quent paper,[23] (+)-hexahelicene was shown to exhibit a negative dichroism for the β band, which again suggests that the (−)-enantiomer must have the P configuration. It is interesting to note that the (+)-heterohelicenes, (−)-hexahelicene, and (+)-IX have also in common a very strong positive dichroism associated with the β' band. Since the origin of this band is uncertain and might differ for the various compounds, it is somewhat speculative to adopt this observation as a general rule. The investigation of more types of helicenes and heterohelicenes is needed to see whether such simple rules can be used safely for the correlation of their CD spectra. In addition, unambiguous proof of the absolute configuration of hexahelicene remains desirable.[35,36]

Experimental Section

Uv spectra (in cyclohexane solution) were measured with a Beckman DB-G spectrophotometer, ORD spectra (in chloroform solution) were determined with a Polarimatic 62 instrument, and CD spectra (in methanol solution) with a Roussel-Jouan Dichrographe II.

Table II. Uv Absorption Maxima (mμ) and Log ϵ Values[a]

Compd	
I	210 (4.54), 243 (4.75), 257 (4.41), 268 (4.37), 295 (3.80), 320 (4.20), 334 (4.29), 353 (3.63), 371 (3.76)
II	216 (4.75), 230 (4.67), 243 (4.65), 273 (4.47), 305 (3.94), 319 (3.90), 352 (4.22), 368 (4.27), 384 (3.98)
III	215 (4.62), 235 (4.60), 246 (4.50), sh 262 (4.48), 278 (4.28), 300 (3.85), 313 (3.82), sh 346 (4.21), 358 (4.26), 384 (3.95)
IV	227 (4.76), 253 (4.58), 277 (4.53), sh 317 (4.06), sh 324 (4.11), 329 (4.16), sh 355 (3.85), 372 (4.30), 391 (4.40)
V	218 (4.66), 229 (4.64), 277 (4.41), 316 (4.10), 330 (3.84), sh 356 (3.93), 371 (4.24), 391 (4.35)
VI	216 (4.72), 242 (4.64), sh 260 (4.47), 294 (4.27), 301 (4.22), 309 (4.22), 328 (3.87), sh 352 (4.03), 367 (4.28), 385 (4.30), sh 392 (4.23).
VII	215 (4.85), 225 (4.87), sh 250 (4.74), 359 (4.19), 376 (4.35), 412 (4.00), 435 (4.06).

[a] Cyclohexane solution, sh = shoulder.

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(35) I. Tinoco, Jr., and M. P. Freeman, *J. Phys. Chem.*, **61**, 1195 (1957).

(36) This is especially so since the results of recent calculations again do not favor Moscowitz's assignment (see footnote 9 of ref 1b).

Polar and Stereochemical Effects in the Addition of Triphenylaluminum to Para-Substituted Diphenylacetylenes[1,2]

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Abstract: To gain an understanding of the electronic factors governing the addition of the carbon–aluminum bond (carbalumination) to unsaturated hydrocarbons, the mechanism of the addition of triphenylaluminum to the triple bond of para-substituted diphenylacetylenes was investigated. The para substituents (Z) employed were the $(CH_3)_2N$, CH_3O, CH_3, CH_3S, H, Cl, CF_3, and CH_3SO_2 groups, but the acetylenes with the latter two substituents failed to react normally. The other acetylenes generally underwent stereospecific cis carbalumination to give a mixture of the two isomers, **6** and **7**, the logarithm of whose ratio correlated linearly with the Hammett σ values of the para substituent ($\rho = -0.713$) (see eq 2). The regioselectivity and cis stereospecificity, as well as the rate-retarding effect of donor solvents, are in accord with a kinetically controlled, electrophilic attack of the trivalent aluminum center on the triple bond, possibly with a bridging phenyl group diminishing the positive character on the acetylenic carbon.

The discovery of the ability of group IIIA metal alkyls and hydrides to add readily to unsaturated carbon–carbon bonds has transformed the whole field of hydrocarbon chemistry. Organoaluminum compounds have received particular attention during the past decade, both as stoichiometric reagents for forming new hydrocarbon skeletons[4] and as Ziegler–Natta catalyst components for the polymerization of olefins or acetylenes.[5] Despite the abundant progress in the synthetic applications of aluminum alkyls,[6] little is known about the stereochemistry, electronic factors, and kinetic details of the basic carbalumination reaction, that is, the addition of the carbon–aluminum bond to unsaturated carbon–carbon linkages.

The carbalumination of the acetylenic linkage appeared to be a most promising way of assessing both the polar and stereochemical factors determining the mode of addition of carbon–aluminum bonds to carbon–carbon unsaturation. Although the initial work of Wilke and Müller[7] with symmetrically substituted acet-

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(1) Part XVI of the series, "Organometallic Compounds of Group III," devoted to carbometallation and hydrometallation of unsaturated carbon–carbon bonds.

(2) Previous related parts: *J. Organometal. Chem.*, 21, 21, 285 (1970); 16, P55 (1969); 12, P33 (1968); 11, P7, P50 (1968); 8, 53 (1967); *ibid.*, 4, 415 (1965); 2, 184 (1967); *J. Amer. Chem. Soc.*, **88**, 2213, 2976 (1966); **86**, 4221 (1964); 84, 3605, 3830 (1962); *J. Org. Chem.*, 31, 3419 (1966).

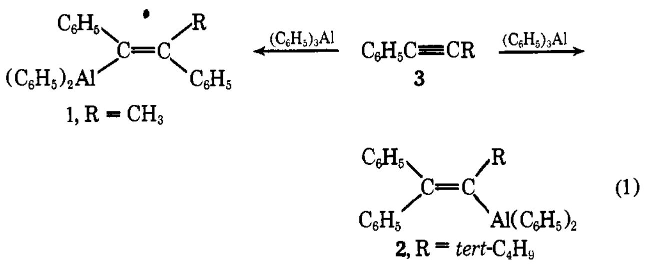
(3) National Aeronautics and Space Administration Trainee, 1963–1966.

(4) K. Ziegler, *et al.*, *Justus Liebigs Ann. Chem.*, **629**, 1 (1960); H. Lehmkuhl, K. Ziegler, and H.-G. Gellert, in "Houben-Weyl Methoden der organischen Chemie," Vol. XIII/4, E. Müller, Ed., Thieme Verlag, Stuttgart, 1970.

(5) *Cf.* the excellent review by J. P. Kennedy and A. W. Langer, Jr., *Fortschr. Hochpolym.-Forsch.*, **3**, 508 (1964).

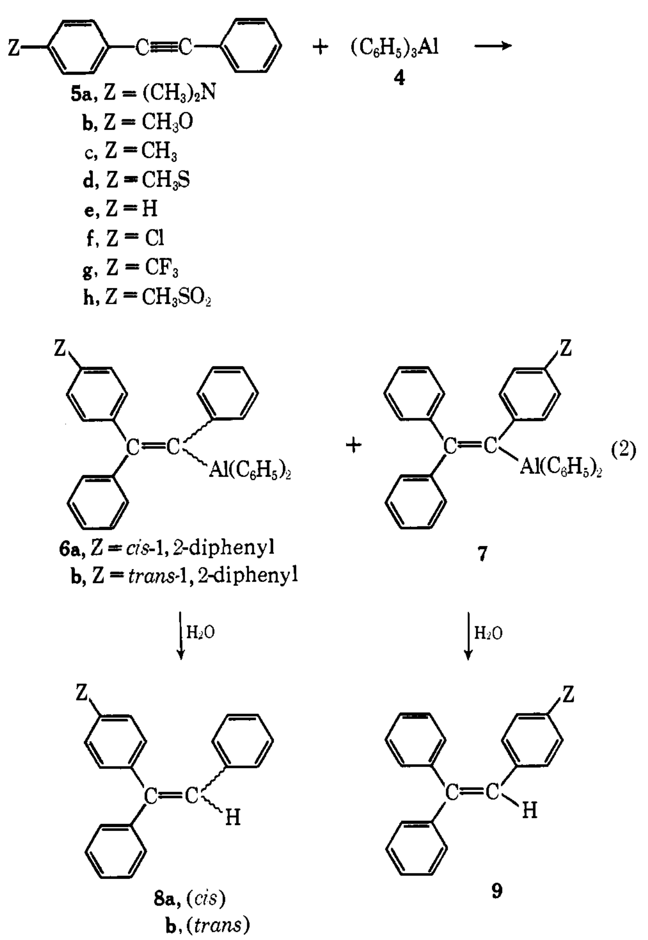
(6) *Cf.* the excellent review by G. Bruno, "The Use of Aluminum Alkyls in Organic Synthesis," Ethyl Corporation, Baton Rouge, La., 1970, p 75, with 473 references.

ylenes uncovered the cis nature of the carbalumination with triethylaluminum, further studies with unsymmetrically substituted acetylenes showed that the regiospecificity[8] of carbalumination is sensitive to both polar[9] and steric[10] factors. A comparison of the behaviors of methylphenylacetylene and *tert*-butylphenylacetylene toward triphenylaluminum is illustrative: the former gives >95% adduct **1**, while the latter yields **2** as the only discernible product. Furthermore, with monosubstituted acetylenes the metallation of the acetylenic hydrogen occurs in preference to carbalumination;[11,12] indeed, triphenylaluminum reacts readily with either 1-hexyne or phenylacetylene to form the corresponding 1-alkynyl(diphenyl)aluminum in excellent yield.[12]



In order to elucidate the mechanism of the carbalumination of unsaturated hydrocarbons, the present investigation has studied the addition of triphenylaluminum (**4**) to a series of para-substituted diphenylacetylenes (**5**). By choice of substituents (Z) that exert an electronic influence on the triple bond, but which are chemically compatible with **4**, we hoped to observe a change in the ratio of adducts **6** (cis or trans) and **7**. Since any steric factors in the addition reaction (*cf.* the behavior of **3**) would be avoided in the region of the triple bond, any change in the ratio of products might then be related to electronic parameters of the Hammett type. The nature of the electronic influence exerted by substituent Z would be pivotal in deciding whether carbalumination by triphenylaluminum might involve carbanionic attack by negatively polarized carbon, electrophilic attack by trivalent aluminum, or homopolar addition of the carbon–aluminum bond. Moreover, the addition of triphenylaluminum to these acetylenes would permit a more sensitive test of the cis or trans stereochemistry of carbalumination than heretofore possible. Direct formation of a mixture of **6a** and **6b**, due to steric hindrance to cis addition, or the isomerization of an initially formed adduct, should show up in the product analysis of **8**. Conclusions on the stereochemistry of **6a** and/or **6b** based upon that of the hydrolysis products, **8a** and **8b**, would be valid, since vinylaluminum compounds are known to undergo hydrolysis with retention of stereochemistry.[7,9]

The present article describes the variation in the direction of carbalumination (ratio of **6** to **7**) as Z in **5** was changed from a $(CH_3)_2N$, CH_3O, CH_3, CH_3S to a Cl group. When Z was a CF_3 or CH_3SO_2 group, carbalumination was markedly suppressed and overshadowed by competing reactions of the substituent Z itself. Furthermore, the stereochemistry of addition was observed to be sensitive to the nature of the Z substituent. The mechanistic conclusions permissible in the light of these results are assessed here, but a more detailed discussion of reaction mechanisms will be reserved for a subsequent paper dealing with an overall kinetic study of the carbalumination of acetylenes.



Results

Triphenylaluminum (**4**) was chosen as the organoaluminum addend, because its moderate reactivity facilitated handling and gave conveniently measurable rates of reaction. In addition, its melting point (243°) permitted samples of high purity to be obtained by recrystallization. The para-substituted diphenylacetylenes selected as substrates comprise a series ranging from a member with the highly electron-donating $(CH_3)_2N$ group to that with the highly electron-withdrawing CF_3 group. The acetylenes, **5a**–**5h**, were synthesized according to published procedures, except for the *p*-dimethylamino, *p*-methylthio, and *p*-methylsulfonyl derivatives, which were prepared for the first time. The carbalumination depicted in eq 2 was performed at 180.0 ± 0.1° in mesitylene solution under nitrogen, until the acetylene was consumed. The reasonable reproducibility of the isomer ratio, **6**:**7**, with variation in the size of the carbalumination run is consistent with an irreversible addition of **4** to **5** under these conditions.[13]

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

(8) A. Hassner, *J. Org. Chem.*, **33**, 2684 (1968).

(9) *Cf.* J. J. Eisch and W. C. Kaska, *J. Amer. Chem. Soc.*, **88**, 2213, 2976 (1966), for qualitative electronic considerations of the carbalumination of alkynes.

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

(11) T. Mole and J. R. Surtees, *Chem. Ind. (London)*, 1727 (1963).

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

(13) Ongoing studies on competitive additions of R_1–Al *vs.* R_2–Al bonds to alkynes have, as their goal, the evaluation of addition ten-

Table I. Distribution of Triarylethylene Isomers from Para-Substituted Diphenylacetylenes and Triphenylaluminum

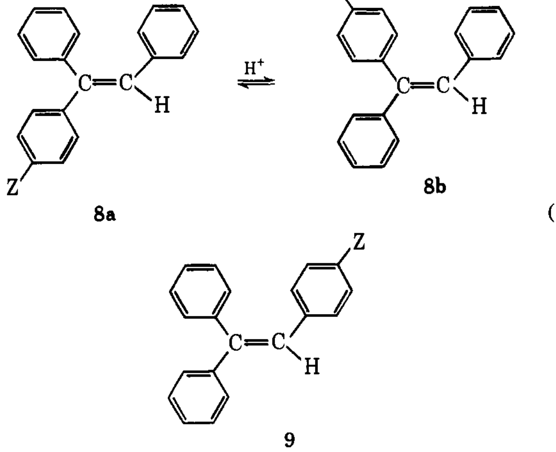
Z	Relative percentages: 1,2-Diphenyl, **8b** (trans)	Relative percentages: 1,1-Diphenyl, **9**	Log **8/9**	σ_p	σ_p^+	CH_3 signal, δ, ppm[d]: **8a**	CH_3 signal, δ, ppm[d]: **8b**	CH_3 signal, δ, ppm[d]: **9**
$(CH_3)_2N$	79.3[a]	20.7	0.583	−0.83	−1.7	3.00	3.02	2.94
CH_3O	58.7	41.3	0.153	−0.268	−0.778	3.68	3.70	3.60
CH_3	56.4	43.6	0.111	−0.170	−0.311	2.38	2.40	2.28
CH_3S	48.5	51.5	−0.026	0.00	−0.604	2.40	2.42	2.33
Cl	40.5	59.5	−0.167	+0.227	−0.114			
CF_3	*b*							
CH_3SO_2	c							

[a] This percentage comprises 60.0% of the *trans*-1,2-diphenyl and 19.3% of the *cis*-1,2-diphenyl isomers, but they both result from the same orientation in carbalumination. [b] No normal addition, but rather possible azulene formation, seemed to occur. [c] No normal addition, but rather attack on the sulfone group, seemed to occur. [d] Signals for 10% solutions in CCl_4.

A subsequent reaction, namely the cyclization of adducts **6** and **7** with the formation of benzaluminoles,[9] is known to take place in the vicinity of 200°. Any such cyclic products would, however, yield the same products, **8**:**9**, upon hydrolysis and thus not alter the ratio of isomeric products. Further reaction of triarylvinylaluminum systems, such as **6** and **7**, with additional acetylene, which yields derivatives of indene, naphthalene, and tetraarylethylene,[14] is known to be insignificant under these conditions.

Hydrolytic work-up of the reaction products gave an analyzable mixture of triarylethylenes in the cases where Z in **5**–**9** equaled $(CH_3)_2N$, CH_3O, CH_3, CH_3S, and Cl, but not where Z equaled CF_3 and CH_3SO_2. The *p*-trifluoromethyldiphenylacetylene underwent no smooth carbalumination, but possibly underwent dimerization to an azulene derivative. The *p*-methylsulfonyldiphenylacetylene was exceptionally unreactive; even under vigorous conditions it underwent no discernible carbalumination but rather seemed to suffer carbon–sulfur bond scission. With the other acetylenes, the reaction products were identified and analyzed by several methods. First, the triarylethylenes having Z equal to $(CH_3)_2N$, CH_3O, and CH_3S were separated into isomers **6b** and **7** by column chromatography. Second, authentic samples of stereoisomers **6a**, **6b**, and **7**, where Z = CH_3O and Cl, were synthesized by known routes and used to develop nmr (CH_3 signal) and infrared (CH_3O, Cl) methods of analyzing the triarylethylene mixtures. Third, for all the triarylethylenes containing a methyl group, it was found that isomers **6a**, **6b**, and **7** possessed individually discernible nmr signals, whose integration provided a quantitative analysis of the reaction mixture directly. Fourth, the empirical relation of the chemical shifts of these methyl groups was established, wherein the peak farthest downfield was **8b**, the *trans*-1,2-diphenyl isomer, the peak *ca.* 0.02 ppm upfield from this was **8a**, the *cis*-1,2-diphenyl isomer, and the peak *ca.* 0.1 ppm upfield was **9**, the 1,1-diphenyl isomer (Table I).

Finally, the structural assignment and quantitative analysis of the isomers in a reaction mixture were greatly assisted by the following technique of acid-catalyzed isomerization (eq 3). Since only two isomers, out of the possible three (**8a**, **8b**, and **9**), were obtained in all cases but one (Z = $(CH_3)_2N$), the nmr analysis could be performed on the reaction mixture directly to give the ratio of two isomers. That this ratio was that of **8b** to **9** was demonstrated by heating the reaction product with a trace of acid, recovering the organic product, and then repeating the nmr analysis. The nmr peak most downfield was diminished and a new peak, characteristic of **8a**, appeared at *ca.* 0.02 ppm downfield.



(3)

The peak at 0.1 ppm upfield (due to **9**) suffered no change relative to the sum of the signals of **8a** and **8b**.

The foregoing considerations lead to the conclusion that exclusively a cis carbalumination occurred in every case, except for *p*-*N*,*N*-dimethylaminodiphenylacetylene, where a small amount (25% isomer **8**) of apparent trans-carbalumination product (**8a**) was detected. Since there is reason to believe that isomerization of initially formed **6b** was the real source of **8a** (Z = $(CH_3)_2N$), the total of **8a** and **8b** in this case is used in correlating the product ratio **8**:**9** with electronic parameters (Table I, Figures 1 and 2).

The relative percentages of the triarylethylene isomers, **8b** and **9**, found in the successful carbaluminations of the acetylenes **5** are listed in Table I, along with Hammett σ_{para} and Hammett–Brown σ_{para}^+ values of the Z substituents involved. The plot of the logarithm of the fraction, **8/9**, *vs.* the Hammett σ_{para} values is given in Figure 1; for comparison, a trial plot of the same

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dencies and, hopefully, an assessment of bridging factors in different R groups.

The actual magnitude of $\Delta\rho$ may also be dependent upon the temperature of the carbalumination and upon the ratio and concentration of the reagents used. Since carbalumination of the acetylenes **5** could be achieved not only by **4**, but in the later stages of the reaction by **6** and **7** also, the observed $\Delta\rho$ may be a composite of $\Delta\rho$ due to each reagent. Also, the dimer–monomer equilibria of **4** and other aluminum aryls would be important in determining $\Delta\rho$. In any case, all carbaluminations were carried out under comparable conditions: at the same concentrations, at 180°, and to completion.

(14) J. J. Eisch and R. L. Harrell, Jr., *J. Organometal. Chem.*, 20, 257 (1969).

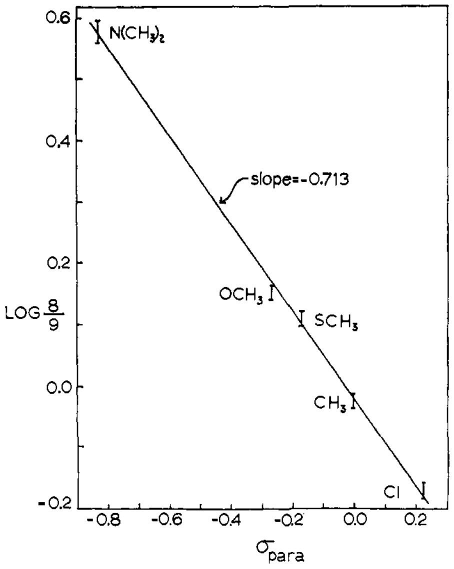


Figure 1. Plot of the logarithm of the product ratio of the isomeric triarylethylenes, **8**/**9**, obtained from triphenylaluminum and the para-substituted diphenylacetylenes, *vs.* the Hammett σ values of the para substituent.

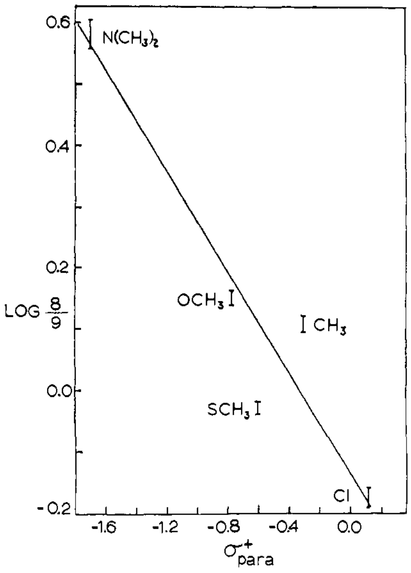


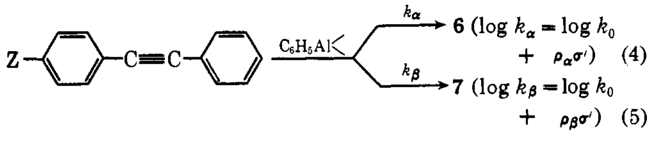
Figure 2. Trial plot of the logarithm of the product ratio of the isomeric triarylethylenes, **8**/**9**, *vs.* the Hammett–Brown σ^+ values of the para substituent.

function *vs.* the Hammett–Brown $\sigma_{\text{para}}{}^+$ values is shown in Figure 2. The choice of the fraction, **8**/**9**, rather than **9**/**8**, is not entirely arbitrary; in this way a negative value is obtained for $\Delta\rho$ and this is consistent with the later kinetic studies that show the reaction rate being increased by electron-donating substituents. An estimate of the accuracy of the percentages **8b** and **9** can be obtained for the reaction of **5b**, where both nmr and infrared spectroscopy were used for the product analysis. The percentage of isomer **8b**, Z = CH_3O, with its standard deviation was 58.7 ± 0.63. The standard deviation is thus 1.1% of this percentage, so we have assumed this limit of uncertainty for the ordinates of Figure 1 and 2.

The straight line in Figure 1 could be drawn satisfactorily through the points by the method of least squares, and a slope of −0.713, having a standard deviation of ±0.012, could be obtained. The plot in Figure 2 was not cleanly linear, but the points were scattered about a test straight line.

Discussion

From the foregoing evidence and from previous work on the carbalumination of alkynes,[7,9] it is concluded that the addition of triphenylaluminum to para-substituted diphenylacetylenes occurs in a kinetically controlled, cis fashion. The one apparent exception to cis stereospecificity, **5a**, will be discussed later on. The Hammett linear free energy correlation for a series of related reactions is invoked here for two competing reactions of the same substrate, namely the two orientations (**6** and **7** of eq 2) in which cis carbalumination can occur. If the partial rate factor leading to **6** is termed k_α and that leading to **7** k_β, one can write Hammett relations comparing either k_α or k_β with the partial rate factor for the unsubstituted diphenylacetylene, k_0



$$\xrightarrow{C_6H_5Al<} \begin{cases} \xrightarrow{k_\alpha} \mathbf{6}\ (\log k_\alpha = \log k_0 + \rho_\alpha\sigma') & (4) \\ \xrightarrow{k_\beta} \mathbf{7}\ (\log k_\beta = \log k_0 + \rho_\beta\sigma') & (5) \end{cases}$$

Subtracting eq 5 from eq 4 gives

$$\log \frac{k_\alpha}{k_\beta} = (\rho_\alpha - \rho_\beta)\sigma'$$

Since the reactions are competitive, irreversible processes under these conditions, the ratio of rate constants is equal to the ratio of the products, **6**:**7** or **8**:**9**. The difference of the ρ values, $\rho_\alpha - \rho_\beta$, can be symbolized by a composite reaction constant, $\Delta\rho$, and the following Hammett relation for the present study derived

$$\log \frac{8}{9} = (\Delta\rho)\sigma' \qquad (6)$$

From the data in Table I and the plots presented in Figure 1 ($\sigma' = \sigma$) and in Figure 2 ($\sigma' = \sigma^+$), the better correlation of the logarithm of the product ratio, **8**:**9**, was found with the classic Hammett σ values, rather than with Hammett–Brown σ^+ values. These results suggest that the trend in electronic influences on the carbalumination reaction resemble more nearly those involved in the ionization of benzoic acids[15a] than those involved in the solvolysis of cumyl chlorides.[15b]

The slope of the plot in Figure 1, −0.713 ± 0.012, is accordingly equal to $\Delta\rho$, a measure of the sensitivity of carbalumination to electron availability at the triple bond of the alkyne. As the σ value becomes more negative, the proportion of isomer **8** increases and, as the next publication will show, the overall rate of carbalumination increases. Without overanticipation of such subsequent kinetic studies, the present results on isomer distribution can be interpreted as strongly supporting electrophilic attack by the aluminum reagent on the acetylenic linkage. In effect, the electron-donating character of Z in **10** is pitted against that of a para-H in **11** in determining the differences in the free energies of activation ($\Delta\Delta F^{\ddagger}$) for transition states **10** and **11**. Although the negative sign of $\Delta\rho$ shows that the formation of the new aluminum–carbon bond (solid

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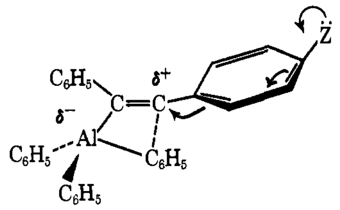
[15] (a) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958); (b) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).



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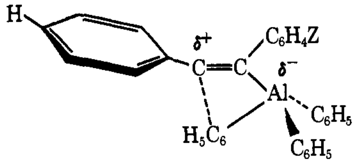

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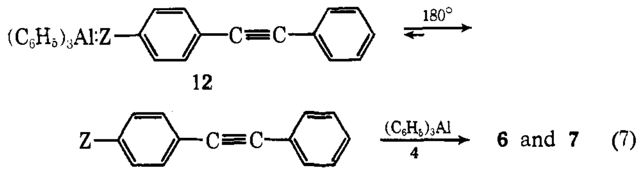
lines in **10** and **11**) has made more progress in the transition state than the new carbon–carbon bond (dashed bonds), the absolute magnitude of $\Delta\rho$, 0.7, is modest, compared with those of other recognized electrophilic processes. The addition of chlorine, for example, to compounds of the type $RC_6H_4CH{=}CHCOC_6H_5$ in acetic acid solution exhibits a ρ of -4.5,[16] and the bromination of substituted benzene nuclei can yield a ρ of -12.1.[15b] A possible explanation for the small magnitude of $\Delta\rho$ in the carbalumination is that the adding phenyl group, participating as a π base (dashed lines in **10** and **11**), may further diminish the positive charge on the acetylenic carbon.[13]

The conclusion that the carbalumination reaction occurs *via* electrophilic attack by the aluminum center on unsaturated carbon is also supported by the adverse effect of donor solvents on the reaction. When *p*-methoxydiphenylacetylene was heated with **4** in cineole solution for 4 hr at 180°, the starting acetylene was recovered essentially unchanged. The complex formed between **4** and cineole under these conditions is unable to achieve carbalumination, presumably since the requisite tricoordinate aluminum cannot be freed from its stable cineole etherate. The inertness of complexes of **4** and some donor molecules in carbalumination raises a question on the behavior of para-substituted diphenylacetylenes, **5**, toward triphenylaluminum, **4**. Should not substrates in **5**, where Z = $(CH_3)_2N$, CH_3O, or CH_3S, lead to equally inert complexes, **12**? How then does the carbalumination take place? The known behavior of anisole with **4** is instructive: the two form below 100° a stable complex, which dissociates into its components upon heating.[17] Since the present work on isomer distribution was done at 180°, dissociation into components and the attack by unsolvated **4** and **5** apparently circumvent the inertness of complex **12** to ready carbalumination (eq 7).



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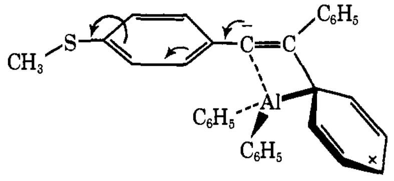
5

(7)

A word about other possible reaction mechanisms for carbalumination is in order. The likelihood of a homolytic cleavage of the phenyl–aluminum bond of **4** in the carbalumination is very small. The generally clean cis stereospecificity and the absence of telltale products (biphenyl, phenylmesitylene, or bimesityl) argue against any process involving "free" phenyl radicals. The credibility of an addition initiated by nucleophilic attack by negatively polarized phenyl group, $C_6H_5^{\delta-}Al^{\delta+}(C_6H_5)_2$, is also feeble. Usually such a muted "carbanionic" attack is fostered by donor solvents, since such solvates accentuate anionic heterolysis (*cf.* alkyllithium reagents in tetrahydrofuran or in tetramethylethylenediamine[18]). The retarding effect of donor solvents on carbalumination, cited above, however, is at variance with such a nucleophilic view. Furthermore, the orientation observed with *p*-methylthiodiphenylacetylene (**5d**) is pertinent to this consideration. Since sulfur is known to be able to expand its octet, nucleophilic attack on **5d** might be expected to give a ratio of **8**/**9** < 1.0. In either case, the carbanionic character would be stabilized by $d\pi$–$p\pi$ bonding with sulfur (**13**). Actually, the ratio of **8**/**9** is *ca.* 1.0, with experimental error. Therefore, an electrophilic mechanism is in best agreement with the known stereospecificity and regioselectivity of this carbalumination process. The question of a π-complex intermediate in these additions will be taken up in our publications dealing with the kinetics of carbalumination and of hydralumination.



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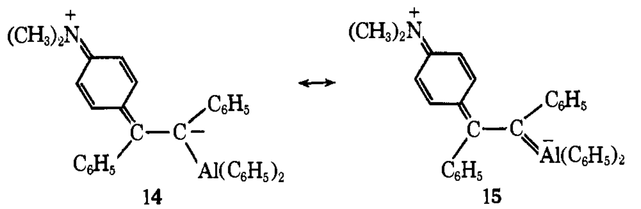
Finally, the cis stereospecificity observed in those carbaluminations of **5**, where Z = CH_3O, CH_3S, CH_3, and Cl, is consistent with the established mode of electrophilic addition to acetylenes in haloboration[19] and in acetoxymercuration.[20] In the case of **5a**, where Z = $(CH_3)_2N$, the best explanation for the production of both cis and trans adducts, **6a** and **6b**, is that some of the initially formed cis adduct underwent isomerization in the reaction mixture at 180°. That only this adduct underwent isomerization may be ascribable to the powerful electron donation by the $(CH_3)_2N$ group. Resonance forms such as **14** and **15** may contribute to a lowering of the barrier to rotation about the double bond.



14 **15**

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[16] P. B. D. de la Mare and N. V. Klassen, *Chem. Ind.* (*London*), 498 (1960).

[17] T. Mole, *Aust. J. Chem.*, **16**, 801 (1963).

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Experimental Section[21]

Preparation of Starting Materials. Triphenylaluminum was prepared in the previously published manner.[9] Although the highly purified product was employed for kinetic studies (mp 241–243°, from toluene), the lower melting product (mp >227°) was equally satisfactory for determining the stereochemistry and orientation for the addition of this organometallic to the para-substituted diphenylacetylenes.

The para-substituted diphenylacetylenes were prepared (a) by the interaction of copper(I) phenylacetylide with para-substituted iodobenzenes,[22] (b) by a sequence of a mixed benzoin condensation, benzil formation, and bishydrazone preparation, and oxidation to the acetylene by mercury(II) oxide, or (c) by the rearrangement of 1-halo-2,2-diarylethylenes. All known compounds, the parent diphenylacetylene,[23] and its *p*-chloro, *p*-methoxy,[24] *p*-methyl,[25] and *p*-trifluoromethyl relatives,[26] were purified until their melting points, as well as their infrared and ultraviolet spectral data, were in agreement with published values.

The following new acetylenes were synthesized.

(a) *p*-*N*,*N*-Dimethylaminodiphenylacetylene. The copper(I) phenylacetylide necessary for the Stephens–Castro acetylene synthesis was prepared advantageously in the following manner. To a mechanically stirred solution of 50.8 g (0.50 mol) of freshly distilled phenylacetylene in 600 ml of 95% ethanol were added 32 ml of concentrated ammonium hydroxide and 53.2 g (0.50 mol) of 93% copper(I) chloride. After the reaction vessel was flushed with nitrogen, the suspension was stirred at room temperature for 7 hr. Upon collection on a Büchner filter, the greenish yellow powder was washed five times with water, thrice with 95% ethanol, and thrice with ether. After drying *in vacuo* for 2 hr, 70 g (85%) of the product was obtained.

In 200 ml of anhydrous, reagent-grade pyridine, 14.8 g (0.60 mol) of *p*-iodo-*N*,*N*-dimethylaniline (mp 78.5–79.5°)[27] and 10.0 g (0.60 mol) of copper(I) phenylacetylide were heated under reflux for 24 hr in a nitrogen atmosphere. The reaction mixture was taken up in 1.2 l. of ether, and the solution was then washed with six 150-ml portions of water, dried over anhydrous magnesium sulfate, and thereupon passed through an alumina column. Upon evaporation of the solvent 11.9 g (90%) of product was obtained, mp 105–107°. Two recrystallizations from 95% ethanol provided colorless crystals, mp 110.5–112°. Prolonged exposure to air caused some discoloration.

Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.52; H, 6.83; N, 6.70.

Spectral data showed C≡C stretch of medium intensity at 2230 cm^{-1} in CS_2; $\lambda_{\max}^{\mathrm{EtOH}}$ 323 mμ (ϵ 32,500), 221 (9600); nmr (10% in CCl_4) CH_3 singlet at δ 3.2 ppm.

(b) *p*-Methylthiodiphenylacetylene. *p*-Methylthioiodobenzene (mp 43.5–44.5°, lit.[28] mp 43.5°) was prepared by adapting the known procedure for the preparation of iodobenzene.[29] A mixture of 7.47 g (0.030 mol) of *p*-methylthioiodobenzene, 5.0 g (0.030 mol) of copper(I) phenylacetylide, and 100 ml of anhydrous pyridine was heated under reflux for 10 hr. The light brown reaction suspension was extracted with three-200 ml portions of ether and thereupon the combined ether extracts were washed successively with three 200-ml portions of 10% hydrochloric acid, a portion of 5% sodium bicarbonate solution, and a portion of water. Removal of solvent from the dried ether extract provided 6.62 g (91%) of crude product. Decolorization was effected by passage of the product through an alumina column and elution with a 3:1 mixture of hexane and benzene. One recrystallization from methanol gave 4.49 g (62%) of colorless needles, mp 91.5–92.5°.

Anal. Calcd for $C_{15}H_{12}S$: C, 80.32; H, 5.39; S, 14.29. Found: C, 80.65; H, 5.42; S, 14.06.

Spectral data showed C≡C stretch of weak intensity at 2200 cm^{-1} in CS_2; $\lambda_{\max}^{\mathrm{EtOH}}$ 319 mμ (ϵ 30,600), 302 (34,900), 224 (14,100); nmr (10% in CCl_4) CH_3 singlet at δ 2.50 ppm.

(c) *p*-Methylsulfonyldiphenylacetylene. *p*-Iodophenyl methyl sulfone (mp 117.5–118.5°, lit.[28] mp 117–118°) was prepared from *p*-methylthioiodobenzene by oxidation with hydrogen peroxide. As in the preceding procedure, a mixture of 14.1 g (0.050 mol) of *p*-iodophenyl methyl sulfone, 8.33 g (0.050 mol) of copper(I) phenylacetylide, and 170 ml of pyridine yielded 7.15 g (56%) of crude product, mp 153–159°. Chromatographic decolorization and recrystallization from methanol provided colorless needles, mp 162.5–163.5°.

Anal. Calcd for $C_{15}H_{12}O_2S$: C, 70.29; H, 4.72; S, 12.50. Found: C, 70.22; H, 4.68; S, 12.49.

Spectral data showed C≡C stretch of medium intensity at 2250 cm^{-1} in $CHCl_3$; $\lambda_{\max}^{\mathrm{EtOH}}$ 308 mμ (ϵ 27,900), 291.5 (30,100), 246 (9000), 224 (13,000); nmr ($CHCl_3$) CH_3 singlet at δ 3.18 ppm.

Preparation of Authentic Triarylethylenes. The expected reaction products from the interaction of triphenylaluminum, respectively, with *p*-methoxydiphenylacetylene and with *p*-chlorodiphenylacetylene, followed by hydrolysis, were synthesized, in order to permit an assignment of the stereochemical mode of addition (cis or trans) and to provide pure samples for quantitative analysis by spectroscopy.

(a) 1,1-Diphenyl-2-*p*-anisylethylene. Ethyl *p*-anisylacetate [bp 96–98° (0.4 mm); $n^{24}\mathrm{D}$ 1.5060 (lit.[30] bp 138–140° (7 mm); $n^{24}\mathrm{D}$ 1.5070)] was treated with *p*-chlorobenzylmagnesium chloride and the resulting carbinol dehydrated to yield 1,1-diphenyl-2-*p*-anisylethylene. Recrystallization from petroleum ether (bp 30–60°) gave 4.2 g of colorless, fluffy needles, mp 82.5–83.5° (lit.[31] mp 84–85°).

(b) *trans*-1,2-Diphenyl-1-*p*-anisylethylene. *p*-Anisyl Grignard reagent, prepared from 18.7 g (0.10 mol) of *p*-bromoanisole and 2.43 g (0.10 g-atom) of magnesium in 65 ml of anhydrous ether, was treated with 12.0 g (0.061 mol) of benzyl phenyl ketone dissolved in 45 ml of anhydrous ether. Customary work-up and evaporation of volatile impurities from the dried ether extract gave 15.4 g (89%) of crude 1,2-diphenyl-1-*p*-anisylethanol. Without further purification, the carbinol was dehydrated by distillation under reduced pressure in a Hickman still to yield 8.3 g (58%) of a mixture of *cis*- and *trans*-1,2-diphenyl-1-*p*-anisylethylene. Chromatography of 6.0 g of this material on a 50 × 1.5 cm column of freshly reactivated alumina (200° for 30 hr), using hexane as eluent, resulted in a partial separation of the isomers. Recrystallizations of the early fractions from hexane gave 1.4 g of colorless needles of the trans isomer, mp 90–91°; $\lambda_{\max}^{\mathrm{MeOH}}$ 305 mμ (ϵ 23,000) (lit.[32] mp 90–91°).

(c) 1,1-Diphenyl-2-*p*-chlorophenylethylene. This compound was prepared by the dehydration of the alcohol formed upon hydrolysis of the Grignard reaction product of *p*-chlorobenzyl chloride with benzophenone. A published method[33] was modified by using a 1:1 molar ratio of Grignard reagent to ketone and adopting the specific directions for the preparation of triphenylethylene.[34] Usual work-up provided 38.6 g (100%) of crude 1,1-diphenyl-2-*p*-chlorophenylethanol. Dehydration was accomplished by treating this product with several drops of 20% sulfuric acid and heating it in a Hickman still under reduced pressure. The distillate was recrystallized several times from ethanol to give colorless needles: mp 76–77°; $\lambda_{\max}^{\mathrm{EtOH}}$ 302 mμ (ϵ 22,600), 233 (19,100) (lit.[33] mp 76–77°).

(d) *cis*- and *trans*-1,2-Diphenyl-1-*p*-chlorophenylethylenes. These compounds were prepared separately by adaptation of published

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(21) Melting points were obtained on samples in capillary tubes (sealed under nitrogen for the case of triphenylaluminum) by use of a Thomas-Hoover apparatus, and are corrected. Infrared spectra were recorded on a Perkin-Elmer Infracord or a grating spectrophotometer, Model 337; ultraviolet spectra on a Cary instrument, Model 15; and nmr spectra on a Varian spectrometer, Model A-60. The chemical shifts are expressed either in hertz (cycles per second) or in parts per million (δ values) relative to internal tetramethylsilane. All manipulations involved in the preparation, reactions, and transfer of organoaluminum compounds were performed under an atmosphere of dry, oxygen-free nitrogen, the details of which are given in *J. Amer. Chem. Soc.*, **88**, 2213, 2976 (1966). The only procedural departure in the present work was the use of reduced copper, B. T. S. Katalysator (Badische Anilin & Soda Fabrik, A.G.), for the deoxygenation of the nitrogen. All hydrocarbon solvents which came into contact with triphenylaluminum were of reagent grade and were dried by refluxing over and distilling from sodium under an atmosphere of nitrogen.

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methods.[35,36] *trans*-1,2-Diphenyl-2-*p*-chlorophenylethylene, colorless needles, had mp 91.0–92.5°; λ_{max}^{EtOH} 299 mμ (ε 18,700), 233 sh (18,900), 227 (19,100) (lit.[37] mp 92–93°, 89–90°). *cis*-Diphenyl-2-*p*-chlorophenylethylene was obtained as thick platelets, mp 63.5–65.0° (lit.[37] mp 63–64.5°, 62–63°).

Infrared spectra of the individual cis and trans isomers in carbon disulfide were compared to determine how effective the separation had been. The cis isomer exhibited a strong peak at 772 cm^{-1} and medium peaks at 732, 590, and 574 cm^{-1}, which were not detectable in the spectrum of the trans isomer. Conversely, the trans isomer displayed a strong peak at 740 cm^{-1} and moderate peaks at 732 and 567 cm^{-1}, which were not discernible in the spectrum of the cis isomer.

Isomer Distribution Studies in the Addition of Triphenylaluminum to Para-Substituted Diphenylacetylenes. (a) General Reaction Conditions. These reactions were conducted in a 50-ml, two-necked flask equipped with a three-way stopcock adapter as a nitrogen inlet and with a short air condenser surmounted by another three-way stopcock adapter. In a nitrogen-filled glovebox the diarylacetylene, the triphenylaluminum, and the dry mesitylene in the molar ratio 1.0:1.05:8.1 were weighed into the reaction vessel. Most reaction runs employed *ca.* 2.5–3.5 g of triphenylaluminum and 12–15 ml of mesitylene. After removal from the glovebox the apparatus was flushed thoroughly with nitrogen by alternate evacuation and refilling. The flask was then placed in an electrically heated oil bath thermostatically maintained at 180.0 ± 0.1°. During the 4-hr heating period under nitrogen gentle refluxing of the mesitylene was observed. The cooled reaction mixture was treated with 25 ml of deoxygenated water (boiled to one-third its volume under nitrogen) and then with 25 ml of dilute hydrochloric acid or, in the reaction of *p*-*N*,*N*-dimethylaminodiphenylacetylene, with dilute sodium hydroxide solution. The organic hydrolysis products were extracted into benzene, the extracts were dried over anhydrous calcium sulfate, and the solvent (benzene and mesitylene) was finally driven off on a rotary film evaporator under reduced pressure, until constancy of residue weight was attained. Typically 93–99% of the expected weight of product was isolated by this procedure.

(b) Analysis of the Mixtures of Reaction Products. The absence of any starting diarylacetylene was demonstrated, either by the absence of its appropriate methyl signal, where applicable, in the nmr spectrum of the crude product, or by tlc analysis on silica gel with carbon tetrachloride development. Only in the reactions with the *p*-trifluoromethyl- and the *p*-methylsulfonyldiphenylacetylenes was any starting material detected.

In the cases of the *p*-*N*,*N*-dimethylamino-, *p*-methoxy-, *p*-methyl-, and *p*-methylthiodiphenylacetylenes, the mixtures of products could be conveniently analyzed by nmr spectroscopy. The resulting triarylethylenes gave individual methyl peaks whose integrated intensities at 50 Hz provided a reliable quantitative measure of the composition of isomers in the product. The positions of the methyl signals in the reaction products for 10% solutions in CCl_4 are given in Table I.

Structural assignments of the methyl signals for the case of *p*-methoxydiphenylacetylene could be done by direct comparison with the authentic samples synthesized above. In the other runs, a decision between the *cis*- or *trans*-1,2-diphenyl-1-arylethylene, on the one hand, and the 1,1-diphenyl-2-arylethylene, on the other, could be reached by the following isomerization experiment. After a mixture had been analyzed by nmr integration, it was heated in glacial acetic acid with a trace of concentrated sulfuric acid and then recovered by treatment with sodium hydroxide solution and extraction into ether. Removal of ether and repetition of the nmr spectrum revealed a relative diminution in the downfield methyl peak and the appearance of a new, third peak *ca.* 0.02 ppm upfield from the downfield one. The downfield methyl peak accordingly could be attributed to the 1,2-diphenyl-1-arylethylene, since only this isomer could undergo cis–trans isomerization with net chemical change. As support for this assumption it was shown that the nmr methyl signals of authentic samples of *cis*- and *trans*-1,2-diphenyl-1-*p*-anisylethylene have a separation of 0.02 ppm.

The question of the cis or trans character of the 1,2-diphenyl-1-arylethylene was decided by the combined use of reference compounds, comparison of the physical properties of the individually isolated isomers with literature reports, and observed trends in the nmr spectra. Column chromatography on reactivated neutral alumina (200° for 36 hr) was employed to separate the isomeric triarylethylenes and to permit identification of at least one isomer of each pair with an authentic sample or with literature data. Because nmr chemical shifts are concentration dependent, determining whether or not an isolated isomer produced a particular peak in the spectrum of the reaction mixture was not done solely by comparing signal frequencies, but by adding the isomer in question to the reaction mixture, in order to see which nmr peak would then be enhanced.

In the case of *p*-chlorodiphenylacetylene, where an nmr analysis could not be performed, and where the reaction mixture could not be separated by column, thin layer, or gas chromatography, the three possible triarylethylenes had been characterized by previous workers. These isomers were synthesized in the manner described above and were used to verify the presence of only *trans*-1,2-diphenyl-1-*p*-chlorophenylethylene in the reaction mixture and to measure the ratio of the two products by infrared spectroscopy. Infrared analysis was also employed for the *p*-methoxydiphenylacetylene reaction. In this case the results agreed within 1% with those obtained by nmr analysis. Spectra for quantitative analysis were measured with a Perkin-Elmer grating spectrophotometer, Model 337, using 0.1 mm KBr cells and "spectral grade" solvents. Frequencies were selected at which one isomer displayed a well-resolved peak absorption and the other isomer minimal absorption.

Some useful details of the qualitative and quantitative analyses of the individual reaction mixtures are given in the following sections.

(c) *p*-Methoxydiphenylacetylene. Chromatography of 1.03 g of the reaction product on alumina with development by hexane and then a benzene–hexane pair resulted in a separation of the isomers; pure *trans*-1,2-diphenyl-1-*p*-anisylethylene was eluted first.

Analysis of the original reaction mixture by nmr integration gave 58.2 ± 0.5% of the *trans*-1,2-diphenyl and 41.8% of the 1,1-diphenyl isomers. Infrared analysis in carbon disulfide for the trans isomer at 836 cm^{-1} and for the other isomer at 823 cm^{-1} gave 59.3 and 40.7%. The nmr and infrared values were averaged in arriving at the values in Table I. No *cis*-1,2-diphenyl isomer was detected.

(d) *p*-Methylthiodiphenylacetylene. On a column of alumina the product was separated into its isomers by elution with hexane and a hexane–ether (9:1 v/v) pair. The early fractons were recrystallized five times from 95% ethanol to provide fine, colorless needles, mp 102–103°. Buu-Hoi and Hoan report that 1,2-diphenyl-1-*p*-methylthiophenylethylene melts at 100°, but give no evidence as to whether it is the cis or trans isomer. Both the present compound and that of Buu-Hoi[38] give a reddish halochromic response to concentrated sulfuric acid. The methyl peak corresponded to the downfield peak in the nmr spectrum of the reaction mixture. Acid isomerization of the reaction mixture caused this peak to decrease and a new peak to form 0.02 ppm upfield. As all the other known *trans*-1,2-diphenyl isomers have their methyl signals downfield from those of their cis isomers, this isolated compound is concluded to be *trans*-1,2-diphenyl-1-*p*-methylthiophenylethylene. No cis isomer was detected in the reaction product: λ_{max}^{EtOH} 308 mμ (ε 18,100), 267 (25,700), 229 (16,200).

Anal. Calcd for $C_{21}H_{18}S$ (mp 102–103°): C, 83.40; H, 6.00. Found: C, 83.38; H, 6.08.

The latter chromatographic fractions yielded the other isomer, which upon repeated recrystallization from 95% ethanol formed colorless crystals, mp 108–109°. The methyl peak in the nmr spectrum corresponded to the upfield peak in that of the reaction mixture. Since this substance was recovered unchanged upon attempted acid-catalyzed isomerization, its behavior is consistent with its identity as 1,1-diphenyl-2-*p*-methylthiophenylethylene, λ_{max}^{EtOH} 321 mμ (ε 27,400), 235 (15,700).

Anal. Calcd for $C_{21}H_{18}S$: C, 83.40; H, 6.00. Found: C, 83.18; H, 5.89.

Spectral analysis of the reaction mixture by nmr integration yielded 48.5 ± 0.3% of the *trans*-1,2-diphenyl isomer and 51.5% of the 1,1-diphenyl isomer.

(e) *p*-*N*,*N*-Dimethylaminodiphenylacetylene. The reaction mixture was chromatographed on alumina with a benzene–hexane (3:7 v/v) eluent. The early fractions were recrystallized from methanol to give a crystalline product which discolorized slowly upon exposure to air, mp 97–98°. Since the nmr methyl signal corresponded to the downfield methyl peak in the spectrum of the reaction product, and since acid treatment of this substance did cause isomerization (new nmr peak 0.02 ppm upfield; this isomer is as-

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signed the structure of *trans*-1,2-diphenyl-1-*p*-*N*,*N*-dimethylaminoethylene.

Anal. Calcd for $C_{22}H_{21}N$: C, 88.25; H, 7.07; N, 4.68. Found: C, 87.79; H, 7.33; N, 4.84.

Recrystallizations of the later chromatographic fractions under a nitrogen atmosphere from petroleum ether (bp 30–60°) and from methanol yielded air-sensitive, yellow-green crystals, mp 122–123.5°. Ease of decomposition made an elemental analysis difficult, but a measured nmr proton ratio of 2.5 for aromatic plus vinyl protons *vs.* methyl protons was satisfactory. Staudinger and Kon[39] report that 1,1-diphenyl-2-*p*-*N*,*N*-dimethylaminophenylethylene is an air-sensitive, golden green solid, mp 126–127°. Again, this substance possessed an nmr methyl signal corresponding with the upfield signal in the spectrum of the reaction product, and this compound did not exhibit a new nmr methyl signal upon attempted isomerization. Therefore, there is no doubt that it is the 1,1-diphenyl isomer.

The nmr spectrum of the crude reaction mixture displayed three methyl peaks at δ 3.02, 3.00, and 2.94 ppm, the first being due to the isolated *trans*-1,2-diphenyl isomer, the latter attributable to the 1,1-diphenyl isomer. Since the peak at 3.00 ppm also was generated when the pure *trans*-1,2-diphenyl isomer was treated with acid, this absorption is assigned to the *cis*-1,2-diphenyl isomer. Therefore, all three isomers result from the addition of triphenylaluminum to this acetylene. From nmr integration the percentages of products are, therefore, 60.0 ± 0.5% of the *trans*, 19.3% of the *cis*, and 20.7% of the 1,1-diphenyl isomers. In Table I the sum of both cis and trans isomers, 79.3%, is used since both isomers are produced by the addition of the aluminum center to the same acetylenic atom.

(f) *p*-Methyldiphenylacetylene. Column chromatographic separation of the two isomers in the reaction product, using freshly activated alumina and petroleum ether eluent, was unsuccessful. The nmr spectrum of the reaction mixture displayed the usual two methyl peaks, δ 2.40 and 2.28 ppm. Assignment of the peaks to the appropriate isomer was based on analogy with the previous cases ($(CH_3)_2N$, CH_3O, CH_3S), where the trans 1,2-isomer always gave the most downfield methyl peak in the nmr spectrum. In addition, the behavior upon acid-catalyzed isomerization is in complete agreement with this assignment. Thus, the nmr spectrum of the isomerized product showed a diminution of the downfield peak and the emergence of a new peak 0.02 ppm upfield from it. The nmr analysis of the original reaction mixture showed 56.4 ± 0.3% of the *trans*-1,2-diphenyl and 43.6% of the 1,1-diphenyl isomers.

(g) *p*-Chlorodiphenylacetylene. Repeated attempts to separate the product mixture by column chromatography over activated neutral alumina failed to yield either pure isomer. Thin layer chromatography and color development with chromic acid spray assured the absence of the starting material (orange spot) in the mixture of triarylethylenes (green spot). Absence of infrared absorption at 574 and 590 cm^{-1}, wave numbers characteristic of the *cis*-1,2-diphenyl isomer, gave assurance that only the *trans*-1,2-diphenyl and 1,1-diphenyl isomers were present.

By reference to the infrared spectra of authentic samples, extinction coefficients were calculated at 724, 730, 740, and 772 cm^{-1}. Analysis of the reaction mixture revealed the presence of 40.2 ± 0.6% of the *trans*-1,2-diphenyl and 59.8% of the 1,1-diphenyl isomers.

(h) *p*-Trifluoromethyldiphenylacetylene. The former of these diphenylacetylenes underwent extensive decomposition when treated with triphenylaluminum, as evidenced by the immediate development of a deep purple color upon mixing the reagents. After reaction at 145° for 2 hr and hydrolytic work-up a dark, gummy product was obtained. Column chromatography on alumina with a benzene–hexane (1:1 v/v) eluent gave intensely purple fractions whose infrared spectra were almost completely devoid of absorptions characteristic of the CF_3 group.[40] Consideration decomposition, possibly related to the aluminum bromide catalyzed dimerization of diphenylacetylene to 1,2,3-triphenylazulene,[41] appeared to have been favored over the expected, simple addition.

In an attempt to moderate the reactivity of triphenylaluminum, the reaction was repeated in anisole solution (in which the aluminum compound exists as a solvate <100° [17]) at 79° for 20 hr. Hydrolysis of the violet solution showed that much *p*-trifluoromethyldiphenylacetylene had not reacted and again purple products had arisen.

(i) *p*-Methylsulfonyldiphenylacetylene. Reaction of a 2.50-g sample with triphenylaluminum in mesitylene at 180° for 4 hr and usual work-up gave 2.4 g of a pale yellow powder whose nmr showed only one methyl peak and an aromatic proton pattern resembling the starting diphenylacetylene. Recrystallization of the product from methanol gave enrichment in starting material, mp 155–160° (starting material, mp 162–163°). Thin layer chromatography of the crude product on silica gel with ethyl acetate–benzene (3:7 v/v) development showed that much starting material (R_f 0.44) and two minor components traveling ahead of the acetylene (overlapping, R_f 0.73) were present.

Heating 1.0 g (3.91 mmol) of the acetylene, 1.07 g (4.15 mmol) of triphenylaluminum, and 4.6 ml of mesitylene at 180° for 46 hr and hydrolytic work-up gave an acrid odor of sulfur dioxide. The isolated yellow powder was shown by thin layer chromatography to contain less than 10% of starting material. The principal reaction products (overlapping spots, R_f 0.73, blue and yellow by ultraviolet detection, brown and yellow by chromic acid spray) were not the expected *p*-methylsulfonyltriphenylethylenes, as such products would be expected to have R_f values lower than the starting material. Rather than carbalumination of the acetylenic linkage, some reaction involving the SO_2 linkage, yet to be elucidated, had occurred.

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