry hexane. The organic filtrate was dried with anhydrous calcium sulfate and the solvent was removed. Distillation of the organic residue (shown by glpc analysis to contain no *trans*-β-methylstyrene) gave a fraction containing mainly the deuterated *cis* olefin, bp 70–71° (20 mm). The pure deuterated *cis*-β-methylstyrene was collected by use of a 6-ft, 30% silicone oil-on-firebrick column. A mass spectrometric analysis of this compound on a Consolidated Electrodynamic spectrometer, Model 21-1038, at an ionizing voltage of 6.5 v showed the presence of only 2.7% nondeuterated *cis*-β-methylstyrene, together with a smaller amount of dideuterated olefin, in deuterated product thus obtained.[20]

The positions of the deuterons in *cis*-β-methylstyrene were determined by recording the nmr spectra of both the nondeuterated and the deuterated olefin under identical sample and instrumental conditions. The nmr spectrum of the nondeuterated olefin at 60 Mc possessed chemical shifts and coupling constants for the proton resonances in complete agreement with published values.[21] The spectrum of the deuterated olefin was changed considerably: the α-vinyl absorptions at $\delta = 6.3$ ppm were broadened into one peak, the β-vinyl absorptions were now a quartet centered at 5.65 ppm with each peak split into a triplet from spin coupling with deuterium ($J_{\mathrm{H_1D}}$ (expected) = 1.75 cps, $J_{\mathrm{H_1D}}$ (found) = 1.8 cps); and the methyl signal occurred as a doublet at 1.77 ppm. Integration of the proton peak areas showed the presence of 82 ± 2% of the deuterons at the α-vinyl carbon and 18 ± 2% at the β-vinyl carbon.

From the distillation residue obtained in isolating the olefin a crop of deuterated *cis,cis*-2,3-dimethyl-1,4-diphenyl-1,3-butadiene was obtained, mp 132–133°. Its nmr spectrum showed a resonance for phenyl, a poorly resolved vinyl and a broadened, nonsplit methyl signal in intensities of 10:0.91:6.04.

J. Deuteriolysis of a 2:1 Reaction Mixture of 1-Phenylpropyne and Diisobutylaluminum Hydride. As in part C, except that heating period was 7 days. Deuteriolysis was conducted as in part I. The symmetrical diene was allowed to crystallize out of the crude, solvent-free product and the mother liquor was distilled; the unsymmetrical diene boiled at 60° under 0.1 mm. Recrystallization from heptane gave the pure *cis,cis*-1-deuterio-2,4-dimethyl-1,3-diphenyl-1,3-butadiene, mp 62–64°. Its nmr spectrum consisted of a phenyl resonance at 7.25 (intensity of 9.4), a quartet for the vinyl proton at C_4 (6.0 ppm, $J_{\mathrm{H,CH_3}} = 7.0$ cps, intensity of 1.0), a singlet for the methyl at C_2 (2.09 ppm, 3.0), and a doublet for the methyl at C_4 (1.60 ppm, $J_{\mathrm{CH_3,H}} = 7.0$ cps, 3.0).

K. Infrared Spectrum of Vinylaluminum Adducts. As in part B, the vinylaluminum adduct mixture was prepared. When the resulting product was placed under 0.01 mm at room temperature, only a small amount of 1-phenylpropyne could be recovered. An infrared spectrum of the orange-red oil displayed a sharp band of moderate intensity at 1562 cm^{-1}, assigned to the C=C stretch of the α,β-unsaturated organoaluminum system.[22] Despite the apparent absence of the C≡C band the red oil did yield some 1-phenylpropyne upon hydrolysis.

Reaction of Tetraphenylpropyne with Diisobutylaluminum Hydride. A. Hydrolytic Work-up. A solution of 5.75 g (0.0167 mole) of tetraphenylpropyne in 75 ml of dry toluene was heated with 2.8 g (0.020 mole) of diisobutylaluminum hydride at reflux. After 36 hr the orange solution was hydrolyzed and the organic solvent was distilled. A glpc analysis of the crude residue showed the presence of some starting alkyne, ethylbenzene, 62% of triphenylmethane, and 38% of a second component. The triphenylmethane was separated by fractional recrystallization from benzene, mp 94.0–94.5°. Recrystallization of other crystal crops from ethanol yielded a solid, mp 124–125.5°.

Anal. Calcd for $C_{27}H_{22}$: C, 93.60; H, 6.40; mol wt, 346. Found: C, 93.80; H, 6.30; mol wt (Rast), 370.

The infrared spectrum in carbon tetrachloride did not have any absorption in the aliphatic C—H stretch region, nor at 965 cm^{-1} where *trans*-CH=CH deformations are expected. The nmr spectrum displayed phenyl singlets at 7.00 ($(C_6H_5)_3C$) and 6.68 ppm and vinyl hydrogen resonances at 6.89 and 6.60 ppm. The integrated areas were in the ratio of 15:5.2:1.0:1.0. The vinyl peak at 6.60 ppm was assigned to the $=CHC_6H_5$ peak, since the following deuteriolysis experiment suggested a greater percentage of deuterium at this position (*cf.* *cis*-β-methylstyrene in part I).

Finally, this hydrocarbon depressed the melting point greatly when admixed with authentic 1,1,1,3-tetraphenylpropane. However, treatment of this hydrocarbon in acetic acid with hydrogen in the presence of 5% palladium-on-charcoal catalyst yielded 1,1,1,3-tetraphenylpropane, mp 127–128° (mmp). Hence, this coumpound is *cis*-1,3,3,3-tetraphenylpropene.

B. Deuteriolytic Work-up. As in the foregoing, the same amounts of reagents in toluene were heated for 48 hr at 90° and an additional 48 hr at 110°. The orange-red reaction mixture was poured into a mixture of pentane and 10 g of 99.8% pure deuterium oxide. Usual work-up gave a toluene layer which contained (glpc) ethylbenzene, 60.4% of triphenylmethane, and 39.6% of *cis*-1,3,3,3-tetraphenylpropene, but no styrene or phenylacetylene. Upon separation the triphenylmethane was shown to be 90 ± 1% α deuterated by nmr integration. The nmr spectrum of the *cis* olefin revealed the presence of 56% of $C{=}C(D)C_6H_5$ and 44% of $C{=}C(D)C(C_6H_5)_3$.

To demonstrate the triphenylmethane is inert to $(C_4H_9)_2AlH$, a solution of the two reactants was refluxed in toluene for 4 days. Neither an orange color nor a gas evolution (possibly H_2 or C_4H_{10}) was observed.

Reaction of Diphenylacetylene with Diisobutylaluminum Hydride. A solution of 7.93 g (0.0557 mole) of the hydride and 9.94 g (0.0557 mole) of the acetylene in 100 ml of heptane was heated at 50° for 48 hr. Hydrolysis of an orange aliquot and glpc analysis on a 3-ft, 5% silicone gum rubber-on-firebrick column revealed the presence of *cis*-stilbene, diphenylacetylene, and *trans*-stilbene in a 15.5:2:1 ratio. Recrystallization of the organic product from the aliquot out of glacial acetic acid yielded 29% of *cis,cis*-1,2,3,4-tetraphenyl-1,3-butadiene.

Further heating of the remaining organoaluminum solution at 90° for 24 hr and hydrolytic work-up showed the presence of a small amount of bibenzyl, together with the main components of *trans*- and *cis*-stilbenes in a 4.4:1 ratio. The relative amount of

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(19) We are indebted to Dr. Robert Summitt, Corning Glass Co., for suggesting this purification procedure.

(20) The cooperation of Mr. Frank Drogoz of the University of Michigan is gratefully acknowledged.

(21) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 238, 239.

(22) G. Wilke and H. Müller, *Ann.*, **629**, 222 (1960).

the diene obtained by recrystallization was 26%. Characteristic infrared bands for bibenzyl (900 and 1150 cm^{-1}) were prominent in the latter mother liquors from the diene.

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Factors Governing the Reaction of the Benzyl Grignard Reagent. I. Reactions with Acetaldehyde, Chloral, and Trifluoroacetaldehyde

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Contribution from the Chemical Laboratories of Purdue University, Lafayette, Indiana 47907. *Received January 3, 1966*

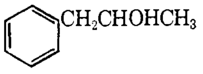
Abstract: The reaction of the benzyl Grignard reagent with acetaldehyde, chloral, and trifluoroacetaldehyde has been studied in detail. The products of the reaction with acetaldehyde are concentration dependent. With a 1:1 equivalency of Grignard to aldehyde, the principal product of the reaction is *o*-(2-hydroxypropyl)phenylmethylcarbinol. Benzylmethylcarbinol is a minor product and practically no *o*-tolylmethylcarbinol is produced. With a 3:1 equivalency of Grignard to aldehyde, all three products are formed. The intermediate leading to the diol product has been trapped out by adding trimethylchlorosilane to the reaction mixture at a time when hydrolysis would normally have been effected. The literature directions for the preparation of benzyltrichloromethylcarbinol from chloral could not be duplicated. Instead, halogen-metal exchange seemed to occur with the formation of bibenzyl and polymeric products. Also contrary to literature reports, it has been shown that benzyltrifluoromethylcarbinol is only a minor product when the benzyl Grignard reacts with trifluoroacetaldehyde. The products of this reaction are likewise dependent upon the relative concentrations of the Grignard and aldehyde. They are completely analogous to those obtained with acetaldehyde in that α, *ortho*, and diol products are formed.

The proclivity of the benzyl Grignard reagent to produce *ortho*- and *para*-substituted products in addition to the expected α has intrigued organic chemists through the years.[1] The so-called "abnormal reactions" of this reagent were first inadvertently noted by Grignard himself. In treating benzylmagnesium chloride with "polyoxymethylene," he characterized the product as the expected β-phenylethanol.[2] Tiffeneau and Delange[3] later disclosed that the material which Grignard had actually prepared was instead *o*-tolylcarbinol. Since this time, numerous examples have appeared in the chemical literature describing similar anomalies when the benzyl Grignard reacts with a variety of other reagents.

Unfortunately most of the early work in this field was hampered by the lack of adequate analytical techniques. The usual analytical method employed was oxidation of the crude reaction product to a mixture of benzoic, phthalic, and terephthalic acids. Such a method has two obvious flaws: (1) the yield of oxidation products is seldom quantitative and minor products can thus be overlooked; (2) one cannot safely extrapolate back to the structure of the materials which upon oxidation gave rise to the benzoic and phthalic acids.

Our laboratory is presently engaged in a broad, systematic research program designed to shed light, if possible, on those factors which influence benzylic-type Grignard reagents from reacting, on occasion, normally (*i.e.*, yield α products), and, under other circumstances, abnormally (*i.e.*, to form *ortho* and *para* products). In the present paper we are reporting the reaction of benzylmagnesium halides with acetaldehyde, chloral, and trifluoroacetaldehyde.

Acetaldehyde. Siegel[4] and co-workers, in an excellent series of papers, have studied the reaction between benzylmagnesium chloride and a variety of aldehydes. They report that the product of the reaction with acetaldehyde is a mixture of benzylmethylcarbinol (I) and *o*-(2-hydroxypropyl)phenylmethylcarbinol (II). They were unable to detect any *o*-tolylmethylcarbinol (III) in the reaction product. A similar pattern was noted for higher homologs like propionaldehyde, *n*-butyraldehyde, etc. It was pointed out that these results were in contrast to the reaction of the benzyl Grignard with formaldehyde in which only *o*-tolylcarbinol[5] is produced.



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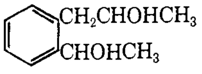

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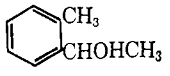

III

We repeated the reaction of the benzyl Grignard with acetaldehyde using a 1:1 and 3:1 equivalency of Grignard reagent to aldehyde, respectively. The products of

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(1) See H. Gilman and J. E. Kirby, *J. Am. Chem. Soc.*, **54**, 345 (1932), for some pertinent literature references.

(2) M. V. Grignard, *Bull. Soc. Chim. France*, [3] **29**, 953 (1903).

(3) M. Tiffeneau and R. Delange, *Compt. Rend.*, **137**, 573 (1903).

(4) (a) S. Siegel, S. K. Coburn, and D. R. Levering, *J. Am. Chem. Soc.*, **73**, 3163 (1951); (b) see also S. Siegel, W. M. Boyer, and R. R. Jay, *ibid.*, **73**, 3237 (1951).

(5) As will be pointed out in the next paper in this series, this is an oversimplification in the case of formaldehyde.