Steric Effects in the Hydralumination, Carbalumination, and Oligomerization of *tert*-Butyl(phenyl)acetylene[1]

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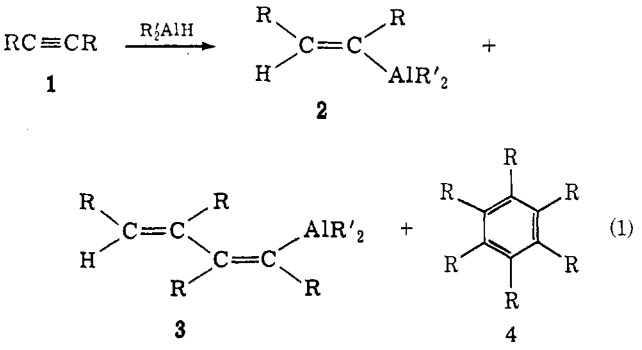
The hydralumination and subsequent reductive oligomerization of *tert*-butyl(phenyl)acetylene under the action of diisobutylaluminum hydride were examined. With a 1:1 equivalent ratio of reagents hydralumination proceeded (a) exclusively in a regiospecific cis fashion at 50°; (b) principally in a trans manner at 110°; and (c) preponderantly in a bis hydraluminating fashion at 140°. With a 2:1 ratio of alkyne:hydride and prolonged reaction time, the principal hydrolyzed product was *cis,cis*-1,4-di-*tert*-butyl-2,3-diphenyl-1,3-butadiene. Finally, by heating the alkyne with a small proportion of hydride, the reduced trimer, *cis,cis,cis*-1,3,6-tri-*tert*-butyl-2,4,5-triphenyl-1,3,5-hexatriene, was also obtained upon hydrolysis. The diene and triene were found to undergo conrotatory and, apparently, disrotatory ring closures, respectively. In addition, the clear-cut controlled hetero reductive dimerization of *tert*-butyl(phenyl)acetylene with a different alkyne, methyl(phenyl)acetylene, was achieved, leading to *cis,cis*-4-*tert*-butyl-2-methyl-1,3-diphenyl-1,3-butadiene. Finally, the carbalumination of *tert*-butyl(phenyl)acetylene by triphenylaluminum occurred regiospecifically to form 3,3-dimethyl-1,1-diphenyl-1-butene. The regiochemistry of the hydralumination observed here is shown to be consistent with a polar view, but that of the carbaluminations is seen to require a steric explanation. The nature of suitable activated complexes and the possible role of π-complex intermediates in the reductive oligomerization of alkynes are briefly considered.

The hydralumination of alkynes with dialkylaluminum hydrides is a valuable synthetic route to substituted vinylaluminum compounds. In a stereospecific fashion, the resulting adducts can, in turn, be (a) hydrolyzed to give cis alkenes[2,3] or trans alkenes;[3-5] (b) carbonated, with[6] or without[7] complexation with methyllithium, to yield substituted acrylic acids; (c) halogenated to provide vinylic halides;[4c,8,9] or (d) treated with various reagents, such as aldehydes[4b,6,8] or unsaturated hydrocarbons,[2,3,4b,10] to extend the carbon chain.[11] Competitive with the hydralumination of the alkyne are the reductive dimerization and the cyclotrimerization reactions,[2,3,12] which yield, upon hydrolytic work-up, *cis,cis*-1,3-alkadienes and hexasubstituted benzenes, respectively (eq 1). Although these reactions have been viewed[2] as simply consecutive steps in the concatenated pathway, **1** + RC≡CR → **2** → **3** → **4**, a survey of known interactions of organoaluminum compounds with alkynes has led to the alternative proposal of π-complex intermediates for such processes.[12]



1 **2** **3** **4**

The study of substituted acetylenes[3,5] has already demonstrated the importance of polar factors in the regioselectivity of hydralumination. Examination of sterically hindered acetylenes now appeared worthwhile for elucidating the pathways of the reductive dimerization and the cyclotrimerization reactions. To this end, we have examined the behavior of *tert*-butyl(phenyl)acetylene (**5**) toward diisobutylaluminum hydride (**6**). Through the presence of bulky R groups in **1**–**4** it was expected that the competing processes depicted in eq 1 might more readily be dissected and that certain previously undetected intermediates might be uncovered. Furthermore, the carbalumination of this same alkyne with triphenylaluminum also was of interest. From such a study we hoped to assess steric factors for a straightforward insertion analogous to the proposed process, **2** + RC≡CR → **3**.

Results

Hydralumination and Carbalumination of *tert*-Butyl(phenyl)acetylene.—Heating a 1:1 mixture of the acetylene **5** and the hydride **6** at 50° gave, upon hydrolysis, a 94% yield of *cis*-β-(*tert*-butyl)styrene (**7**) and a 6% yield of *cis,cis*-1,4-di-*tert*-butyl-2,3-diphenyl-1,3-butadiene (**8**). By hydrolysis of a similar reaction mixture with deuterium oxide, it was established from the nmr spectrum of **7** that only the olefinic hydrogen adjacent to the phenyl group was deuterated. Similarly it was found that only one of the two identical olefinic hydrogens in diene **8** was deuterated. The organoaluminum precursors (**9** and **10**) involved are, accordingly, those shown in eq 2. Even though the acetylene was already consumed after 24 hr, the ratio, **7**:**8**, changed during the next 24 hr from 98:2 to 94:6. This indicates that **9** slowly dissociated into **5** and **6**,

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[1] Part XXII of the series, "Organometallic Compounds of Group III," devoted to carbometalation and hydrometalation. Previous part: J. J. Eisch and S. G. Rhee, *J. Organometal. Chem.*, **42**, C73 (1972).

[2] G. Wilke and H. Müller, *Justus Liebigs Ann. Chem.*, **629**, 222 (1960).

[3] J. J. Eisch and W. C. Kaska, *J. Amer. Chem. Soc.*, **88**, 2213 (1966).

[4] For the principally trans hydralumination of alkynes with $LiAlH_4$ in THF, *cf.* (a) E. F. Magoon and L. H. Slaugh, *Tetrahedron*, **23**, 4509 (1967), and (b) J. J. Eisch and M. W. Foxton, Abstracts, Third International Symposium on Organometallic Chemistry, 1967, p 340, and ref 5. For trans hydralumination of alkynes with $Li[Al(i\text{-}C_4H_9)_2(CH_3)H]$ in monoglyme, *cf.* (c) G. Zweifel and R. B. Steele, *J. Amer. Chem. Soc.*, **89**, 5085 (1967).

[5] J. J. Eisch and M. W. Foxton, *J. Organometal. Chem.*, **11**, P50 (1968); *J. Org. Chem.*, **36**, 3520 (1971).

[6] G. Zweifel and R. B. Steele, *J. Amer. Chem. Soc.*, **89**, 2754 (1967).

[7] J. J. Eisch and M. W. Foxton, *J. Organometal. Chem.*, **11**, P7 (1968).

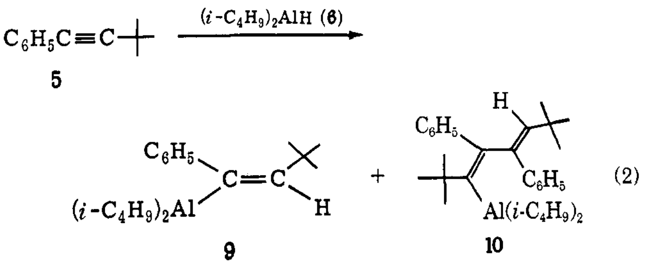
[8] G. Zweifel and C. C. Whitney, *J. Amer. Chem. Soc.*, **89**, 2753 (1967).

[9] *Cf.* J. J. Eisch and W. C. Kaska, *ibid.*, **88**, 2976 (1966), for the stereospecific iodinolysis of carbon–aluminum bonds.

[10] G. Zweifel, J. T. Snow, and C. C. Whitney, *ibid.*, **90**, 7139 (1968).

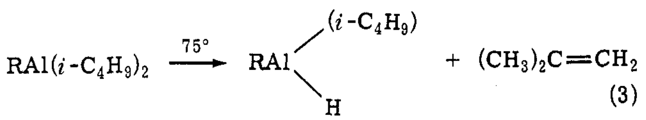
[11] H. Lehmkuhl, K. Ziegler, and H.-G. Gellert in "Houben-Weyl Methoden der Organischen Chemie," Vol. XIII/4, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1970, pp 204–258.

[12] J. J. Eisch, R. Amtmann, and M. W. Foxton, *J. Organometal. Chem.*, **16**, P55 (1969).

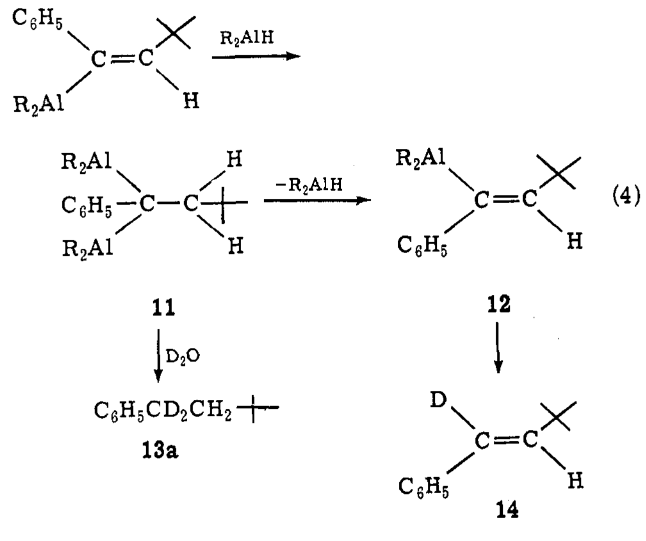


since the material balance of reactants and products did not reveal any new products.

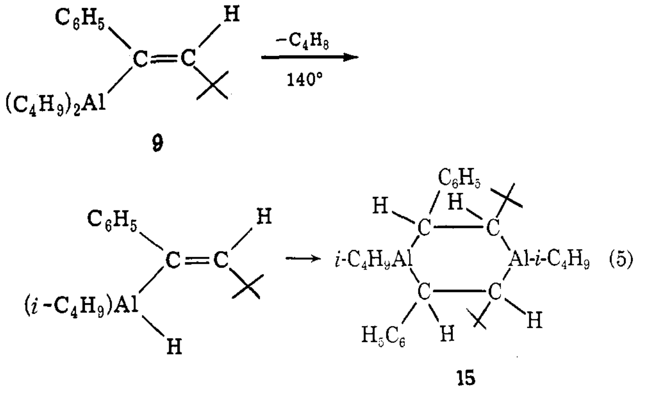
A similar hydralumination reaction mixture as above was heated for 48 hr-periods at 75°, at 110°, and finally at 140°. Hydrolytic and deuterolytic work-up revealed changes in the nature of the products. At 75°, both bis hydralumination (16%) leading to **11** and isomerization (35%) leading to the trans isomer of **9** occurred. Since more bis hydralumination occurred than could be accounted for by the remaining 6% of **6**, some of the isobutyl groups in **9** and **10** clearly had been lost as isobutylene and additional Al–H bonds had been generated[13] (eq 3–4).



$$\mathrm{RAl}(i\text{-}C_4H_9)_2 \xrightarrow{75°} \mathrm{RAl}\begin{smallmatrix}(i\text{-}C_4H_9)\\ \mathrm{H}\end{smallmatrix} + (CH_3)_2C{=}CH_2 \qquad (3)$$



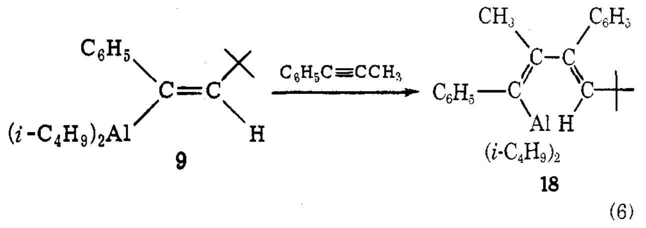
Previous work has offered strong evidence for the intermediacy of bis hydraluminated products like **11** in the cis,trans isomerization of vinylaluminum compounds.[3] The lability of adducts such as **11** was further revealed when the temperature was raised to 110°; the amount of **11** sank to 6%; and 68% of the product was now the trans adduct **12**. As a seeming contradiction to this finding, however, it was observed that heating for another 48 hr at 140° and then hydrolyzing led to the formation of 91.5% of the 3,3-dimethyl-1-phenylbutane (**13**). Only 2% of the cis olefin **7**, 6% of the trans olefin **14**, and 0.5% of the diene **8** remained. However, hydrolysis with deuterium oxide and nmr examination of **13b** showed that the deuterium was now distributed between the carbon α to the phenyl (61%) and the β carbon (39%). Since geminal adducts like **11** were apparently unstable at >100° and since the large amount of bis hydralumination revealed the importance of eq 3 at 140°, we propose that the increased amount of **13b** arose principally from a 1,4-dialuminacyclohexane intermediate (**15**) (eq 5).



Again, a 1:1 mixture of the acetylene **5** and hydride **6** were heated for 48 hr to yield a 94:6 mixture of **9** and **10**. Then 1 more equiv of acetylene **5** was introduced. After 16 hr at 50° the reaction mixture was hydrolyzed to give 33% of diene **8**, 38% of cis olefin **7**, and 29% of remaining acetylene **5**. Continued heating at 50–70° eventually gave >80% of diene **8**, and no other isomeric diene or oligomer could be detected.

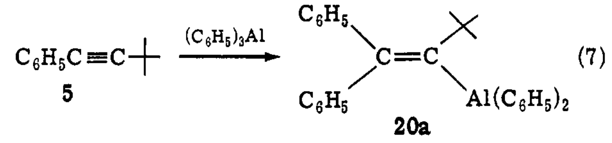
When 5:1 mixtures of the acetylene **5** and hydride **6** were maintained at 70–140°, again high yields of diene **8** were realized. However, when 7.5:1.0 mixtures were heated without solvent for 4 days at 140–160°, a new hydrocarbon, which proved to be *cis,cis,cis*-1,3,6-tri-*tert*-butyl-2,4,5-triphenyl-1,3,5-hexatriene (**16**), was also obtained.

Furthermore, it proved possible to achieve a controlled reductive heterodimerization of two different alkynes. Thus, after **9** was formed from a 1:1 mixture of *tert*-butyl(phenyl)acetylene (**5**) and hydride **6**, 1 equiv of methyl(phenyl)acetylene was introduced and the reaction mixture was heated at 50–60°. Upon hydrolysis, a 26% yield of *cis,cis*-4-*tert*-butyl-2-methyl-1,3-diphenyl-1,3-butadiene (**17**), uncontaminated by any other diene (except **8**, which was originally present), was isolated. By work-up of part of the reaction mixture with D_2O and nmr examination of **17**, it was revealed that deuteration occurred only at the 1 position of the butadiene. Hence, the aluminum precursor was **18**, as in eq 6.

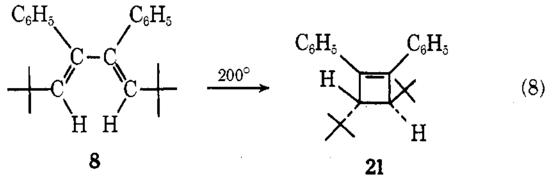


Finally, *tert*-butyl(phenyl)acetylene (**5**) was carbaluminated with triphenylaluminum (**19**) with difficulty, requiring prolonged heating at 90–110°. However, a single product, 3,3-dimethyl-1,1-diphenyl-1-butene (**20**), was isolated in good yield, showing that the reaction had formed **20a** regiospecifically (eq 7).

[13] K. Ziegler, H. Martin, and F. Krupp, *Justus Liebigs Ann. Chem.*, **629**, 14 (1960).



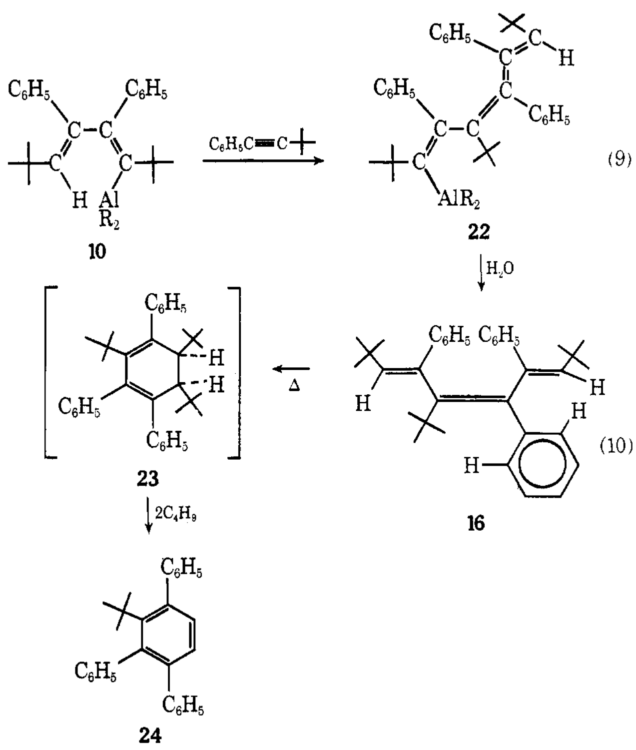
Structure Proofs of the Reaction Products.—The positions of the carbon–aluminum bonds in precursors **9**, **10**, **11**, **12**, **15**, and **18** could readily be ascertained by hydrolyzing with D_2O[3] and comparing the nmr spectra of the deuterated hydrocarbons with those of the hydrocarbons themselves. The stereochemical structure of the *cis,cis*-1,4-di-*tert*-butyl-2,3-diphenyl-1,3-butadiene (**8**) follows from (a) the two identical vinylic protons at 5.03 ppm (*cf.* nmr spectrum of **7**, where C_6H_5CH is at 6.38 and t-C_4H_9CH is 5.52 ppm); (b) the failure of **8** to be metalated by *n*-butyllithium in THF, thus ruling out that the protons at 5.03 ppm could be allylic; and (c) the facile thermal, conrotatory[14] ring closure of **8** to yield *trans*-3,4-di-*tert*-butyl-1,2-diphenylcyclobutene (**21**) (eq 8).



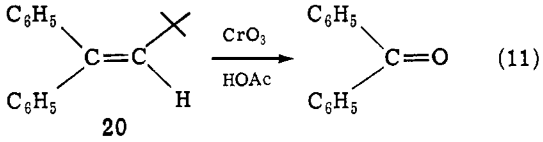
Isomeric with **8**, **21** had no nmr absorptions in the region 5.0–7.0 ppm, but instead displayed a two-proton singlet at 2.82 ppm. The ultraviolet spectrum of **21** displayed its long-wavelength maximum at 282 nm (*cf.* *cis*-stilbene, λ_{max} 280 nm), whereas the long-wavelength maximum in **8** was at 230 nm (*cf.* *cis*-*β*-*tert*-butylstyrene, λ_{max} 220 nm). The foregoing evidence, taken together with other spectral data for **8**, rules out the cis,trans and trans,trans forms, as well as isomeric structures where the positions of the *tert*-butyl and phenyl groups would be different.

The assignment of the structure *cis,cis,cis*-1,3,6-tri-*tert*-butyl-2,4,5-triphenyl-1,3,5-hexatriene to the reductive trimer **16** follows from the following considerations: (a) the presence of dissimilar, unsplit vinyl protons at 5.41 and 5.51 ppm, respectively; (b) the occurrence of three distinct signals for the three *tert*-butyl groups; (c) the presence of two protons split into multiplets at 5.72–5.90 ppm and 13 protons at 6.5–7.05 ppm, suggesting that two aromatic protons were abnormally shielded; and (d) the fact that the vinyl protons at 5.41 and 5.51 ppm resembled the chemical shift of t-C_4H_9CH in **7** (5.52 ppm). Finally, the possible formation of **16** from organoaluminum precursor **10** (eq 9) and the pyrolysis of **16** to yield 3-*tert*-butyl-1,2,4-triphenylbenzene (**23**) (eq 10) are consistent with the structural assignment.

As shown in **16** (eq 10), the ortho protons of the 4-phenyl will tend to lie in the shielding cones of the flanking 2- and 5-phenyl groups. Also to be noted is that the transformation **16** → **24** can be viewed as a thermally allowed, disrotatory ring closure of a 1,3,5-hexatriene,[14] followed by aromatization through the thermolysis of two relatively labile allylic–*tert*-butyl, carbon–carbon bonds.



The carbalumination of **5** by **19** was shown to yield only 3,3-dimethyl-1,1-diphenyl-1-butene (**20**) in the following manner: (a) gas chromatographic analysis of the reaction hydrolysate uncovered only **5** and **20**; (b) attempted acid-catalyzed isomerization of **20** was unsuccessful, whereas a 1,2-diphenylethylene would have yielded two isomers;[15,16] and (c) chromic acid oxidation of **20** yielded benzophenone (eq 11).



Finally, the sole diene obtained from the sequential reaction of hydride **6**, first with *tert*-butyl(phenyl)acetylene (**5**) and then with methyl(phenyl)acetylene, was shown to be *cis,cis*-4-*tert*-butyl-2-methyl-1,3-diphenyl-1,3-butadiene (**17**) as follows: (a) the unsplit vinyl proton at 5.88 ppm was assigned to *tert*-C_4H_9CH and the vinyl multiplet at 6.0 ppm to the C_6H_5CH (*cf.* **7**); (b) the methyl protons were split into a doublet (J = 1.0 Hz) and this fact excludes it from the 1 and 4 positions of the diene; and (c) all known homodimerizations of ordinary alkynes yield products of cis,cis configuration.

Discussion

The regiochemistry of hydraluminating triple bonds can readily be rationalized in terms of polar factors fostering electrophilic attack by the aluminum center (**25**), although, alternatively, an argument based on steric factors is possible. For the case of *tert*-butyl(phenyl)acetylene (**5**) the exclusive formation of **9**, compared with the 82:18 mixture of adducts **26** and **27** obtained from methyl(phenyl)acetylene (**28**), can be

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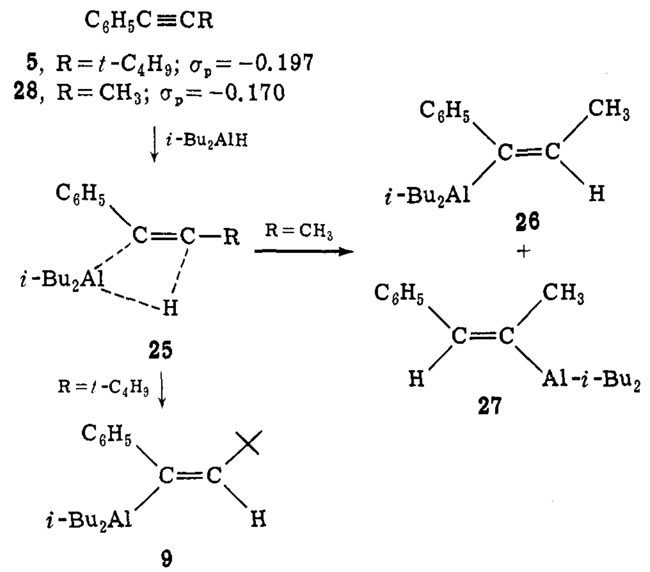
[14] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim, 1970, p 45.

[15] J. J. Eisch and C. K. Hordis, *J. Amer. Chem. Soc.*, **93**, 2974 (1971).

[16] J. J. Eisch and J. M. Biedermann, *J. Organometal. Chem.*, **30**, 167 (1971).



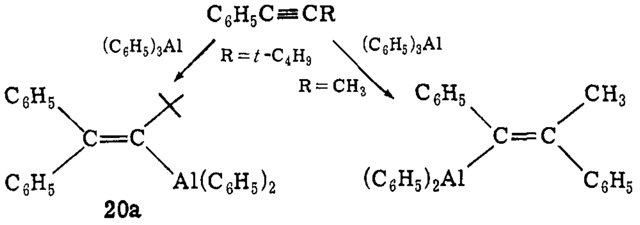
$C_6H_5C{\equiv}CR$

5, $R = t\text{-}C_4H_9$; $\sigma_p = -0.197$

28, $R = CH_3$; $\sigma_p = -0.170$

ascribed to the superior electron-releasing effect of the *tert*-butyl group, as mirrored in its σ_{para} value.

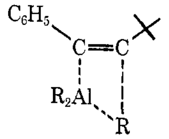
In contrast, this polar explanation cannot be extended to account for the carbalumination of **5**, either by triphenylaluminum or by **9**. Thus, the high regioselectivity in carbaluminating **28** (>95%) is just the reverse of that observed with **5**.



20a

Since Stuart–Briegleb models of **5** and **19** show that the phenyl group behaves effectively as the larger group, in comparison with the splayed out diphenylalumino group, then the formation of **20** from **5** can be ascribed to steric factors operative in a four-center transition state similar to **25**. Such a steric explanation could be likewise invoked to rationalize the formation by an "insertion" process of **10** from **9**, of **18** from **9**, and of **22** from **9**. Possibly steric factors even intervene in the apparent dimerizing hydralumination, leading to the formation of **15**, a case where vicinal bis hydralumination of an alkyne becomes more significant than the usual geminal bis hydralumination.[2]

Although the importance of steric factors in the carbalumination and in the reductive oligomerization of *tert*-butyl(phenyl)acetylene is clear from these considerations, serious objections can be raised concerning the usual coplanar four-center transition state **29**. Examination of Stuart–Briegleb models shows that nonbonded interactions between C_6H_5 and R_2Al and between *tert*-C_4H_9 and R severely impede a close approach of the C≡C and Al—R bonds, when all these centers lie in a plane. On the other hand, when these bonds approach each other in a perpendicular orientation (**30**), nonbonded interactions are minimized and the four centers can easily be brought into appropriate contact. The direction of Al—R bond addition would then be determined by the torsional interactions in passing from **30** to the adduct. By slight modification of this view, the steric factor could be considered as operating through the preferential dissolution of a π-complex intermediate **31a**. Because of the Lewis acidity of unsolvated organoaluminum compounds, the Al covalent radius of 1.26 Å, and the C≡C bond length of 1.20 Å, structures **30** and **31a** are probably equally good models for the activated complex.



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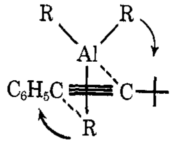

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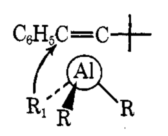

31a, $R_1 = $ vinyl, aryl

b, $R_1 = H$

c, $R_1 = R = Cl$

Finally, some remarks on the combined hydralumination and carbalumination reactions involved in eq 1 are in order. When *tert*-butyl(phenyl)acetylene (**5**) was subjected to these conditions, regiospecific hydralumination and reduction dimerization were likewise observed, but not the direct formation of a hexasubstituted benzene **4**. Instead, a reductive trimerization yielding **16** was found for the first time. Such products can be rationalized as arising from sequential insertions of alkynes into C—Al bonds,[2] *e.g.*, **2** → **3** or **9** → **10** → **22**, while the formation of **4** from **3** has been viewed as a Diels–Alder reaction or as an insertion, followed by dehydralumination.[2] Our finding of the open-chain reduced trimer **16**, considered together with the unlikelihood of dienes such as **3** and **10** assuming cisoid conformations, argues strongly against a Diels–Alder pathway to **4**. As to considering such alkyne oligomerizations as sequential insertions (**9** → **10** → **22**), it is true that the hetero reductive dimerization of two different alkynes occurs in accord with this view (eq 6). However, some reservations on the generality of this insertion mechanism should be entertained. Hydraluminated adducts, such as **2** and **9**, begin to dissociate into alkyne and R_2AlH in the temperature range (50–90°) where apparent insertion occurs. It is then possible that π-complex intermediates (**31b**) are the substrates actually responsible for the oligomerizations. The utility of the π-complex hypothesis in unifying many aspects of organoaluminum chemistry has already been discussed.[12] It is noteworthy that, contemporaneous with our report, Whitesides and Ehmann[17] published a masterly study of the cyclotrimerization of 2-butyne-*1,1,1*-d_3 by aluminum chloride (as well as by other catalysts). Their mass spectral analyses of the hexamethylbenzene obtained were consistent with the intervention of an intermediate of cyclobutadiene-like symmetry. Their results and our results on the oligomerization of alkynes by AlE_3 (E = Cl, H, or R) are consistent with a Lewis acid dimerization of alkynes, possibly *via* π complexes of the type **31b** or **31c**. This view is similar to that of Roberts and Sharts[18] for the chlorinative dimerization of 2-butyne (Smirnov–Zamkov reaction).

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[17] G. M. Whitesides and W. J. Ehmann, *J. Amer. Chem. Soc.*, **91**, 3800 (1969).

[18] J. D. Roberts and C. M. Sharts in "Organic Reactions," Vol. 12, A. C. Cope, Ed., Wiley, New York, N. Y., 1962, p 17.

Experimental Section

The techniques necessary for the manipulations and reactions of organoaluminum compounds under an atmosphere of oxygen-free and dry nitrogen have been described previously.[3] Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are corrected. The following instrumentation for spectral measurements was employed: (a) infrared spectra in carbon tetrachloride solution or in a potassium bromide disc with a Perkin-Elmer Model 137 Infracord; (b) ultraviolet spectra with a Cary Model 15 spectrophotometer; (c) nmr spectra recorded with internal tetramethylsilane reference on the δ scale, with a Varian Model A-60 instrument; and (d) mass spectra with a Varian-MAT Model CH-5 spectrometer. Gas-liquid chromatographic analyses were performed with an F & M instrument, Model 720, with dual, 6-ft columns of 10% silicone rubber dispersed on Chromosorb.

The diisobutylaluminum hydride was obtained from Texas Alkyls Corp. and was fractionally redistilled before use. *tert*-Butyl(phenyl)acetylene,[5] methyl(phenyl)acetylene,[3] and triphenylaluminum[9] were prepared and purified as previously described.

Reactions of Diisobutylaluminum Hydride with *tert*-Butyl(phenyl)acetylene. A. Temperature of 50° and Equivalent Ratio of 1:1.—A solution of 14 mmol of diisobutylaluminum hydride and 14 mmol of *tert*-butyl(phenyl)acetylene (**5**) in 15 ml of dry hexane was maintained at 50° for 48 hr. Hydrolytic work-up and glc analysis showed the presence of 94% of *cis*-β-(*tert*-butyl)styrene (**7**) and 6% of *cis,cis*-1,4-di(*tert*-butyl)-2,3-diphenyl-1,3-butadiene (**8**). Distillation of **7** at 74–76° (15 mm) left a solid residue of **8**. The identity of **7** was established by comparing its refractive index, ultraviolet absorption, and nmr spectrum with published data[19] for **7**: nmr (CCl_4) δ 0.95 (s, 9 H, t-C_4H_9), 5.52 (center, d, $J_{\alpha\beta} = 12.5$ Hz, β H), 6.38 (center, d, $J = 12.5$ Hz, α H to phenyl), 7.08 (s, 5 H, C_6H_5).

The reduced dimer **8** was recrystallized from methanol to yield colorless needles: mp 162–163° (repetition of melting giving lower melting range; *cf. infra*); uv λ_{max} (cyclohexane) 230 nm (sh, ϵ 20,680), 218 (24,300), 211 (sh, 21,980); nmr (CCl_4) δ 0.72 (s, 9 H), 5.03 (s, 1 H), 7.0–7.26 (m, 5 H).

Anal. Calcd for $C_{24}H_{30}$: C, 90.55; H, 9.45; mol wt, 318.5. Found: C, 90.37; H, 9.56; mol wt (osmometric in C_6H_6), 338; mol wt (mass spectrometric at 70 eV), 318 (P).

B. Temperature of 50° with a 1:1 Reactant Ratio Followed by Deuterium Oxide Work-Up.—As in part A, a run was maintained at 50° for 48 hr. One-half of the reaction mixture was treated with deuterium oxide (99.8%) and then worked up in the usual way. The nmr spectrum of the *cis*-β-(*tert*-butyl)styrene (**7**) showed no sign of the doublet centered at 6.38 ppm (vinyl H α to phenyl) and the signal of the β-vinyl H at 5.52 ppm was now a characteristic triplet ($J = 2$ cps). The ratio observed for the phenyl H:β-vinyl H signals of 5:1 gave the assurance that only α deuteration had taken place. The isolated dimer **8** was shown to be deuterated at one of its identical terminal vinyl positions (nmr signals of *tert*-butyl H:vinyl H, 18:1.

The remaining half of the reaction mixture was maintained for an additional 72 hr at 50°. Work-up with deuterium oxide revealed no change in the labeling of **7**, *i.e.*, no β-vinyl deuteration.

C. Reactants in a 1:1 Ratio at Higher Temperatures.—As in part A, the reactants were maintained at 50° for 48 hr, after which a glc analysis showed complete consumption of the acetylene. The reaction mixture was then heated for 48-hr periods at successively higher temperatures and then analyzed examining hydrolyzed samples by nmr and vpc: (1) 75°, 45% *cis*-β-(*tert*-butyl)styrene (**7**), 16% 3,3-dimethyl-1-phenylbutane (**13**), 35% *trans*-β-(*tert*-butyl)styrene (**14**), and 4% *cis,cis*-1,4-di(*tert*-butyl)-2,3-diphenyl-1,3-butadiene (**8**); (2) 110°, 26% **7**, 5% **13**, 68% **14**, and 1% **8**; (3) 140°, 2% **7**, 91.5% **13**, 6% **14**, and 0.5% **8**.

D. Reactants in a 1:2 Ratio of Diisobutylaluminum Hydride to tert-Butyl(phenyl)acetylene.—As in part A, the reactants were heated in a 1:1 ratio at 50° for 48 hr (complete consumption of acetylene). An additional 1 equiv of **5** was then introduced and the reaction mixture was maintained at 50° for another 16 hr. The ratio of products in a hydrolyzed aliquot was now 33% of dimer **8**, 38% of cis olefin **7**, and 29% of remaining acetylene **5**.

E. Reaction of *tert*-Butyl(phenyl)acetylene with a Small Amount of 6.—A mixture of 13 mmol of **6** and 91 mmol of **5** was heated at 50–60° without solvent for 2 hr and then at 175–180° (bath temperature) for a period of 6 days. During this time a yellow color developed, which persisted even after hydrolysis. Gas chromatographic analysis on a 4-ft Carbowax column showed the presence of the starting acetylene **5** and the cis olefin **7**. Analysis on a 2-ft silicon rubber column also revealed the presence of symmetrical diene **8** and a small amount of its cyclobutene relative **21** (column temperatures of 180 and 190°, respectively). Finally, at 260° a component was detected which proved to be the reductive trimer **16**, *cis,cis,cis*-1,3,6-tri-*tert*-butyl-2,4,5-triphenyl-1,3,5-hexatriene.

The crude reaction product was heated at 80° (0.5 mm) to remove residual **5** and **7** and the distillation residue then was fractionally crystallized from methanol to yield the symmetrical diene **8**. The methanolic mother liquor was freed of solvent and the residue was chromatographed on a neutral alumina–silver nitrate (4%) column (2.5 × 150 cm) with the rigorous exclusion of light from the column. Elution was successively conducted with 600 ml of hexane, 200 ml of hexane–benzene (9:1, v/v), 200 ml of hexane–benzene (3:1, v/v), and 200 ml of benzene. By mass spectrometry and nmr spectroscopy the fractions containing **16** were identified. (There is some evidence for the presence of a reductive tetramer as well.[20]) After 120 ml of eluate the fractions containing **16** began to be collected, and the next 400 ml yielded 1.1 g of crude **16**. Recrystallization from methanol gave 900 mg of **16**: mp 117–119°; uv λ_{max} (cyclohexane) 242 nm (sh, ϵ 16,000), 199 (52,000); ir (KBr) 1625 (m), 1585 (m), 1450 (s), 1360 (s), 1200 (s, br), 1075 (m), 1030 (m), 915 (s), 870 (s), 790 (s), 765 (s), and 695 cm^{-1} (s, br); nmr ($CDCl_3$) δ 0.78 (s, t-Bu), 0.94 (s, t-Bu), 1.1 (s, t-Bu), 5.41 (s, vinyl H), 5.51 (s, vinyl H), 5.72–5.90 (m, 2 H), and 6.5–7.05 (m, 13 H); mass spectrum (70 eV) *m/e* (rel intensity) 476 (P, 43, 420 (P − C_4H_8, 64), 421 (P − C_4H_9, 53), 362 (P − 114, 100), 307 (81), and 261 (55).

Anal. Calcd for $C_{36}H_{44}$: C, 90.71; H, 9.29; mol wt, 476.7. Found: C, 90.68; H, 9.30; mol wt (mass spectrometric at 70 eV), 476 (P).

Reaction of Triphenylaluminum with *tert*-Butyl(phenyl)acetylene.—A solution of 3.61 g (14 mmol) of triphenylaluminum and 2.21 g (14 mmol) of t-butyl(phenyl)acetylene in 25 ml of dry toluene was heated at 90° for 4 days and at the reflux temperature for another 24 hr. A glc analysis on a 6-ft, 5% silicone rubber on firebrick column of a hydrolyzed sample showed the presence of one major, new component (column temperature 255°) and a small amount of starting acetylene. Usual hydrolytic work-up yielded a viscous yellowish liquid. Distillation under reduced pressure provided 2.5 g (75%) of 3,3-dimethyl-1,1-diphenyl-1-butene (**20**) as a colorless liquid: bp 73–75° (0.5 mm); nmr (CCl_4) δ 0.96 (s, t-C_4H_9), 6.02 (s, vinyl H), 7.1 (s, C_6H_5), and 7.21 (br s, C_6H_5).

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.44; H, 8.62.

Structure Proof of 3,3-Dimethyl-1,1-diphenyl-1-butene.—In order to distinguish between the 1,1-diphenyl and the 1,2-diphenyl (cis or trans) isomers for the above-mentioned product (**20**), a 1-ml sample was dissolved in 5 ml of glacial acetic acid containing one drop of concentrated sulfuric acid.[15,16] The solution was warmed at 70° for 8 hr. Usual basic work-up led to the recovered hydrocarbon, whose nmr spectrum was still identical with that of **20**. The absence of any acid-catalyzed isomerization rules against the presence of the 1,2-diphenyl isomer, which ought to have undergone cis,trans isomerization.

A 750-mg sample of **20** was treated with 600 mg of chromic anhydride dissolved in a mixture of 75 ml of glacial acetic acid and 25 ml of water. After 3 hr at 80° the mixture was diluted with water and extracted with ether. The ether extract was dried over anhydrous calcium sulfate and the solvent was then evaporated. The infrared spectrum of the crude residue showed all of the characteristic absorptions of benzophenone. Treatment with 2,4-dinitrophenylhydrazine gave a 65% yield of the benzophenone 2,4-dinitrophenylhydrazone, mp 236–237°, from glacial acetic acid (lit. mp 238°), which did not depress the melting point of an authentic sample.

Isomerization of *cis,cis*-1,4-Di(*tert*-butyl)-2,3-diphenyl-1,3-

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(19) (a) D. Seyferth and G. Singh, *J. Amer. Chem. Soc.*, **87**, 4156 (1965); (b) H. Kristinsson and G. W. Griffin, *ibid.*, **88**, 379 (1966).

(20) Mr. Sue-Goo Rhee established a reliable procedure for the most difficult isolation of reductive trimer **16** and uncovered the first evidence for the reductive tetramer.

butadiene.[21]—Treatment of 1.6 g (5.3 mmol) of **8** with 6 mmol of *n*-butyllithium in 60 ml of anhydrous tetrahydrofuran for 6 hr at 0° did not lead to any development of color. Work-up with deuterium oxide and examination of the recovered **8** by nmr spectroscopy showed that the vinyl hydrogens at 5.03 ppm had not been metalated.

A 2.0-g sample of **8** was heated under nitrogen for 9 hr at 200 ± 5°.[22] The nmr spectrum of the product in CCl_4 showed new absorptions at δ 0.92 (s) and 2.82 (s). The ratio of these peaks, ascribable to **21**, to those of **8** at 0.72 and 5.03 was 5:2. Fractional recrystallization from methanol first yielded crops of recovered **8**, followed by rhombic crystals, **21**. Repeated crystallization provided a pure sample of *trans*-3,4-di-*tert*-butyl-1,2-diphenylcyclobutene (**21**): mp 88–88.5°; uv λ_{max} (cyclohexane) 282 nm (ϵ 14,620), 227 (23,850), and 208 (21,280); nmr (CCl_4) δ 0.92 (s, *t*-C_4H_9), 2.82 (s, cyclobuta H), and 7.32 (s, C_6H_5).

When the rhombic crystals, in turn, were heated at 200° for 3 hr, needles of **8** were found to sublime out of the melt.

Anal Calcd for $C_{24}H_{30}$: C, 90.55; H, 9.45; mol wt, 318.5. Found: C, 90.67; H, 9.50; mol wt (mass spectrometric at 70 eV), 318 (P).

Sequential Reaction of Diisobutylaluminum Hydride with *tert*-Butyl(phenyl)acetylene, Followed by the Addition of Methyl(phenyl)acetylene.—As in part A, a run was maintained at 50° for 48 hr, after which a glc analysis showed complete consumption of the acetylene. Then 14 mmol of freshly distilled methyl(phenyl)acetylene were added and the reaction mixture was maintained at 50–60° for 4 days. Thereupon the reaction mixture was divided into two parts, one part of which was hydrolyzed and the other part worked up with deuterium oxide (99.8%).

The hydrolyzed portion was analyzed by glc and nmr spectroscopy and was shown to contain 32% of *cis*-β-*tert*-butylstyrene (**7**), 32% of unreacted methyl(phenyl)acetylene (**28**), 10% of the symmetrical dimer **8**, and 26% of a new dimer **17**. No mono- or dimeric-reduced products of methyl(phenyl)acetylene alone were detectable. Distillation under reduced pressure gave a pale yellow, viscous liquid, bp 145–150° (0.50 mm), whose analytical data were consistent with its identity as *cis,cis*-4-*tert*-butyl-2-methyl-1,3-diphenyl-1,3-butadiene: nmr (CCl_4) δ 0.91 (s, *t*-C_4H_9), 2.01 (d, CH_3, J = 1.0 Hz), 5.88 (s, vinyl H), 6.0 (m, br, vinyl H), 7.13 (br s, C_6H_5), and 7.24 (m, C_6H_5).

Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 90.98; H, 8.63.

The portion of the reaction mixture worked up with D_2O yielded a monodeuterated form of **17**, whose nmr spectrum showed no signal at 6.0 ppm and whose doublet at 2.01 ppm was now a sharp singlet. These data place the deuteron at the 1 position of **17**.

Pyrolysis of the Reductive Trimer 16 of *tert*-Butyl(phenyl)acetylene.—A sample of the reductive trimer **16** in a capillary tube was heated in an oil bath. Over 300° bubbling was observed to occur in the clear melt and over 400° the liquid residue evaporated.

Pyrolysis of 500 mg of **16** in an nmr tube for 45 min at 250–300°, dissolution of the product in $CDCl_3$, and recording of the spectrum uncovered multiplets at 2.7 and 5.4 ppm (ratio 3:1), in agreement with the presence of isobutylene. The crude yellow product (one sharp nmr peak at 0.99 ppm) was treated with charcoal and then recrystallized from a hexane–ethanol pair (1:1, v/v) to provide 300 mg of needles with a faint yellow cast, mp 146–148°, of 3-*tert*-butyl-1,2,4-triphenylbenzene (**24**): nmr ($CDCl_3$) δ 0.99 (s, 9 H), 6.75 (m, 12 H), and 7.04 (br s, 5 H); mass spectrum (70 eV) m/e (rel intensity) 362 (P, 84, 347 (P − CH_3, 100), and 306 (P − C_4H_8, 44); uv λ_{max} (cyclohexane) 230 nm (sh, ϵ 32,000) and 219 (ϵ 35,000).[23]

Anal Calcd for $C_{28}H_{26}$: C, 92.78; H, 7.23. Found: C, 92.60; H, 7.35.

Preparation of Authentic 3,3-Dimethyl-1-phenylbutane by Catalytic Reduction of *tert*-Butyl(phenyl)acetylene.—A solution of 4.75 g (30 mmol) of **5** in 25 ml of freshly distilled ethyl acetate was shaken with 500 mg of a 10% palladium-on-charcoal catalyst under an atmosphere of hydrogen at 45 psi. After a 2-hr treatment at 25° usual distillative work-up gave a 90% yield of **13**: bp 213–215°;[24] $n^{23}D$ 1.4822; nmr (neat) δ 0.89 (s, *t*-C_4H_9), 1.25–1.60 (m, CH_2-*t*-C_4H_9), 2.32–2.65 (m, $CH_2C_6H_5$), and 7.08 (s, C_6H_5).

Registry No.—**5**, 4250-82-2; **6**, 1191-15-7; **7**, 3740-05-4; **8**, 23764-10-5; **13**, 17341-92-0; **16**, 35323-92-3; **17**, 35323-93-4; **19**, 841-76-9; **20**, 23586-64-3; **21**, 23764-11-6; **24**, 35324-18-6.

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[21] *Cf.* H. H. Freedman, G. A. Doorakian, and V. R. Sandel, *J. Amer. Chem. Soc.*, **87**, 3019 (1965), for the metalation of *cis*-1,2,3,4-tetraphenylcyclobutene by *n*-butyllithium in tetrahydrofuran solution.

[22] G. A. Doorakian and H. H. Freedman, *ibid.*, **90**, 3582 (1968), have reported on the facile thermal cyclization of the sterically hindered diene, *trans*-1-bromo-*cis*-1,2,3,4-tetraphenylbutadiene.

[23] Mr. Csaba Kovacs made the initial observation of this interesting pyrolysis and Mr. Sue-Goo Rhee verified the course of the reaction.

[24] A. E. Bey and D. R. Weyenberg, *J. Org. Chem.*, **30**, 2436 (1965).