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PRELIMINARY COMMUNICATION

PROPOSED π-COMPLEX INTERMEDIATES IN THE REACTIONS OF ORGANOALUMINUM COMPOUNDS WITH ALKYNES. THE BEHAVIOR OF tert-BUTYLPHENYLACETYLENE

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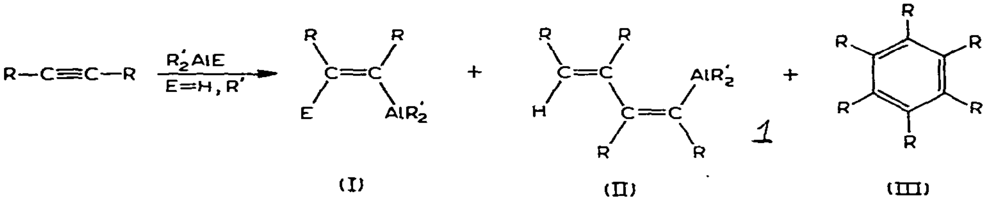
In pioneering research Wilke and Müller established that not only does the triple bond of alkynes add carbon–aluminum or hydrogen–aluminum bonds (I)[1, 2], but that dialkylaluminum hydrides can effect reduction (I, E = H), reductive dimerization (II) or cyclotrimerization of the alkyne, depending upon the alkyne: R'_2AlH ratio[3] (eq. 1):



(1)

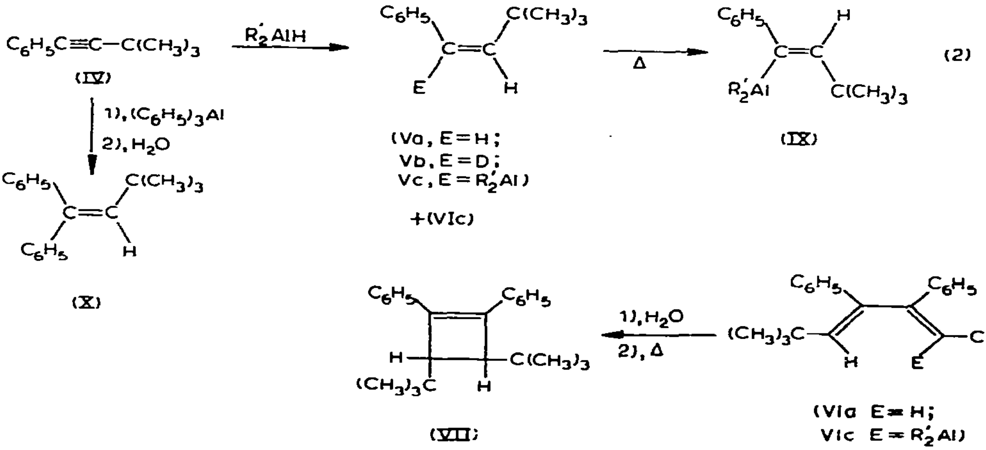
As a reaction pathway it was suggested that II arises from I simply by the insertion of an alkyne unit selectively into the vinyl–aluminum bond. In turn, III was thought to result from a Diels–Alder addition of alkyne to II and the subsequent loss of R'_2AlH from the intermediate adduct[3]. The products I–III, then, were felt to result from three consecutive reactions. Parallel findings on the insertion of symmetrical alkynes into the carbon–aluminum bonds of R_3Al and R_2AlR' types were interpreted as supporting this concatenated scheme.

As part of a program designed to shed light on the mechanism of alkyne–organoaluminum interactions, the behavior of terminal[4] and unsymmetrical alkynes[5, 6] toward R'_2AlH and toward $(C_6H_5)_3Al$ has been scrutinized in this Laboratory. We now find that the behavior of tert-butylphenylacetylene, taken together with our previous results with terminal alkynes[4] and methylphenylacetylene[5, 6], and with those of Wilke and Müller[1, 3], can best be explained in terms of steric factors operative on an intermediate π-complex. At the same time, we propose that products I–III are not formed in the consecutive manner suggested by Wilke and Müller, but that again a π-complex pathway presents a superior integration of the known facts.

Thus, the hydrogen–aluminum bond of diisobutylaluminum hydride and the phenyl–aluminum bond of triphenylaluminum add to the triple bond of tert-butylphenylacetylene (IV) to place the R'_2Al group on different carbon atoms. Furthermore, the reductive dimer of IV is exclusively one isomer (eq. 2). Heating 0.014 mole of tert-butylphenylacetylene (IV) with 0.014 mole of diisobutylaluminum hydride in 15 ml dry heptane under a nitrogen atmosphere for 48 h, at 50° and then hydrolyzing gave 94% of *cis*-β(tert-butyl)styrene[7] (Va) and 6% of a white solid VIa, m.p. 162–163°. Repetition of the reaction and work-up by treatment with deuterium oxide (99.8% pure) yielded Vb, completely and exclusively deuterated (NMR analysis) at the carbon α to the phenyl group, *i.e.* $C_6H_5CD{=}CH(t\text{-}C_4H_9)$ (eq. 2). There was no sign of deuterium at the carbon β to the phenyl group; therefore the R'_2Al group had been attached only to the α carbon in Vc. The structure of VIa was assigned as *cis,cis*-1,4-di-t-butyl-2,3-diphenyl-1,3-butadiene on the basis of proper elemental analyses, molecular weight, spectroscopic data, and the failure of attempted metallation with $n\text{-}C_4H_9Li$ in ether. Heating VIa at 200° for 3h leads to the formation of a solid VII, m.p. 88.5° whose properties are consistent with *trans*-3,4-di-t-butyl-1,2-diphenylcyclobutene, presumably formed from VIa by a thermal conrotatory[8] ring closure[9]. Other isomeric structures for VIa can be rejected on the basis of spectral or chemical properties.

Upon heating to 100° adduct Vc underwent 6% diadduct formation (VIII), yielding 1-phenyl-3,3-dimethylbutane upon hydrolysis, and principally isomerization to IX (68%); prolonged heating at 140° led to 92% VIII and less than 1% of VI. Prolonged heating of Vc at 50° gave a modest increase in dimer (2→6%, 2 days).

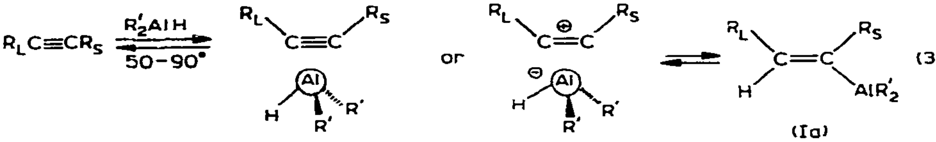
Heating IV with $(C_6H_5)_3Al$ in refluxing toluene gave, upon hydrolysis, > 95% 1,1-diphenyl-3,3-dimethyl-1-butene (X). The possibility of the 1,2-diphenyl isomer was dismissed, since the NMR spectrum of X was unchanged after attempted acid isomerization and since X yielded benzophenone upon chromic acid oxidation.



In trying to rationalize the mode of insertion of IV into the carbon–aluminum bonds of $(C_6H_5)_3Al$ or exclusively into the vinylic–aluminum bond of Vc, Stuart–Briegleb models of four-center transition states revealed no clear steric grounds for explaining these preferences. Although electronic factors demonstrably play a role in the addition of $(C_6H_5)_3Al$ to *para*-substituted tolanes, where steric factors are equalized[10], an electronic explanation for IV → X is unacceptable, since methylphenylacetylene adds

$(C_6H_5)_3Al$ in the reverse sense[6] (>95%). In addition to these difficulties, an acceptable mechanism must accommodate the following remarkable aspects of the alkyne insertion and oligomerization (I–III) reactions of aluminum alkyls [1-3]: (*a*) Acetylene does not undergo metallation, but, in fact, participates more readily than ethylene in carbon–aluminum insertions. Monosubstituted alkynes, however, undergo metallation as a prominent course[4]. (*b*) The oligomerization sometimes proceeds to the dimeric or trimeric stage, but never beyond to tetrameric or higher stages. (*c*) Although acetylene itself inserts into the C_4H_9–Al bond of (iso-$C_4H_9)_3Al$ at 20°, 3-hexyne or tolane inserts exclusively at 60° into the vinyl–aluminum bond of I ($R' =$ iso-C_4H_9; $R = C_2H_5$ or C_6H_5). (*d*) Although acetylene inserts into the C_2H_5–Al bond of $(C_2H_5)_3Al$ below 60° in a strict 1:1 ratio to yield diethyl(*trans*-1-butenyl)aluminum, 3-hexyne reacts with $(C_2H_5)_3Al$ to yield upon hydrolysis exclusively 1,1,2,3,4-pentaethyl-1,3-butadiene. No triethylethylene-(3-ethyl-3-hexene) was formed, regardless of the ratio of reactants. Conversely, $(C_2H_5)_3Al$ reacted with tolane to yield only monoadduct (ethylstilbene) and never any penta-substituted butadiene. (*e*) Attempts to add triisobutylaluminum to 3-hexyne and to tolane at 80° led to isobutylene evolution and to products of types I and II. (*f*) A Diels–Alder reaction on II as a route to III would demand that II assume a most hindered *cisoid* conformation[5].

In the following proposal invoking π-complex intermediates (scheme 1), it is postulated that vinylaluminum compounds with a hydrogen β-*cis* to the aluminum center may accomplish apparent "insertions" by forming π-complex species (XI) (R_L = larger group; R_S = smaller group):



(3)

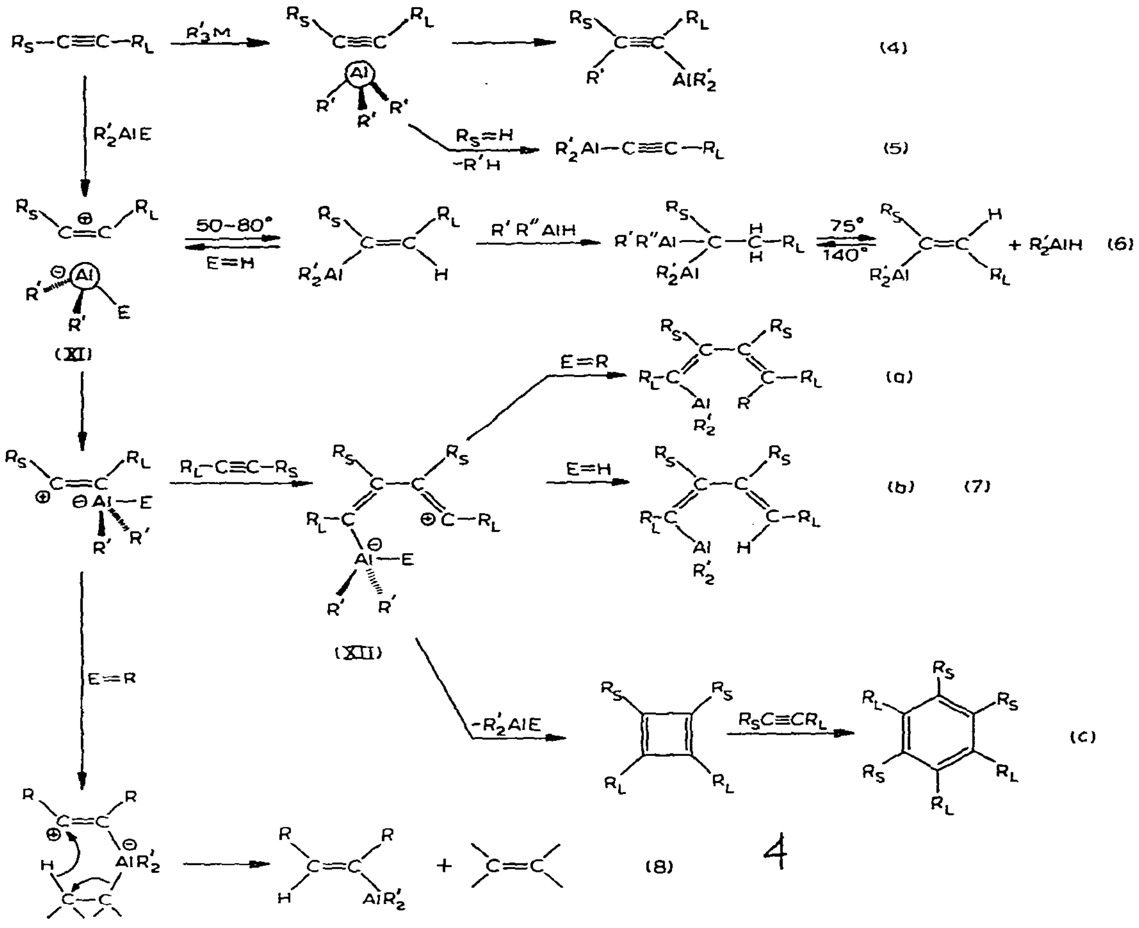
(XI)

(Ia)

(C≡C bond length: 1.20 Å;
Al covalent radius: 1.26 Å)

Of course, genuine alkyne insertions into carbon–aluminum bonds are well-documented[3, 5], but this scheme recognizes that adduct Ia begins to dissociate into alkyne in the temperature range (50–90°) where apparent "insertion" occurs. Also, the exclusive insertion of alkyne in vinylic–aluminum bonds in II or Vc, and the lack of any isobutylaluminum insertion is accounted for (*cf. supra*).

In Scheme 1: (*a*) the selectivity in the direction of carbon–aluminum or hydrogen–aluminum bond additions to alkynes is principally influenced by the steric perferences in disrupting the π-complex (eq. 4,5); (*b*) the apparent superior reactivity of vinylic–aluminum over alkyl–aluminum bonds is related to the ease of the former in forming the necessary intermediate XI; (*c*) the nature of the dimers in the reductive oligomerization of unsymmetrical alkynes can be rationalized in a clear fashion, as can the limitation of the oligomerization to the cyclic trimeric stage (eq.7c); (*d*) the heightened reactivity of acetylene over that of ethylene can be correlated with the stronger π-donor character of the former[11]; the metallation of terminal acetylenes with the alignment of R' in R_3Al with the acetylenic hydrogen (eq.5); (*e*) the failure to find monoadducts (*e.g.*,



Scheme 1.

($(C_2H_5)_3Al$ with 3-hexyne or $(i\text{-}C_4H_9)_3Al$ with tolane, eq.8) or 1:2 adducts (*e.q.*, with $(C_2H_5)_3Al$ and tolane) in certain cases is explicable, since the scheme (eq.4,6,7a,b,c) does not demand that the adducts have the consecutive relation given them by Wilke and Müller[3]; (*f*) the isomerization of the *cis*-adduct of IV to the *trans* adduct (*e.g.*, IX) prevents dissociation to alkyne and hence inhibits dimer formation (*e.g.*, VI), even at high temperatures; and (*g*) the cyclobutadiene pathway suggested in eq.7c should mean that organoaluminum compounds containing no Al–H bonds will also be able to trimerize alkynes via complexes like XI, XII in eq.7c. Indeed, when triphenylaluminum and diphenylacetylene (1:2) are heated at 200° considerable amounts of hexaphenylbenzene are formed[12]. The similarity between this proposed pathway and a rational view of the trimerization of 2-butyne to hexamethyl–Dewar-benzene by aluminum chloride[13] is readily apparent.

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