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ORGANOMETALLIC COMPOUNDS OF GROUP III

XXXIV *. STERIC FACTORS IN THE CARBALUMINATION OF OLEFINS. THE QUESTION OF THE ANOMALOUS, REDUCED REACTIVITY OF OLEFINS VERSUS ACETYLENES

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Summary

In order to understand the reasons for the anomalous, reduced reactivity of olefins toward electrophilic carbalumination, compared with that of acetylenes, the reactivity, stereochemistry and regiochemistry of a series of acyclic and cyclic olefins in carbalumination with triphenylaluminum were investigated. The following substrates underwent reaction between 80 and 225°C with decreasing ease in the order: norbornadiene > *cis*-β-methylstyrene > *trans*-β-methylstyrene ~ 1,2-dihydronaphthalene ~ 1,1-dimethylindene > *cis*-1,2-diphenylethylene > 3,3,3-triphenylpropene > *trans*-1,2-diarylethylenes ~ phenylcyclopropanes. The stereochemistry of the mono- and bis-carbaluminations of norbornadiene was shown to be *syn, exo*. The regiochemistry observed with unsymmetrical olefins could readily be rationalized by a steric effect operative in the preferential collapse of an olefin—$(C_6H_5)_3Al$ π-complex. Besides carbalumination, several other reactions were observed with these olefins: (1) *cis,trans*-isomerization of acyclic olefins; (2) metallation of vinylic carbon atoms by $(C_6H_5)_3Al$; (3) elimination of $(C_6H_5)_2AlH$ from carbalumination adducts; (4) by inference from the foregoing reaction with certain systems, epimerization at sp^3-hybridized carbon—aluminum bonds; and (5) decarbalumination with carbon—carbon bond scission. These side reactions were considered together with relative reactivities, stereochemistry and regiochemistry in developing energy profiles

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* For previous part, see ref. 9.

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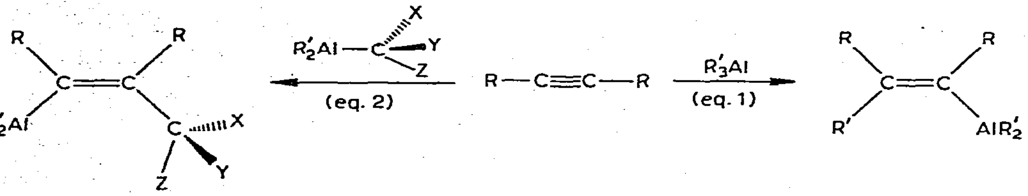
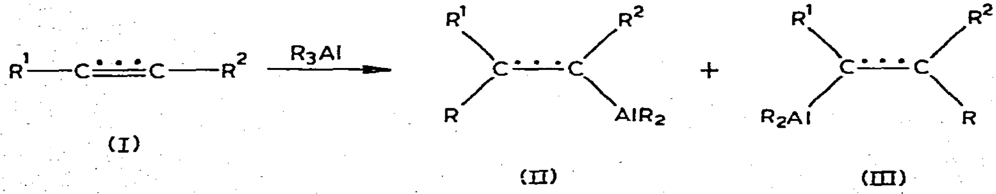
for the carbalumination of olefins and acetylenes. The reduced reactivity of olefins is thought to arise from steric factors that destabilize a π-complex with $(C_6H_5)_3Al$ and that cause a trapezoidal-like transition state to be of higher energy and rate-determining. The higher reactivity of acetylenes is ascribed to less steric hindrance both to π-complexation with $(C_6H_5)_3Al$, and to the collapse of the complex via a trapezoidal configuration. For acetylenes, it is judged that the formation of an intimate π-complex is rate-determining.

Introduction

The addition of alkylaluminums to the carbon—carbon unsaturation of olefins or acetylenes, fist observed by Ziegler and co-workers [1], is a reaction of great potential for the systematic construction of carbon skeletons. Furthermore, the course of these carbaluminations has been shown to be both stereoselective and regioselective. The pronounced stereoselectivity is seen in the exclusive *syn*-addition of alkyl- or aryl-aluminums to alkynes [2—7], the *exo*-carbalumination of bicyclic olefins [8], the exclusive *exo,syn*-addition of arylaluminums to substituted benzonorbornadienes [9] and the insertion of an alkyne into an sp^3-hybridized carbon—aluminum bond with retention of configuration at carbon [10] (eqns. 1, 2):



Equally important in achieving preferential carbon—carbon bond formation is the regioselectivity of carbalumination, namely the proportion of *syn*-isomers II and III arising from an olefin or acetylene (I, eqn. 3):



(3)

By proper choice of R^1 and R^2 (e.g., with phenyl and *p*-substituted phenyl groups for alkynes [5,6], or with 6-substituted benzonorbornadienes for olefins [9]), any steric influence on the isomer ratio can be canceled out. Thus, a study of the isomer ratio II : III resulting from the addition of triphenylaluminum to *p*-substituted diphenylacetylenes [5] and to 6-substituted benzonorbornadienes [9] has permitted a separate evaluation of the electronic influences. Moreover, with certain of these substituted acetylenes and olefins, the overall relative reactivities toward carbalumination could also be determined. These combined regioselectivity and reactivity studies have shown that an electron-donating R^1 substituent enhances the rate of carbalumination and increases the proportion of adduct II (cf. eq. 3). Such results, taken together with those of detailed kinetic, solvent and stereochemical studies, lead, rather convincingly, to a reaction mechanism involving an electrophilic attack by monomeric R_3Al on the carbon—carbon π-bond.

However, one discordant aspect of this otherwise harmonious mechanistic view is the relative reactivities of olefins and acetylenes: toward carbalumination, a given acetylene is far more reactive than the similarly substituted olefin. Acetylene, for example, undergoes rapid carbalumination by triethylaluminum in the range of 40—60°C, while ethylene requires a temperature of 150°C for a similarly rapid reaction [2]. More telling is the behavior of diphenylacetylene and the *cis*- and *trans*-diphenylethylenes toward triphenylaluminum in refluxing mesitylene (ca. 175°C): the acetylene undergoes complete reaction in 4 h; the *cis*-olefin is inert after 40 h at the same temperature and only slowly reacts when heated neat with $(C_6H_5)_3Al$; and the *trans*-olefin is inert to $(C_6H_5)_3Al$ when heated neat at 200°C. This reduced reactivity of olefins versus acetylenes is clearly anomalous, for all previous studies of electrophilic additions to carbon—carbon unsaturation have shown olefins to be distinctly more reactive than acetylenes [11].

The present study of the behaviour of olefins upon carbalumination was undertaken, therefore, to learn the reasons for this anomalous, reduced reactivity. To this end, various substituted acyclic and cyclic olefins, as well as cyclopropanes, have been subjected to carbalumination by triphenylaluminum. The reactivity and regiochemistry exhibited by these hydrocarbons have then been employed to show how the energy profile for the carbalumination of olefins differs from that of acetylenes.

Results

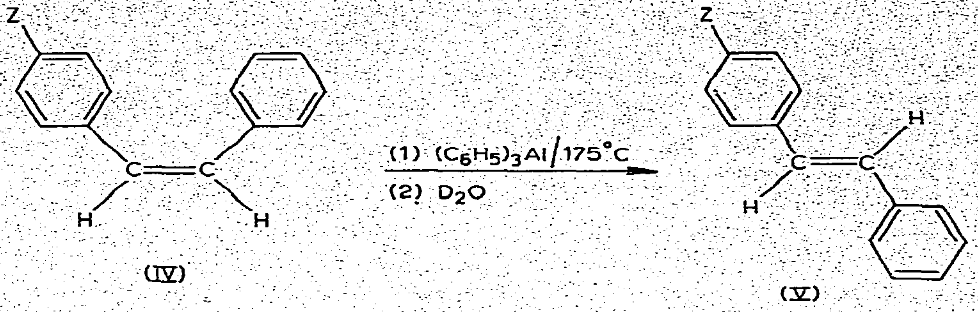
Reactivity and side reactions

The olefins examined (Table 1) underwent carbalumination with great differences in rate: norbornadiene was the most reactive, undergoing both mono- and bis-carbalumination in refluxing benzene solution; while di- and tri-phenylated olefins were among the least, requiring temperatures well over 215°C without solvent for significant reaction (*cis*- and *trans*-diphenylethylenes, 1-phenylcyclopentene and 3,3,3-triphenylpropene). Cyclopropanes, such as the 1-phenyl and 1,1-diphenyl derivatives, were also unreactive to $(C_6H_5)_3Al$ below 200°C and above 200°C very slowly reacted to yield several products. With these unreactive olefins and even with those that did undergo carbalumination under 200°C (1,1-dimethylindene, the *cis*- and *trans*-β-methylstyrenes and 1,2-dihydronaphthalene), a number of other reactions competed with, or occurred subsequent to, the carbalumination of the olefinic linkage. First of all, at 175°C (temperature of refluxing mesitylene under nitrogen) both *cis*-diphenylethylene and Z-1-phenyl-2-*p*-tolylethylene were isomerized into their *trans*-isomers by agency of $(C_6H_5)_3Al$ without the occurrence of any discernible carbalumination or metallation of the hydrocarbon (eqn. 4).

TABLE 1. REACTIONS OF OLEFINIC HYDROCARBONS WITH TRIPHENYLALUMINUM

Olefinic substrate (mmol)	$(C_6H_5)_3Al$ (mmol)	Reaction time (h)	Reaction temp. (°C)	Solvent	Products after H_2O treatment (% yield)
Norbornadiene (50)	10	3	80	Benzene	*exo*-5-Phenylnorbornene[a] (88; 73) *exo,exo*-2,5-Diphenylnorbornane[a] (27)
cis-β-Methylstyrene (50)	50	24	175	Mesitylene	1,2-Diphenylpropane (45) *trans*-1,2-Diphenylpropene (25) n-Propylbenzene (25)
trans-β-*Methylstyrene* (40)	40	24	175	Mesitylene	*cis*-β-Methylstyrene (5) 1,2-Diphenylpropane (8) *trans*-1,2-Diphenylpropene (25) n-Propylbenzene (25) *trans*-β-Methylstyrene (42)
1,1-Dimethylindene (6.2)	6.2	72	190	Decane	1,1-Dimethyl-3-phenylindene (44) 1,1-Dimethyl-2-phenylindene (22) 1,1-Dimethylindan (10) 1,1-Dimethylindene (12) 1,1-Dimethyl-*x*-phenylindans[b] (5)
1,2-Dihydronaphthalene (6)	8	40	175	Mesitylene	3-Phenyl-1,2-dihydronaphthalene (25) 1,2,3,4-Tetrahydronaphthalene (25) 1,2-Dihydronaphthalene (50)
3,3,3-Triphenylpropene (2)	2	72	190		No reaction
3,3,3-Triphenylpropene (2)	2	72	225		Triphenylmethane[c] *trans*-1,2-Diphenylethylene 1,1-Diphenylethylene, tetraphenylpropane
cis-1,2-Diphenylethylene (17)	17	40	175	Mesitylene	*trans*-1,2-Diphenylethylene (50) *cis*-1,2-Diphenylethylene (50)
cis-1,2-Diphenylethylene (6)	6	18	200		1,1,2-Triphenylethane (5) Triphenylethylene (3) 1,2-Diphenylethylene (92 in a *cis,trans*-ratio of 7 : 93).
trans-1,2-Diphenylethylene (5.4)	6.6	18	200		No reaction
Z-1-Phenyl-2-*p*-tolylethylene (3)	4	19	175	Mesitylene	*E*-1-phenyl-2-*p*-tolylethylene (60) *Z*-1-phenyl-2-*p*-tolylethylene (40)
E-1,2-Di-*p*-methoxyphenylethylene (7)	7	48	175		No metallation or carbalumination

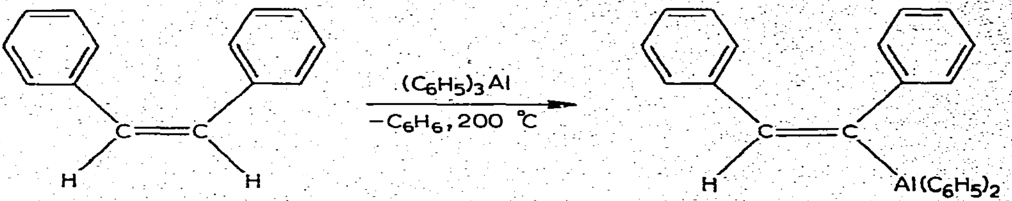
[a] The yield is 88% of monophenyl product based upon $(C_6H_5)_3Al$ furnishing one phenyl group; the yields of the monophenyl and diphenyl derivatives, based upon the total millimoles of products is 73% and 27%, respectively. [b] Probable nature of minor components. [c] Reaction products too intractable to permit of a quantitative analysis.



(4)

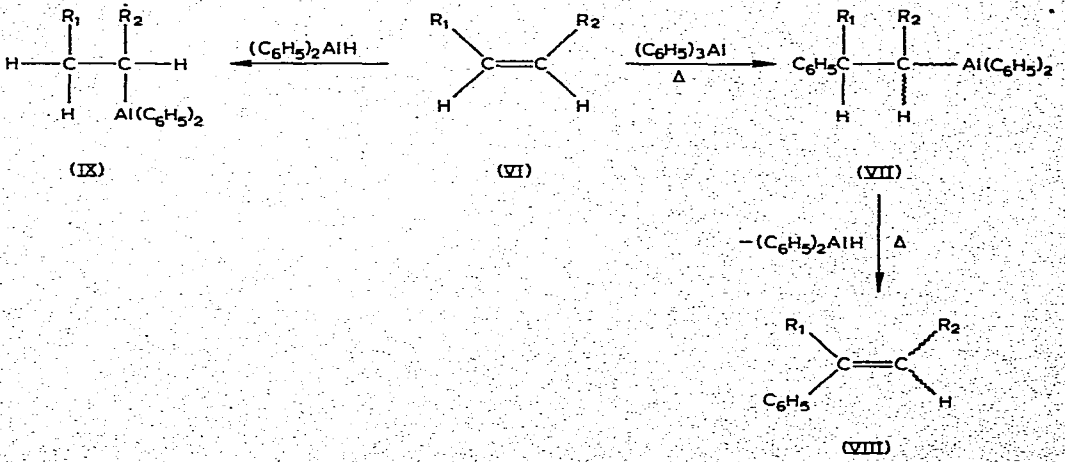
Z = H, CH_3

Secondly, at or above 200°C, *cis*-diphenylethylene, and possibly 1,1-dimethyl-2-phenylindene (cf. infra), underwent slow metallation at the vinylic carbon (eqn. 5).



(5)

Thirdly, all but the highly reactive norbornadiene underwent the thermal loss of $(C_6H_5)_2AlH$ from the initial carbalumination adduct; the $(C_6H_5)_2AlH$ generated then effected the hydralumination of the starting olefin (eq. 6-7). There are certain mechanistic implications as to the stereochemistry of carbalumination (VI → VII), hydralumination (VI → IX) and dehydralumination (VII → VIII) that deserve consideration, but this will be deferred (cf. Discussion).



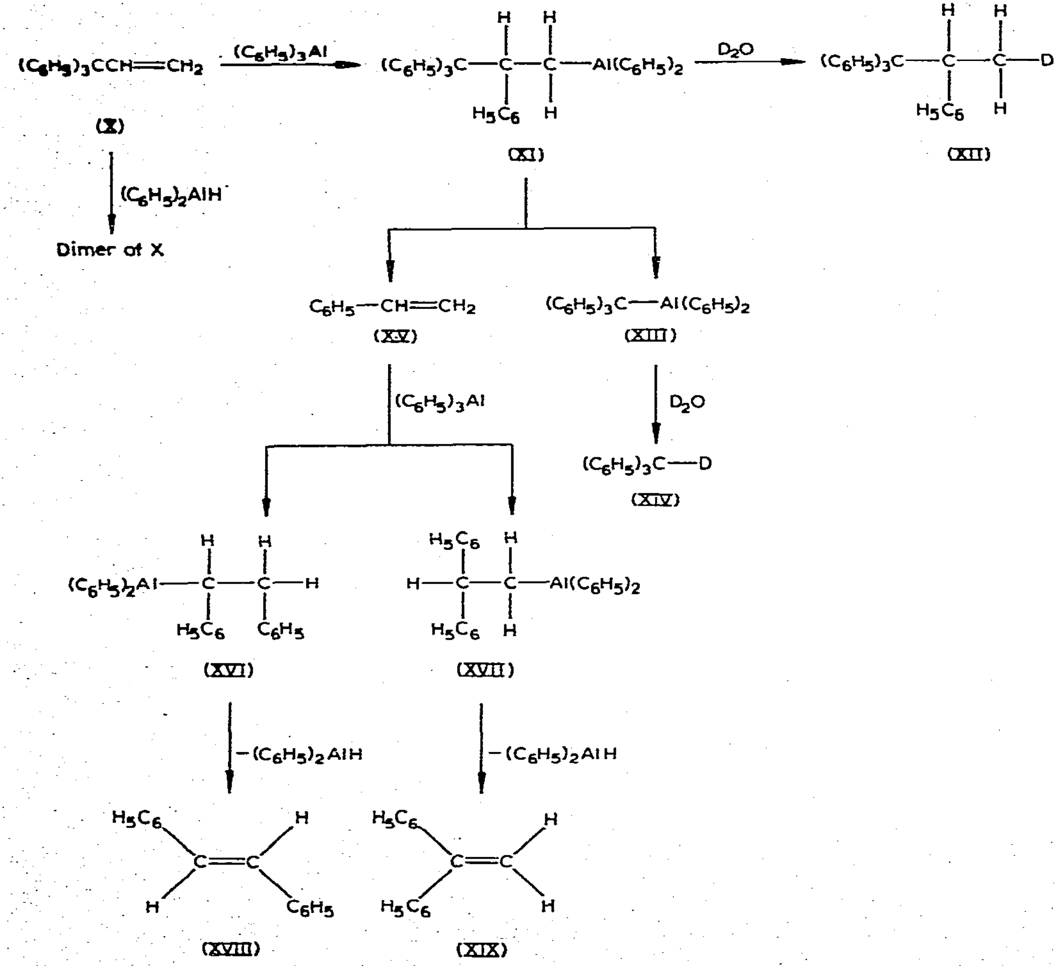
(6)

(7)

Fourthly, in contrast with 1-octene, which is carbaluminated by $(C_6H_5)_3Al$

at 150°C, 3,3,3-triphenylpropene (X) reacted with $(C_6H_5)_3Al$ only at >220°C and then gave rise to carbon—carbon bond fragmentation products. Work-up with D_2O led to the isolation of triphenylmethane, *trans*-stilbene, 1,1-diphenylethylene and products suggestive of the carbalumination and dimerization of X. The triphenylmethane was shown by NMR spectroscopy to be extensively deuterated on the α carbon and the diphenylethylenes to be significantly deuterated by mass spectrometry. These products can be rationalized in terms of steps precedented in previous studies (Scheme 1). The direction of carbalumination to form XI is similar to that observed with 1-octene [7]; the elimination of a trityl aluminum compound XIII from XI has already been precedented in the reaction of diisobutylaluminum hydride with phenyl(trityl)acetylene [4]; and

SCHEME 1

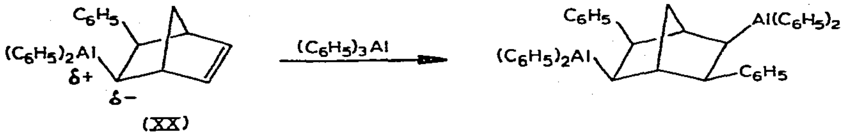


the carbalumination of styrene to yield both regioisomers XVI and XVII is analogous to the known hydralumination of XV where both modes of addition are realized [12]. Moreover, the elimination of diphenylaluminum hydride from XVI and XVII to yield the diphenylethylenes XVIII and XIX has been noted when many such carbalumination adducts are heated above 150°C [7]. Finally, the detection of deuterated XVIII and XIX suggests that these hydrocarbons undergo metallation by $(C_6H_5)_3Al$ under the extreme reaction conditions, just as with *cis*-diphenylethylene.

Stereochemistry and regiochemistry

As is supported in detail in the Experimental section, the mono- and bis-carbaluminations of norbornadiene were shown to occur exclusively in an *exo*, *syn*-manner. Because *syn*-addition is also the preferred pathway for the carbalumination of alkynes [2—7] and benzonorbornadienes [9], it is most likely that acyclic and cyclic olefins generally exhibit an analogous stereochemistry in such additions.

The regiochemistry shown by the mono-adduct of norbornadiene (XX) (eq. 8), 1,2-dihydronaphthalene (XXI, eq. 9), and the *cis*- and *trans*-β-methylstyrenes (XXIII, eq. 10) was apparently specific; only one regioisomer was detected.



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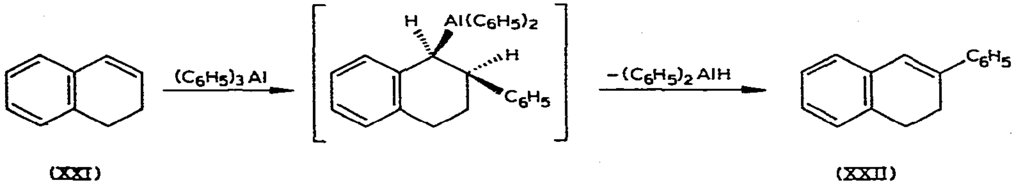

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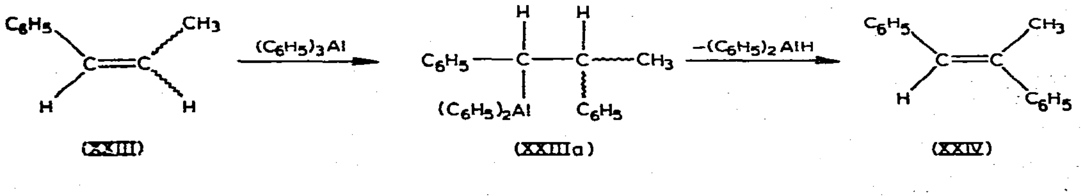
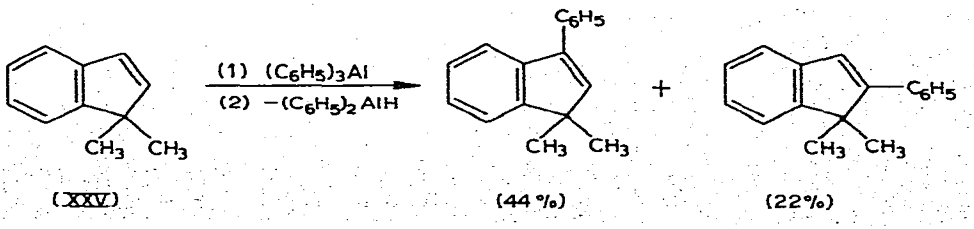


(10)

With 1,1-dimethylindene (XXV), both regioisomers were formed (eq. 11).



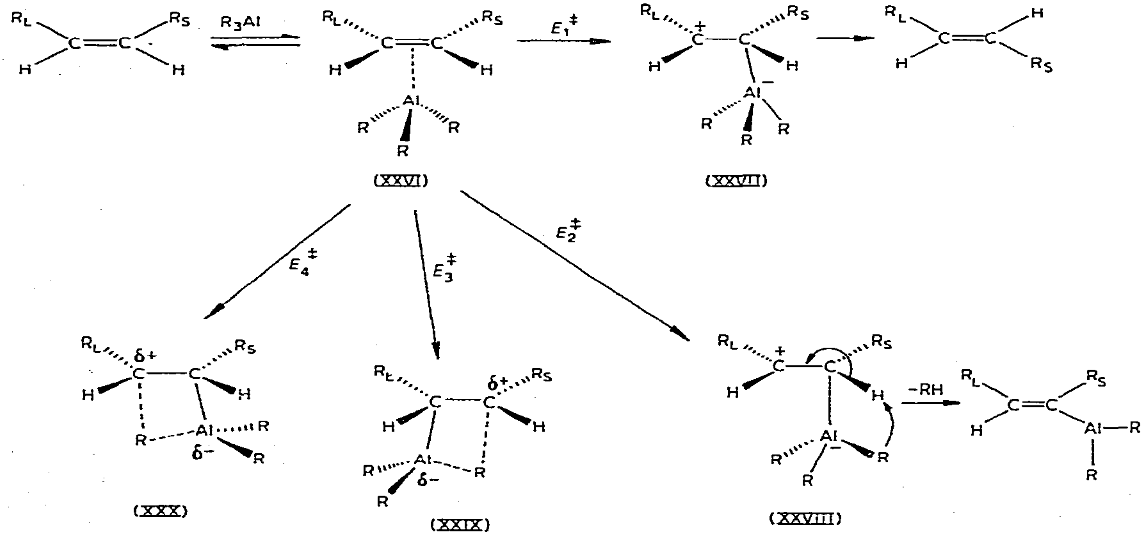
(11)

Discussion

Reactivity and regiochemistry

Since the polar effects operative in both the carbalumination of diphenylacetylenes [5,6] and benzonorbornadienes [9] are similar, the origin of the anomalous reactivity of olefins must lie in steric effects. But to learn at just what stage of the reaction such steric effects are involved, it is important to examine the regioselectivity and the competing reactions. Both the isomerization (eq. 4) and the metallation (eq. 5) of *cis*-diarylethylenes are competitive with the carbalumination. A reasonable mechanistic interrelation of these processes can be formulated in terms of a reversibly formed π-complex (XXVI), which slowly leads to transition states for isomerization (XXVII, σ-complex configuration), metallation (XXVIII, four-center) or carbalumination (XXIX and XXX, R_L and R_S signify larger and smaller groups, respectively) (Scheme 2) *. The reactions observed for *cis*-diphenylethylene suggest that the activation energies are thus ordered: $E_1^{\neq} < E_2^{\neq} \sim E_3^{\neq} = E_4^{\neq}$. Any regioselectivity in carbalumination would then arise when steric factors would cause preferential migration of the R group from aluminum to vinylic carbon ($E_3^{\neq} \neq E_4^{\neq}$ in XXIX and XXX). The gauche interactions encountered between R and R_S, compared with that between R and R_L, should make $E_3^{\neq} < E_4^{\neq}$. This conclusion is in accord with the regioselectivities observed with the internal olefins examined in this study (eq. 8—11). For the mono-carbalumination adduct XX, it should be noted that molecular models show that the $(C_6H_5)_2Al$ group can exert a steric effect on the close approach of a second $(C_6H_5)_3Al$ to the double bond.

SCHEME 2



In ascribing the foregoing regioselectivities to steric control, it is difficult to

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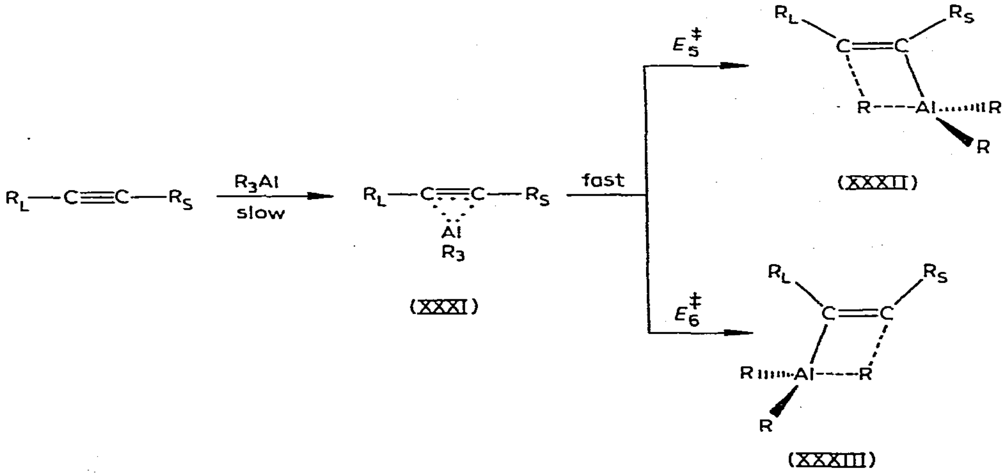
* Cf. the steric factors determining the direction of collapse for π-complexes thought to be intermediates in the hydralumination and carbalumination of alkynes [8,13].

dismiss the possible contributions of polar factors. The carbalumination of XX might be ascribable to the influence of the polar carbon—aluminum bond in XX to further electrophilic attack. Likewise, the electron-release of *sp*^{3}- versus *sp*^{2}-carbon in XXI and XXIII might determine the direction of carbalumination (cf. charge separations in XXIX and XXX). But the undeniable influence of a steric influence is seen in indene XXV, where electronic considerations would have predicted that the 2-phenyl isomer would predominate (eq. 11). As further substantiation of the steric control operative in this observed regioselectivity, it should be recalled that methylphenylacetylene is carbaluminated almost exclusively by $(C_6H_5)_3Al$ to yield the 1-alumina-*cis*-1,2-diphenylpropene adduct. In contrast, t-butylphenylacetylene yields solely the α-alumina-3,3-dimethyl-1,1-diphenyl-1-butene adduct. Clearly, at least one of these regiospecificities must be ascribed to a steric effect [13].

Recent consideration of the carbalumination of benzonorbornadienes and diphenylacetylenes has led to the conclusion that formation of a tight π-complex is rate-determining and that collapse of this complex to form the regioisomers occurs in relatively rapid steps (eq. 12).



(12)

With ordinary olefins, it is clear that π-complexation is not rate-determining, for *cis,trans*-isomerization can, in certain cases, occur faster than carbalumination. The difference in reactivity between alkynes and strained cyclic olefins, on the one hand, and acyclic or cyclic olefins, on the other, seems to be due to the relative energies of the respective π-complexes, XXVI and XXXI, and the transition states for carbalumination, XXIX and XXX versus XXXII and XXXIII. π-Complexation of alkynes with R_3Al should be more intimate than that of olefins, because the latter encounters more *F*-strain (R vs. R_L or R_s or H in XXVI) and *B*-strain (R_L vs. R_S). For these reasons, the π-complex XXVI should be a looser, weaker interaction than XXXI. Furthermore, the olefin transition states XXIX and XXX involve two gauche interactions for the migrating R group and two eclipsing interactions between the R_2Al group and the olefin's substituents. By comparison, the acetylene transition states XXXII and XXXIII have one eclipsing encounter of the migrating R group and two gauche interactions due to the R_2Al group. Taken together with the smaller energy necessary to disrupt a C≡C, rather than a C=C linkage, these considerations suggest that XXIX and XXX should be of relatively greater energy than XXXII and XXXIII. Finally, since the overall carbalumination of an acetylene should be more exoergic than that of the corresponding olefin, one can construct energy profiles for the carbalumination of these hydrocarbons, as illustrated in Fig. 1. This analysis, therefore, attributes the anomalous reactivity of olefins to steric factors that make π-complexation a weaker interaction and group transfer from aluminum rate-determining. The even lower reactivity exhibited by cyclopropanes would arise, accordingly, from an even lower ground-state energy and a diminished π-character of the ring bonds *.

Stereochemistry

Since the stereochemistry of carbalumination and hydralumination of the C=C and C≡C linkages generally is of a *syn*-character [2—8,9,14—16], by the principle of microscopic reversibility decarbalumination and dehydralumination should also be more facile by *syn*-elimination. For this reason, the formation of 3-phenyl-1,2-dihydronaphthalene (XXII) from 1,2-dihydronaphthalene (XXI, eq. 9) and of the phenyl-1,1-dimethylindenes from 1,1-dimethylindene (XXV, eq. 11) require some comment. The loss of $(C_6H_5)_2AlH$ from the expected *syn*-adducts would either have to occur in an *anti*-fashion, or the initial *syn*-

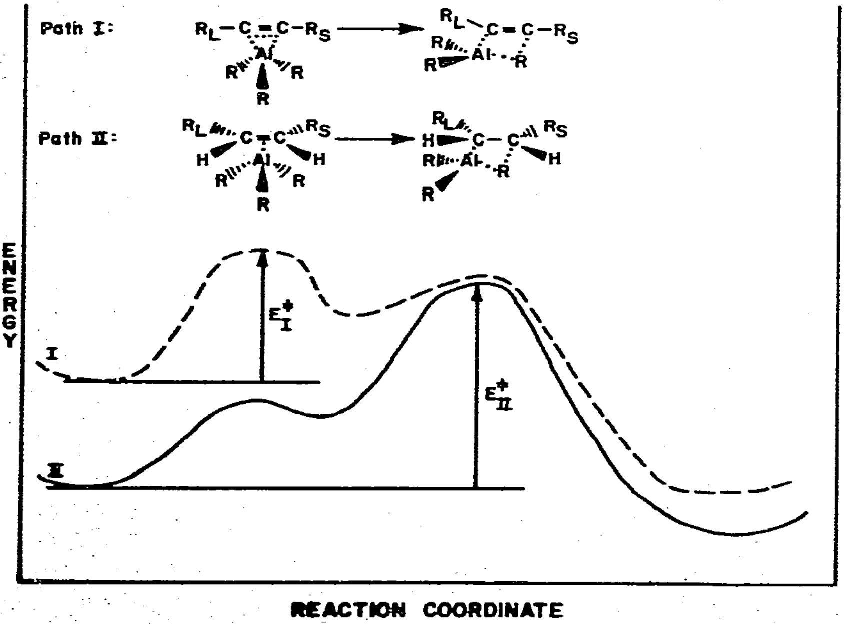


Fig. 1. Suggested Energy Profiles for the hydraluminations of acetylenes (Path I) and olefins (Path II).

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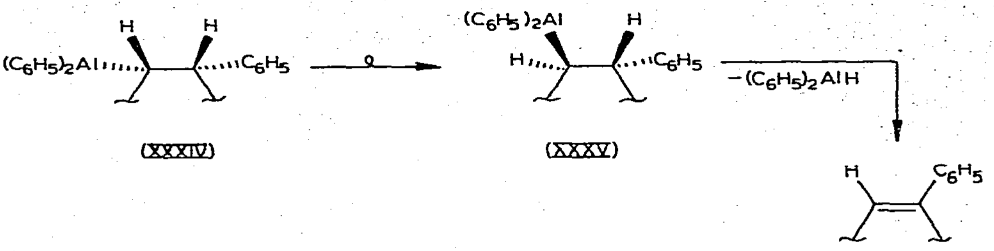
* With suitable modifications, this analysis could be invoked to explain the greater ease with which acetylenes undergo hydralumination or hydroboration, in comparison with olefins. The principal difference would be that the smaller hydride bridging group in XXIX and XXX would encounter smaller gauche repulsions, in XXXII and XXXIII smaller eclipsing interactions. Indeed, for the hydralumination of acetylenes there is again evidence for a π-complex-like transition state [14].

adduct (XXXIV) would have to isomerize to the *anti*-adduct (XXXV), prior to a *syn*-dehydralumination (eq. 13).



(13)

Current studies of configurational change at sp^3-hybridized carbon—aluminum bonds (derived from the *syn*-addition of $(i\text{-}C_4H_9)_2AlD$ to XXV) have shown that the configuration is epimerized at temperatures of 75—100°C [17]. Accordingly, the pathway depicted in eq. 13 is the more probable one for the formation of XXII and the phenyl-1,1-dimethylindenes from the cyclic olefins, rather than an *anti*-dehydralumination.

The formation of *trans*-1,2-diphenylpropene (XXIV) from either the *cis*- or *trans*-β-methylstyrene probably also involves such a configurational change in adduct XXIIIa, prior to a *syn*-loss of $(C_6H_5)_2AlH$ to give the more stable *trans*-isomer (XXIV). Here, however, it cannot be ruled out that any *cis*-1,2-diphenylpropene formed might be isomerized to XXIV, just as with *cis*-diphenylethylene (eq. 5).

Finally, the interesting decarbalumination observed with 3,3,3-triphenylpropene (Scheme 1) has a precedent in the carbon—carbon bond scission observed in the hydralumination of methyl(trityl)acetylene [3]. Such reversal of carbalumination seems to be favored by the release of steric strain in XI and the formation of a carbon—aluminum bond stabilized by partial negative charge dispersal (i.e., trityl [18]).

Experimental

General techniques

The experimental procedures for the preparation, transfer and analysis of triphenylaluminum have been described previously [5,6]. All the following reactions of organoaluminum reagents with olefins were conducted with scrupulously dried and deoxygenated hydrocarbon substrates and solvents under an atmosphere of dry, oxygen-free nitrogen. The olefinic substrates, either synthesized or purchased, were checked for their purity by NMR, thin-layer chromatographic and gas chromatographic analysis before final drying: *cis*-β-methylstyrene [3], *trans*-β-methylstyrene (Eastman), 1,2-dihydronaphthalene (Aldrich, 3 : 1 mixture with tetralin), norbornadiene (Baker), *cis*- and *trans*-stilbenes (Aldrich), *Z*-1-phenyl-2-*p*-tolylethylene [3], *E*-1,2-di-*p*-methoxyphenylethylene [5], cyclopentene [19], 1-phenylcyclopentene, phenylcyclopropane [10], 1.1-diphenylcyclopropane [20], 1,1-dimethylindene [10] and 3,3,3-triphenylpropene [21].

All gas chromatographic analyses were made with a Hewlett—Packard F&M instrument, model 720, equipped with 6′ dual columns of 10% silicone gum rubber on Chromosorb P. The NMR data, which were obtained with a Varian spectrometer, model A60, are reported on the δ-scale (ppm) with reference to internal TMS. Infrared spectra either of neat liquid samples or of solids as 10% solutions (w/w) in CCl_4 were recorded with a Perkin—Elmer spectrophotometer, model 137. Corrected melting points were measured in a Thomas—Hoover, oilbath, capillary apparatus.

General procedure for the interaction of triphenylaluminum with various hydrocarbon substrates

Under an atmosphere of dry nitrogen the triphenylaluminum was placed in a 50- or 100-ml, two-necked flask equipped with a three-way stopcock and a reflux condenser. The purified and dried solvent, benzene or mesitylene, was then distilled directly into the flask, and thereafter the desired amount of olefin was introduced with a nitrogen-flushed hypodermic syringe. Before heating the reaction solution at reflux with magnetic stirring, the charged flask was chilled and then alternately evacuated and refilled with nitrogen three times.

After the appropriate heating period the cooled mixture was treated carefully with water or dilute HCl (or, for deuterium labelling, with 99.8% D_2O) and allowed to stir. Gentle heating under nitrogen was sometimes required to complete the cleavage of all C—Al bonds. Extraction with benzene, drying of the organic layer over anhydrous $CaSO_4$, removal of solvent and a combination of gas chromatographic and spectral analyses then ensued.

The individual reaction conditions and experimental results are given in the following sections.

1. Norbornadiene. A mixture of 4.50 g (50 mmol) of norbornadiene and 2.58 g (10 mmol) of $(C_6H_5)_3Al$ in 25 ml of benzene was heated at reflux for 3 h. Usual work-up, followed by distillation through a 10 × 1 cm Vigreux column, yielded 1.5 g (75%) of *exo*-5-phenylnorbornene, b.p. 79—80°C/0.1 mm Hg, which was identified by its NMR and IR spectra [8a].

The solid distillation residue was recrystallized from 95% ethanol to give 0.80 g of white platelets, m.p. 87—88°C (lit. [8a] m.p. 88°C), which was identified as *exo,exo*-2,5-diphenylnorbornane by spectral and mixture m.p. comparisons [8a].

By adherence to the same reaction procedure, but with work-up by treatment with D_2O, the deuterated counterparts, *exo*-6-deuterio-*exo*-5-phenylnorbornene and *exo,exo*-3,6-dideuterio-*exo,exo*-2,5-diphenylnorbornane, were obtained. Although previous work had determined the *exo*-position of the phenyl groups in these products [8a], the position of the carbon—aluminum bonds remained to be assigned.

By a comparison of the NMR spectra of both the deuterated and the undeuterated forms of *exo*-5-phenylnorbornene and *exo,exo*-2,5-diphenylnorbornane, the stereochemistry of the carbon—aluminum bonds could be ascertained. First of all, in 5-phenylnorbornene the phenyl group must be *exo*, for its NMR spectrum is distincly different from the published spectral data for the *endo*-5-phenylnorbornene [22] (the 6-*exo*-proton signal of the latter at 2.13 ppm is lacking in the present reaction product). Secondly, in the deuterated *exo*-5-

phenylnorbornene the multiple signal between 0.75 and 1.1 ppm corresponds to one proton, and hence the deuteron is at a C(6) position. Thirdly, the NMR spectrum of the dideuterated *exo,exo*-2,5-diphenylnorbornane displays sharper signals than that of the undeuterated compound. Since the *endo*-protons in a bicyclo[2.2.1] system are never noticeable coupled to the bridgehead protons, while the *exo*-protons often have coupling constants ranging from 3.4—4.0 Hz [22—24], the simplification of the NMR spectrum of the dideuterated compound implies that the deuterons are at the *exo*-C(3) and *exo*-C(6)-positions. Finally, the benzylic protons in the 2,5-diphenylnorbornane system appear as an overlapping doublet of doublets centered at 2.58 ppm and having a total width of 14.5 Hz. In the dideuterated compound the benzylic protons appear as a broadened doublet with $J = 8.5$ Hz. This means that a 6 Hz-coupling is lost upon deuteration. Since *cis*-coupling in the ethano-bridge of a bicyclo[2.2.1] system is always larger than the *trans*-coupling, this result means that the deuterons must be *trans* to the *endo*-benzylic proton. Hydrolysis of carbon—aluminum bonds generally occurs stereospecifically [16], so that the finding of *exo* deuterons in the *exo,exo*-2,5-diphenylnorbornane means that carbalumination itself occurred in an *exo-syn*-fashion.

2. 1,1-Dimethylindene. Although no reaction occurred when this hydrocarbon was heated with $(C_6H_5)_3Al$ in dry toluene for 48 h at 110°C, reaction did occur when 900 mg (6.2 mmol) of the indene and 1.60 g (6.2 mmol) were heated in dry decane for 72 h at 190°C. After treatment with a mixture of D_2O and DCl (10 : 1 v/v) and usual work-up, 1.94 g of crude reaction product was obtained. Gas chromatographic analysis on a 12 ft column of 10% silicone gum rubber on Chromosorb W (60—80 mesh) at 200°C showed the presence of three major and three minor (<6%) components. The most volatile product (10%) was shown to be 1,1-dimethylindan-d_3 by NMR spectral comparison with an authentic sample [17]. The second most volatile and the major product (44%) proved to be 1,1-dimethyl-3-phenylindene, as verified by comparison with the NMR spectrum of an authentic sample (NMR ($CDCl_3$): 1.78 (s, Me_2C), 6.68 (s, vinyl) and 7.34—7.9 (m, arom.)). The least volatile product (22%), coming shortly after the second component, has an NMR spectrum in excellent accord with the structure of 1,1-dimethyl-2-phenylindene (NMR ($CDCl_3$)): 1.90 (s, Me_2C), 7.3 (s, vinyl) and 7.5—8.0 (m, arom.), but the low integration of the vinyl proton (Me_2C : H = 10 : 1) may betoken some deuteration at C(3). Approximately 12% of the starting indene was detected, as well as ca. 5% of a component emerging from the chromatograph, just before the phenylindenes. This component is most likely a 1,1-dimethylphenylindan.

3. 1,2-Dihydronaphthalene. A solution of 850 mg of 1,2-dihydronaphthalene (containing 25% of 1,2,3,4-tetrahydronaphthalene: 6 mmol) and 2.0 g (8 mmol) of $(C_6H_5)_3Al$ in 50 ml of mesitylene was heated at reflux for 40 h. Gas chromatographic analysis on a 6 ft column of 10% silicone gum rubber on Chromosorb W showed that 50% of the dihydro compound remained and 25% of a new compound was now present. After collection and recrystallization from 95% ethanol, it melted at 60.0—60.5°C; NMR ($CDCl_3$) 2.70 (m, 4H), 6.49 ((br) s, 1H), 6.75 (s, 4H) and 7.0 (m, 5H), which data indicate a phenyldihydronaphthalene. The 4-phenyl-1,2-dihydro derivative is reported to be a liquid, while the 3-phenyl-1,2-dihydro compound is said to melt at 58°C and to form a 1,3,5-trinitrobenzene complex as orange needles, m.p. 110°C [25]. Since the compound isolated here formed a trinitrobenzene complex of orange needles, m.p. 106—108°C, this substance must be 3-phenyl-1,2-dihydronaphthalene.

4. cis-β-Methylstyrene. A solution of 5.9 (50 mmol) of *cis*-β-methylstyrene and 12.9 g (50 mmol) of $(C_6H_5)_3Al$ in 100 ml of mesitylene was heated to reflux for 24 h. A GLPC analysis of the hydrolyzed product with a 12 ft column of 10% silicone gum rubber on Chromosorb W showed only 5% of remaining olefin, 25% of n-propylbenzene, 25% of *trans*-1,2-diphenylpropene and 45% of 1,2-diphenylpropane. The products were collected individually and identified by NMR, IR and physical data: the diphenylpropene melted at 80—81°C (95% ethanol; lit. [4] 81°C); the diphenylpropane had characteristic signals at 1.29 (d, 3H, $J = 6.5$ Hz) and 2.72 (m, 3H) [26].

5. trans-β-Methylstyrene. A solution of 4.8 g (40 mmol) of *trans*-β-methylstyrene and 10.3 g of $(C_6H_5)_3Al$ in 100 ml of mesitylene was heated at reflux for 24 h. Work-up with D_2O and GLPC analysis showed the formation of 25% of *trans*-1,2-diphenylpropene and 8% of 1,2-diphenylpropane, as well as n-propylbenzene. The diphenylpropene was shown by NMR spectroscopy not to contain any deuterium.

6. Z-1-Phenyl-2-p-tolylethylene. A solution of 653 mg (3 mmol) of this hydrocarbon (>99% pure by GLPC) and 1.08 g (4 mmol) of $(C_6H_5)_3Al$ in 8 ml of mesitylene was heated at reflux for 19 h. Hydrolysis of a one-ml aliquot and GLPC analysis on a 12 ft column of 10% silicone gum rubber on Chromosorb W in a column temperature-programmed run between 150 and 300°C showed only three peaks, even at the lowest detector attenuation, which proved to be solvent, followed by the *cis*- and *trans-p*-methylstilbenes in a 2 : 1 ratio.

Then the remaining reaction mixture was heated at reflux an additional 40 h. Hydrolysis and analysis showed that the *cis : trans* ratio of the stilbenes was now 1 : 1.5, but no trace of any other product was found.

7. Isomeric 1,2-diphenylethylenes. a. A melt of 970 mg (5.4 mmol) of *trans*-stilbene and 1.7 g (6.6 mmol) of $(C_6H_5)_3Al$ was heated at 200°C for 18 h, but the stilbene was recovered unchanged upon hydrolysis.

b. A 1 : 1 mixture of *cis*-stilbene and $(C_6H_5)_3Al$ (17 mmol) was heated to reflux in 50 ml of mesitylene for 40 h. Hydrolysis revealed only a 1 : 1 mixture of *cis*- and *trans*-stilbenes.

c. When a 1 : 1 melt of *cis*-stilbene and $(C_6H_5)_3Al$ (6 mmol) was heated at 200°C for 18 h, hydrolysis and GLPC analysis showed the presence of *cis*- and *trans*-stilbenes (92% in a 7 : 93 ratio), 1,1,2-triphenylethane (5%) and triphenylethylene (3%). All products were collected and identified by NMR, IR and mass spectral data.

d. A neat run, identical with the foregoing, was carried out, but the hydrolysis was done with D_2O. The *cis*-stilbene was isolated by GLPC collection and then analyzed by mass spectrometry. For mass spectral comparison, an authentic sample of *cis*-stilbene (Aldrich) was purified by two successive GLPC collections and then analyzed with an LKB spectrometer, model 9000, at 70 e.V.: the isolated *cis*-stilbene gave a $(P + 1) : P$ ratio of 0.1628 ± 0.0038 (6 scans), while the control sample gave a ratio of 0.1529 ± 0.0066 (5 scans). The isotopic abundance reported for a $C_{14}H_{12}$ molecule is 0.1538. Calculation leads to a deuterium content of 1.0% for the isolated *cis*-stilbene. Repeated NMR integration of the signals of *cis*-stilbene indicates that 1—2% of deuterium is located on the olefinic carbon atom.

e. As a control, the *cis*-stilbene was heated without $(C_6H_5)_3Al$ at 200°C for 18 h; no isomerization was observed.

8. E-1,2-Di-p-methoxyphenylethylene. A solution of this stilbene (1.68 g, 7.0 mmol) and $(C_6H_5)_3Al$ (1.80 g, 7.0 mmol) was heated in 75 ml of mesitylene at reflux for 48 h. After work-up with D_2O a quantitative recovery of the stilbene was obtained. Analysis by GLPC showed no other component, and IR and NMR spectral examination revealed no deuterium incorporation.

9. 3,3,3-Triphenylpropene. Heating a 1 : 1 mixture of this olefin and $(C_6H_5)_3$-Al on a 2 millimolar scale, either for one week in refluxing mesitylene or for 72 h in a neat melt at 190°C, and then treating the mixture with D_2O led to the recovery of only the undeuterated starting olefin.

When a 1 : 1 neat mixture of the reagents (2.0 mmol) was heated at 225°C for 72 h, work-up with D_2O and column chromatographic separation of the crude products (620 mg) on silica gel gave the following products: (a) ca. 1 : 1 mixture of *trans*-stilbene and 1,1-diphenylethylene; NMR ($CDCl_3$): vinyl signals at 7.06 and 5.32 ppm, aromatic multiplet at 7.2—7.65 and a sharp singlet at 7.17 ppm; mass spectrum (70 eV): base peaks at 180, 181 and 182, with ca. same intensity, indicating considerable mono- and di-deuteration; (b) triphenylmethane; NMR ($CDCl_3$): singlets at 5.44 and 7.04 ppm with peak ratio of 160 : 5, indicating ca. 50% deuteration on the α-carbon; mass spectrum (70 eV): strong peaks at 243, 244, 245 and 246 confirmed that ca. 50% monodeuteration had occurred; and (c) higher fractions that could not be resolved; NMR ($CDCl_3$): aromatic absorptions only; mass spectrum (70 eV): prominent peaks at 347 (phenylation of the olefin) and 540 (dimerization of the olefin).

10. Other hydrocarbon substrates. The following hydrocarbons underwent little or no reaction with $(C_6H_5)_3Al$: 1-phenylcyclopentene (mesitylene, 180°C, 24 h), cyclopentene (mesitylene in a Hoke tube, 140°C, 15 h), phenylcyclopane (neat, 190°C, 8 h) and 1,1-diphenylcyclopropane (mesitylene, 180°C, 45 h).

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