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ORGANOMETALLIC COMPOUNDS OF GROUP III

XIVV*. ORIENTATION IN THE HYDRALUMINATION OF CONJUGATED OLEFIN HYDROCARBONS. BEHAVIOR OF ALLYLIC ORGANOALUMINUM SYSTEMS

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Summary

In order to evaluate steric and electronic factors in the hydralumination of p_π- and d_π-conjugated olefins, the following compounds have been treated with diisobutylaluminum hydride: 1,1-diphenylethylene; 1,1-diphenylallene; 1,1-diphenyl-1,3-butadiene; acenaphthylene; triethylvinylsilane; and triphenylvinylsilane. The sites of the resulting carbon—aluminum bonds in the adducts have been deduced by a combination of NMR spectroscopy, hydrolysis with D_2O, oxidation and carbonation. Hydralumination of 1,1-diphenylethylene gave only the 1,1-diphenyl-2-aluminoethane adduct; 1,1-diphenylallene gave a mixture of the 3-alumino-1,1-diphenyl- and 3-alumino-3,3-diphenyl-propenes, whose proportions varied with the Lewis base present; and 1,1-diphenyl-1,3-butadiene gave a mixture of 4-alumino- and 3-alumino-1,1-diphenyl-1-butenes, together with 1-alumino-1,1-diphenyl-2-butene, whose composition was subject to both kinetic and thermodynamic control. Both the vinylsilanes gave a 70/30 mixture of the 1-silyl-1-alumino- and 1-silyl-2-alumino-ethanes with diisobutylaluminum hydride. When triethyl(vinyl)silane was heated with one-third mole of triisobutylaluminum, the ratio of 1- and 2-aluminoethanes fell to 18/82. Finally, acenaphthylene underwent smooth hydralumination to yield 1-acenaphthyl-(diisobutyl)aluminum. Protolysis yielded varying amounts of acenaphthene and its ring protonated isomer, while carbonation yielded only acenaphthene-3-carboxylic acid.

These results show that, in the absence of adverse steric factors, p_π- and d_π-conjugation favor the internal attachment of aluminum in hydralumination. Moreover, in cases where allylic aluminum systems result, the aluminum seems

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* For previous part, see ref. 32.

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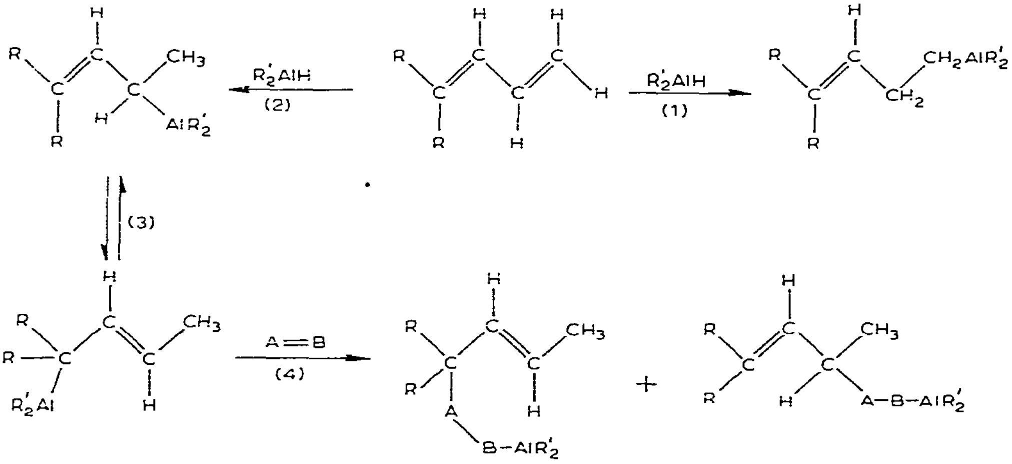
to prefer attachment to the site of highest electron density in the hypothetical anion R$^-$.

Introduction

The hydralumination of conjugated olefinic hydrocarbons warrants further study for two reasons. Firstly, any regioselectivity of Al—H bond addition can offer insight into the electronic and steric factors operative in hydralumination (eqns. 1 and 2) and, secondly, this reaction offers a novel route to allylic organoaluminum compounds (eqn. 2). In the latter case, there exists the possibility of further observing the dynamic character of such allylic compounds (eqn. 3) or of detecting rearrangements in their reactions (eqn. 4).

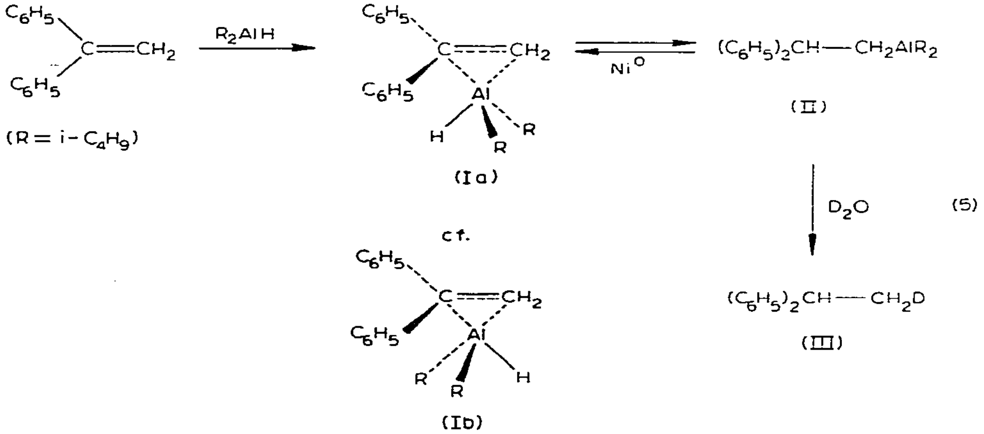


Previous hydraluminations of conjugated polyenes offered encouragement that competing modes of Al—H bond addition (eqns. 1 and 2) would be observed. Thus, although hydralumination of terminal alkenes gives usually 95% of the 1-alumino adduct (eqn. 1) and only 5% of the 2-alumino adduct (eqn. 2) [1], styrene yields up to 24% of the internal alumino product [2]. As a further apparent influence of conjugation on regioselectivity, 6,6-dimethylfulvene adds the Al—H bond to form only the adduct with the aluminum attached to the cyclopentadienyl ring [3]. Since the behavior of styrene and the fulvene suggests the importance of conjugation on regioselectivity, a series of unsymmetrical, phenyl-substituted alkenes was hydraluminated with diisobutylaluminum hydride and the resulting organoaluminum adducts characterized by hydrolysis with water or deuterium oxide. Although allylic aluminum compounds, arising as in eqns. (2) and (3), have a tendency to auto-addition [4,5], it was hoped that such polymerization would be minimized by the use of geminal diphenyl systems (eqns. (1) - (4), R = C_6H_5). Furthermore, in evaluating the effect of conjugation in a broader sense, it was of interest to determine the regioselectivity for the hydralumination of vinylsilanes, such as triethyl(vinyl)silane and triphenyl(vinyl)silane. Since vinylsilanes exhibit chemical properties explicable in terms of d_π—p_π conjugation between silicon and carbon [6,7], their behavior in hydralumination seemed to merit comparison with that of phenylalkenes, where p_π—p_π conjugation obtains.

Results and discussion

The series of geminal diphenyl-substituted hydrocarbons, 1,1-diphenylethylene, 1,1-diphenylallene and 1,1-diphenyl-1,3-butadiene, was chosen as substrate for hydralumination. In addition, acenaphthylene offered a system where the double bond was doubly conjugated with an aromatic nucleus. Vinylsilanes of the type, $R_3SiCH{=}CH_2$ ($R = C_2H_5$ and C_6H_5), were selected for similar hydralumination, in order to learn whether the electronic or steric character of R would lead to significant differences in regioselectivity. After the hydraluminations had been conducted to complete consumption of the unsaturated substrate, the resulting organoaluminum adducts were hydrolyzed with H_2O or D_2O and the hydrocarbons isolated and assayed by a combination of gas chromatography, NMR spectroscopy and mass spectrometry. The results are compiled in Tables 1 and 2.

The interpretation of these results involves the following key considerations: *(a)* whether the hydrocarbons obtained upon hydrolysis accurately reflect the kinds and amounts of organoaluminum precursors; that is, whether hydrolysis occurred without rearrangement; *(b)* whether hydralumination can give kinetically-controlled or thermodynamically-controlled products; *(c)* whether the donor character of the solvent can favor the stability of one allylic organoaluminum isomer over the other (e.g. eqn. 3); and *(d)* whether an allylic organoaluminum isomer of known structure can undergo cleavage reactions with definite rearrangement (eqn. 4). As the ensuing discussion will show, all the foregoing questions can be given an affirmative answer for certain systems. Due to the subtle complexity of allylic aluminum systems, however, it will be seen that generalizations can be very precarious.



Despite the considerable amount of 1-alumino adduct obtained with styrene, the hydralumination of 1,1-diphenylethylene yielded only the 2-alumi-

TABLE 1

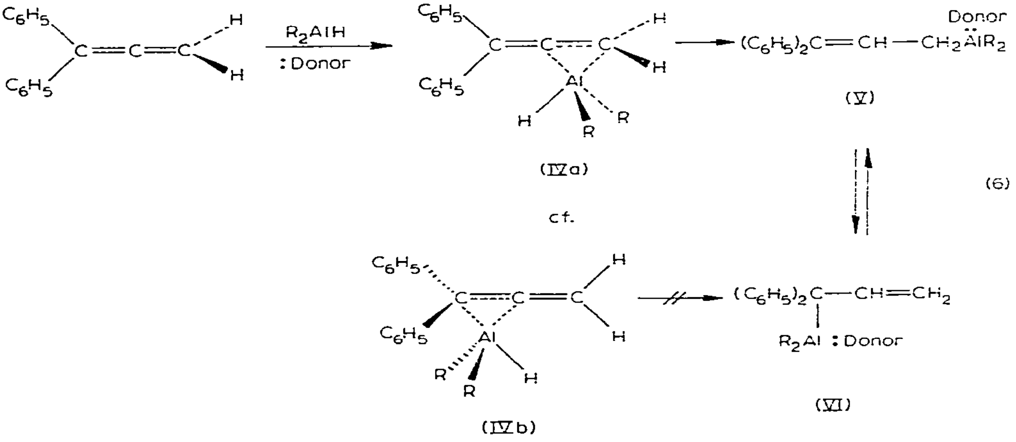
REACTIONS OF 1,1-DIPHENYLALKADIENES WITH DIISOBUTYLALUMINIUM HYDRIDE

Reaction method	Olefin (mole)	Hydride (mole)	Reaction time (h)	Reaction temp. (°C)	Solvent	Product (D_2O or H_2O treatment)	% yield	% conversion
1,1-Diphenylethylene								
A[a]	0.026	0.039	6 36	114 114		$(C_6H_5)_2CH{-}CH_3$	100	100
A	0.026	0.039	36	110		$(C_6H_5)_2CH{-}CH_2D$	100	100
A	0.026	0.039	1 60	145 145		$(C_6H_5)_2CH{-}CH_2D$	100	100
A	0.026	0.039	24 24	145[b] 145		$(C_6H_5)_2CH{-}CH_2D$	100	100
1,1-Diphenylallene								
A	0.0114	0.0114	17	45	Heptane (60 ml)	Polymer		>90
C	0.0114	0.0114	21	68	Heptane (50 ml) Et_3N(0.0114 mol)	$(C_6H_5)_2CHCH{=}CH_2$ $(C_6H_5)_2C{=}CHCH_3$ Polymer	38 22 50	>95
C	0.0114	0.0114	16	68	Heptane (50 ml) Et_3N(0.0114 mol)	$(C_6H_5)CHCH{=}CH_2$ $(C_6H_5)_2C{=}CHCH_3$ Polymer	25 16 35[c]	76
C	0.0114	0.0114	16	68	Heptane (50 ml) Et_3N(0.0114 mol)	$(C_6H_5)_2CD{-}CH{=}CH_2$ $(C_6H_5)_2C{=}CH{-}CH_2D$ Polymer	26 16 33[c]	75
C	0.0114	0.0114	16	68	Heptane (50 ml) Et_2O90.0114 mol)	$(C_6H_5)_2CH{-}CH{=}CH_2$ $(C_6H_5)_2C{=}CH{-}CH_3$ Polymer	37 4 37[c]	78
C	0.0114	0.0114	20	78	Heptane (50 ml) Et_2O(0.0114 mol)	$(C_6H_5)_2CD{-}CH{=}CH_2$ $(C_6H_5)_2C{=}CH{-}CH_2D$ Polymer	32 6 38[c]	76
1,1-Diphenyl-1,3-butadiene								
A	0.029	0.029	21 12 4	108 135 145	Heptane (20 ml) >108° Neat	*trans*-$(C_6H_5)_2CHCH{=}CHCH_3$ $(C_6H_5)_2C{=}CHCH_2CH_3$	60–24 40–76[d]	83
A	0.029	0.029	7	90	Heptane (20 ml)	*trans*-$(C_6H_5)_2CHCH{=}CHCH_3$ $(C_6H_5)_2C{=}CHCH_2CH_3$	64 36[e]	95
A	0.029	0.029	7	90	Heptane (20 ml)	*trans*-$(C_6H_5)_2CDCH{=}CHCH_3$ $(C_6H_5)_2C{=}CHCH_2CH_2D$	62 38	95
A	0.029	0.029	21	110	Heptane (20 ml)	*trans*-$(C_6H_5)_2CHCH{=}CHCH_3$ $(C_6H_5)_2C{=}CH{-}CH_2CH_3$	54 46	

[a] The variations in the methods of admixing the reagents are given in the Experimental. [b] After 24 h at 145° 25 mg of anhydrous nickel(II) acetylacetonate were added. [c] By "polymer" is meant the undistillable residue, which contained various other oligomers, such as (IX). [d] The initial heating period at 108° led to a 60/40 mixture of (XIV)/(XV); after further heating at 145°, the ratio became 24/76. [e] The *meso*- and *d,l*-3,4-dimethyl-1,1,6,6-tetraphenyl-1,5-hexadienes separated from the attempted crystallization of the distillation residues.

no adduct (eqn. 5). The NMR spectrum of (III) displayed a triplet at 4.09 ppm and a doublet of triplets at 1.53 ppm in an intensity ratio of 1.0/2.1, consistent with > 96% deuteration at the methyl group. Even under conditions of equilibration between olefin and R_2AlH, namely, heating with colloidal nickel [2,8], only (III) was formed upon treatment with D_2O showing that (II) is the thermodynamically more stable adduct. Apparently, steric factors operative in the transition state [(Ia) vs. (Ib)] also make it the kinetically favored adduct.

Direct hydralumination of 1,1-diphenylallene led to extensive dimerization and polymerization, rather than to monoreduction. The only well-defined product isolated was 1,1,4,4-tetraphenyl-1-hexene, (IX). By using equimolar amounts of either triethylamine or diethyl ether as a co-solvent, however, the hydralumination could largely be confined to the monoreduction stage. Treatment with D_2O gave a mixture of 1,1-diphenylpropene, (VII), and 3,3-diphenylpropene, (VIII), which were shown by NMR analysis to be deuterated exclusively at C_3 and at C_3, respectively. The NMR spectrum of deuterated (VII) showed the methyl doublet at 1.77 ppm with deuterium splitting and an intensity corresponding to two protons; that of (VII) no longer showed the doublet signal at 4.61 ppm. The proportion of hydrolyzed products, (VII) and (VIII), varied from 42/58 ± 2 for triethylamine to 13/87 ± 2 for diethyl ether. The absence of any of (VII) or (VIII) having a deuteron at C_2 means that only 1-alumino or 3-alumino allylic systems [(V) and (VI)] were initially formed (eqn. 6). From the behavior of 1,1-diphenylethylene it is reasonable to conclude that (VI) is not formed via transition state (IVb), because of strong steric repulsion between the *geminal*-phenyl and *geminal*-isobutyl groups. Rather (VI) would result via (IVa) and (V) by means of an allylic rearrangement. Since the NMR spectra of (V) and/or (VI) could not be observed directly, it is not certain whether the amounts of (VII) and (VIII) accurately reflect the ratio of (V) and (VI). However, it is attractive to consider that steric factors and Lewis basicity should favor the formation of 3-deuterio-1,1-diphenylpropene (eqn. 7); with the smaller ether molecule more of (VI) and hence more of (VIII) would be expected.



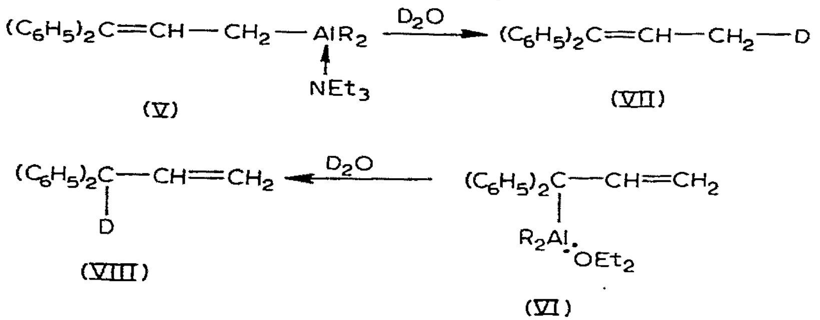
The formation of (IX) in the absence of donor solvent could be depicted

TABLE 2

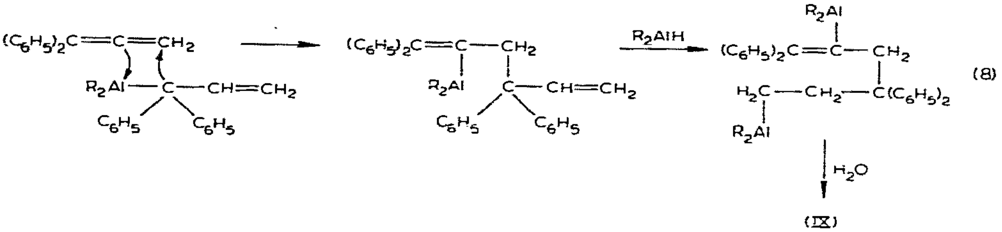
REACTIONS OF VINYLSILANES WITH DIISOBUTYLALUMINIUM HYDRIDE

Reaction method	Olefin (mole)	Hydride (mole)	Reaction time(h)	Reaction temp. (°C)	Solvent	Product (H_2O, D_2O or O_2)	% yield	% recovery
Triethyl(vinyl)silane								
C	0.134	0.144	4	75		$(C_2H_5)_4Si$		95
C	0.134	0.144	4	75		$(C_2H_5)_3SiCHDCH_3$ $(C_2H_5)_3SiCH_2CH_2D$	70 30	100
A	0.100	0.100[a]	15	79		$(C_2H_5)_3SiOH$ $(C_2H_5)_3Si\underset{OH}{C}HCH_3$ $(C_2H_5)_3SiCH_2CH_2OH$	88[b] 9 3	75[c]
A	0.100	0.033[a]	18	165		$(C_2H_5)_3SiOH$ $(C_2H_5)_3Si\underset{OH}{C}HCH_3$ $(C_2H_5)_3SiCH_2CH_2OH$	59[b] 8 33	63[c]
C	0.100	0.100	19	70	Benzene (50 ml)	$(C_2H_5)_3SiOH$ $(C_2H_5)_3Si\underset{OH}{C}HCH_3$ $(C_2H_5)_3SiCH_2CH_2OH$	61[b] 26 13	52[c]
Triphenyl(vinyl)silane								
B	0.020	0.020	40	100	Heptane (50 ml)	$(C_6H_5)_3SiCH_2CH_3$		86
A	0.020	0.020	48	100	Heptane (50 ml)	$(C_6H_5)_3SiCHDCH_3$ $(C_6H_5)_3SiCH_2CH_2D$	70 30	77

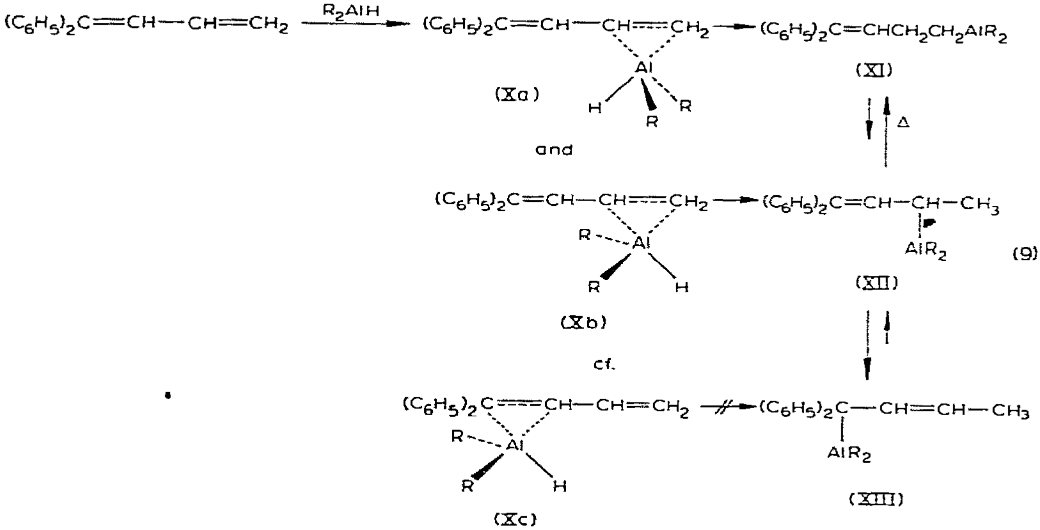
[a] Triisobutylaluminum was used as the source of diisobutylaluminum hydride. [b] Work-up of the organoaluminum adducts involved aerial oxidation. [c] Percent recovered represents the distillable product.



in the following manner. The now predominant (VI) would add to the allene in a 2,3 fashion, followed by a 1,2-hydralumination (eqn. 8). The interactions leading eventually to (IX) are in best accord with sterically governed 1,2-additions to carbon—carbon unsaturation [9].



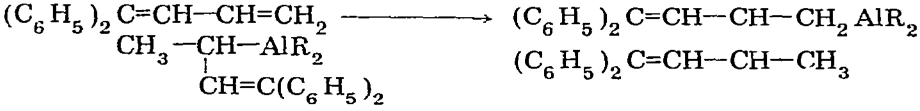
The hydralumination of 1,1-diphenyl-1,3-butadiene at 90° and subsequent treatment with D_2O led to a 60/40 mixture of *trans*-1,1-diphenyl-2-butene, (XIV), and 1,1-diphenyl-1-butene, (XV), which were only deuterated at C_1 and at C_4, respectively. That this product ratio was kinetically controlled was shown by heating the aluminum adducts at higher temperatures before hydrolysis; at 110° the kinetic ratio was 55/45 and at 145° the thermodynamic ratio was 24/76. These results are consistent with the presence of (XI), (XII) and



(XIII) as organoaluminum precursors (eqn. 9). There is no doubt that (XI) is the precursor of the 1-butene, but the 2-butene could arise from (XII) or (XIII), with or without allylic rearrangement, respectively. Because this hydralumination proceeded relatively cleanly at 90°, a direct NMR examination of the aluminum adducts was possible. With reference to the phenyl signal as 10 protons, the vinyl region had an intensity of 1.5 ± 0.05 protons and displayed a triplet centered at 6.05 ppm (*J* 8 Hz) and two partially resolved broad signals at 6.3 and 6.4 ppm (*J* 2 Hz), each having suggestion of hyperfine splitting. Since a hydrolyzed sample gave a 64/36 mixture of (XIV)/(XV), one would expect a vinyl proton count of 1.6 [0.64 × 2H for (XIII) + 0.36 × 1H for (XI)], if the hydrocarbon ratio accurately reflected the ratio of aluminum precursors. If, on the other hand, only (XI) and (XII) were present, a vinyl count of 1.0 would be expected. Since the observed count is 1.5, we conclude that the aluminum precursor of (XIV) is preponderantly, if not exclusively, (XIII). Therefore, hydrolysis with D_2O does appear to label the allylic Al—C bond reliably in this case.

Since a terminal olefinic linkage is far more reactive than an internal bond [10] and since (Xc) is a very unfavorable transition state for a 1,1-diphenylalkene [cf. (Ib)] (Xa) and (Xb) are the most likely routes to (XI) and (XII), respectively. Structure (XIII), the observed allylic aluminum isomer, would then arise from (XII) by rearrangement. The preferential formation of (XI) at higher temperatures would then involve a dehydralumination of (XII) and re-hydralumination to form the more stable product, (XI). Here, thermodynamic control runs counter to kinetic control. Although (XIII) might seem directly obtainable from the diene by a 1,4-hydralumination, such a reaction suffers from the same steric hindrance encountered in the 1,2-additions depicted in (Ib), (IVb) and (Xc).

From certain distillation residues of the hydrolysis products small amounts of *meso*- and *d,l*-3,4-dimethyl-1,1,6,6-tetraphenyl-1,5-hexadiene were obtained. These seemed to have arisen from the following reaction:



$$\begin{array}{lcl} (C_6H_5)_2C{=}CH{-}CH{=}CH_2 & \longrightarrow & (C_6H_5)_2C{=}CH{-}CH{-}CH_2AlR_2 \\ \quad CH_3{-}\underset{\displaystyle CH{=}C(C_6H_5)_2}{\underset{|}{CH}}{-}AlR_2 & & (C_6H_5)_2C{=}CH{-}CH{-}CH_3 \end{array}$$

The hydralumination of acenaphthylene at 90° yielded a monoadduct which by NMR at 35° was shown to have proton intensities and chemical shifts consistent with the acenaphthylaluminum structure (XVI). Depending upon the mode of protolysis and the nature of the reagent, the amount of 1-deuteration can vary from 90 to 50%. Thus, variable amounts of allylic rearrangement occur upon hydrolysis*. On the other hand, carbonation of (XVI) yields exclusively the allylic rearrangement product, acenaphthene-3-carboxylic acid (eqn. 10).

Finally, the hydralumination of both triphenyl(vinyl)silane and triethyl(vinyl)silane, followed by treatment with D_2O and NMR analysis of the products, showed that both silanes gave a 70/30 mixture of 1- and 2-deuterio-

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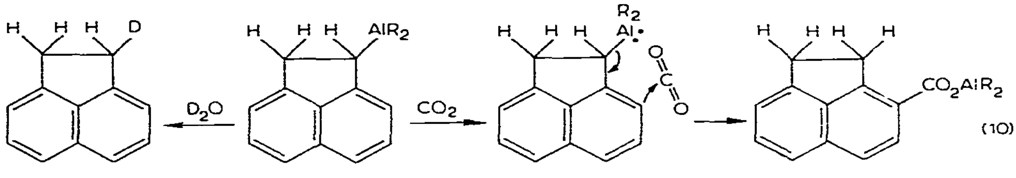
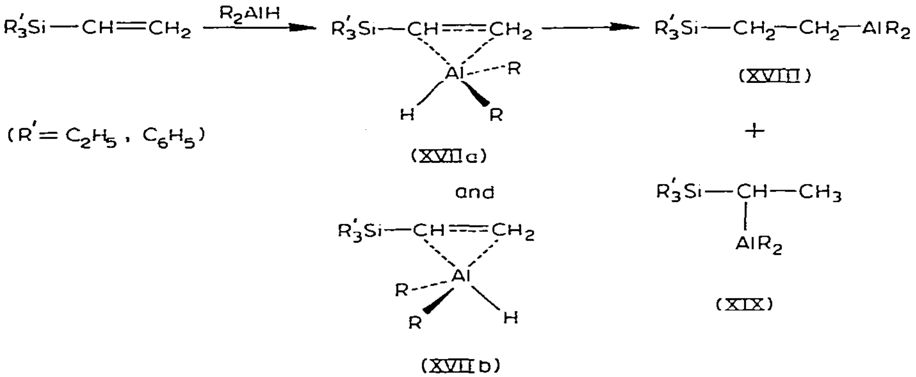
* Unpublished studies by K.C. Fichter of this laboratory.



(XVI)

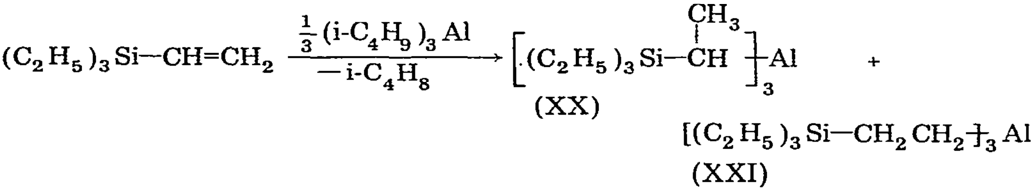
(10)

ethanes (eqn. 11). From these results it is clear that the silicon center, rather than the nature of R', has a significant electronic effect on the regioselectivity. The sterically less favored adduct (XIX), is the major adduct. Although the air oxidation of (XVIII) and (XIX) leads principally to rearrangement products



(11)

[11], the ratio of 1- and 2-trialkylsilylethanols obtained, 67/33 ± 1, is in good agreement with the deuteration results*. The ratio of (XVIII) to (XIX) formed was shown to be sensitive to the steric requirements of the hydraluminating agent. When triethyl(vinyl)silane was heated with one-third mole of triisobutylaluminum (eqn. 12) and the tris(triethylsilylethyl)aluminums air-oxidized, the ratio of the 1- and 2-triethylsilylethanols was 18/82. This indicates that (XXI) was now the principal organoaluminum precursor:



$$(C_2H_5)_3Si{-}CH{=}CH_2 \xrightarrow[-i\text{-}C_4H_8]{\frac{1}{3}(i\text{-}C_4H_9)_3Al} \Big[(C_2H_5)_3Si{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}\Big]_3 Al + [(C_2H_5)_3Si{-}CH_2CH_2]_3Al$$

(XX)

(XXI)

Although some increased amount of the 1-ethanol has also been observed in the hydroboration and oxidation of vinylsilanes [12], these hydralumination results show that either a 1-alumino or a 2-alumino adduct can predominate, depending upon the importance of electronic or steric factors**.

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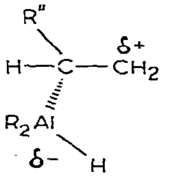
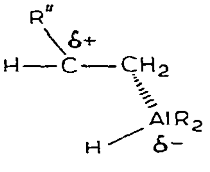
* Although much triethylsilanol arises in this oxidation, it has been shown that this product is formed only through the rearrangement of aluminum hydroperoxides of (XVIII) and (XIX), and not by the hydrolytic cleavage of either triethylsilylethanol. Hence, the ratio of silylethanols is not changed by any β-elimination in this case.

** In the reductive dimerization of vinylsilanes by small amounts of triisobutylaluminum, only β,β-coupling was observed. The ratio of (XVII)/(XIX) was not determined, but the dimerization was attributed to (XVIII) [13].

The foregoing results permit certain comparative observations. First of all, the R_3Si is superior to the phenyl group in favoring internal attachment of aluminum in hydralumination. Since hydralumination has the electronic character of electrophilic attack by aluminum [14], we can conclude that the activation energy for attaining (XXII) is lower than that for (XXIII) when $R'' = R'_3Si$, while the reverse situation obtains when $R'' = C_6H_5$ or alkyl.



(XXII)



(XXIII)

The relatively lower energy of (XXII) can be ascribed to greater availability of electron density at the carbon α to silicon due to $d_\pi-p_\pi$ overlap [7]. The considerable amount of internal aluminum attachment with styrene can analogously be ascribed to some electron density build-up α to phenyl, but this $p_\pi-p_\pi$ effect must be less important than the aforementioned $d_\pi-p_\pi$ effect.

Secondly, where steric factors do not intervene, the $p_\pi-p_\pi$ effect in dienes again favors strongly the internal attachment of aluminum, as in (XIII), when kinetic control of products obtains. Thirdly, allylic aluminum systems, such as (V), (VI), (XII), (XIII) and (XVI), can undergo allylic isomerizations or rearrangement reactions with varying ease. Where spectroscopic or indirect chemical evidence permits some judgment, it appears that discrete isomers, rather than fluxional systems, exist. In the absence of donor solvents, it seems that the aluminum in $R'AlR_2$ attaches itself to the site of highest electron density in the hypothetical anion R'^- [15]. Although such a view would rationalize the preferred formation of (VI), (XIII) and (XVI), it is only a hypothesis to be subjected to more rigorous testing.

Experimental

General procedures

All transfers and addition reactions of organoaluminum compounds were performed under an atmosphere of dry, oxygen-free nitrogen. Apparatus for the preparation of diisobutylaluminum hydride and its reaction with unsaturated hydrocarbons has been described previously [16]. Solvents of reagent grade were distilled from lithium aluminum hydride, when used as media for organoaluminum reactions. The manipulation and hydrolysis of aluminum alkyls were conducted according to procedures already described [17], but additional provisions were made for hydrolyses with deuterium oxide (99.8%). Thus, vessels used to introduce the deuterium oxide were rinsed, while hot, with deuterium oxide and then heated under vacuum. Final cooling ensued under a stream of dry nitrogen. Then dry solvent (anhydrous pentane, ether or benzene) was distilled directly into the vessel and the deuterium oxide added directly from its original ampoule. To this cooled biphasic system was added dropwise a solution of the organoaluminum compound diluted with the same organic solvent. The precipitate of aluminum hydroxide was removed by filtration through a coarse glass frit. The separated organic layer was dried over anhydrous calcium sulfate and the organic products analyzed or isolated by standard methods.

Infrared and ultraviolet spectra were recorded on a Perkin—Elmer double-beam spectrophotometer, model 21 (NaCl optics) and a Cary spectrophotometer, model 14, respectively. Quantitative infrared spectral determinations employed the empirical ratio method [18].

NMR spectral analysis were made on Varian spectrometers, models A-60 and HA-100, employing the integration technique of Jungenickel and Forbes [19]. Hence, the percentage of products so established should be of comparable precision and accuracy. Special analytical problems meriting special comment are the following:

(a) The relative amounts of α- and β-deuteriotetraethylsilanes were determined by recording the spectrum of neat, undeuterated tetraethylsilane and, using the same sample tube and instrument settings, the spectrum of monodeuterated tetraethylsilane. The difference in the heights of the α- and β-proton regions between the two recordings gave the amounts of α- and β-deuteriotetraethylsilanes (± 9%). For the deuterated ethyl(triphenyl)silane (98% monodeuterated by mass spectrometry) the splitting patterns for the α- and β-protons were separable at 100 MHz. Then the total alkyl proton integration was assumed equal to 4.0 protons; accordingly, the amounts of α- and β-deuteration were assignable to within ± 5%.

(b) The position and extent of deuteration in the hydrocarbons from the hydralumination of 1,1-diphenylethylene, 1,1-diphenylallene and 1,1-diphenyl-1,3-butadiene followed from comparison with undeuterated samples and from use of the phenyl peak near 7.2 ppm as an internal standard of 10 protons.

(c) The total deuteration of acenaphthene was estimated to ± 3% by using a sample of hexamethylbenzene as an internal proton-counting standard. The position of deuteration (± 10%) was assigned based upon a published analysis [20].

Total deuterium content was also determined by the falling-drop method [21], as well as by mass spectrometry. Molecular weights were estimated by the Rast method and by mass spectrometry at 70 eV.

Vapor phase chromatography was carried out with a Barber—Coleman unit, model 10, equipped with 10% silicone oil-on-firebrick columns.

Starting materials and products

The following compounds were purchased or prepared according to published procedures: 1,1-diphenylethylene, 1,1-diphenylethane, 1,1-diphenylallene [22,23], 3,3-diphenyl-1-propene [24], 1,1-diphenyl-1,3-butadiene [25], 1,1-diphenyl-1-butene [26], 1,1-diphenylbutane [27], tetraethylsilane [28], ethyl(triphenyl)silane and 3-carbomethoxyacenaphthene [29].

For purposes of spectral comparison, a sample of *trans*-1,1-diphenyl-2-butene (admixed with the simultaneously formed 1,1-diphenylbutane) was prepared from 1,1-diphenyl-1,3-butadiene. Thus, a stirred solution of 14.0 g (68 mmol) of the diene in 100 ml of absolute ethanol and 50 ml of hexane was brought to reflux and then slowly treated with 7.8 g (340 mmol) of sodium, cut in pea-sized pieces. After all sodium had been consumed, the mixture was hydrolyzed cautiously and worked up. The distillation of the separated and dried organic layer yielded 7.5 g of product (b.p. 76 - 77°/0.5 mmHg). Infrared (965 cm^{-1}) and NMR analyses confirmed that only the *trans*-2-butene (75%) and the butane were present.

Acenaphthylene purchased from the Aldrich Chemical Company was chromatographed on Fluorisil and eluted with petroleum ether (boiling range 30 - 60°), m.p. 89 - 91°. Subsequent NMR analysis indicated the presence of 7% acenaphthene (% acenaphthene = $2B \cdot 100/(A + B/2)$, where A and B are the integrated intensities of the aromatic protons and the benzylic protons, respectively). Acenaphthene (Eastman Technical Grade) was recrystallized twice from 95% ethanol and then sublimed, m.p. 93 - 94°.

1-Triethylsilylethanol

1-Triethylsilylethyl chloride [30]. A mixture of 23.0 g (0.18 mol) of tetraethylsilane, 21.6 g (0.16 mol) of sulfuryl chloride and 80 mg of benzoyl peroxide was heated for 3 h under gentle reflux, while the evolved hydrogen chloride was trapped in a sodium hydroxide solution. Subsequent distillation yielded 6.2 g of the chloride (37% conversion), b.p. 96 - 97°/33 mmHg.

1-Triethylsilylethyl bromide [31]. A 250 ml, two-necked, round-bottomed flask was fitted with a thermometer and vertical, 15 cm column filled with glass beads. The column was surmounted by a Y-tube connected to a reflux condenser and to an addition funnel. A charge of 90.0 g (0.63 mol) of tetraethylsilane was permitted to reflux through the column, while 100 g (0.63 mol) of bromine was slowly added to the hot silane vapor from the addition funnel. At the end of the addition the pot temperature had reached 185°. After a crude distillation, bisulfite treatment and redistillation, 14.6 g of the bromide were obtained (10% conversion, b.p. 90 - 91°/8 mmHg, n_D^{25} 1.4720).

1-Triethylsilylethyl acetate [31]. A mixture of 11.9 g of the chloride (0.066 mol), 6.9 g (0.070 mol) of potassium acetate and 10.5 g of glacial acetic acid was heated to reflux for 8 h, diluted with water and then extracted with ether. The ether extracts, after a sodium bicarbonate washing and drying over anhydrous calcium sulfate, were evaporated and distilled to yield 5.3 g (36%) of the acetate.

A similar reaction with the bromide led to a 55% yield.

1-Triethylsilylethanol. A solution of the acetate (7.3 g, 0.036 mol) in 25 ml of anhydrous ethyl ether was added to a slurry of 3.5 g (0.090 mol) of $LiAlH_4$ in 90 ml of ether at such a rate as to maintain gentle reflux. After 3 h at room temperature usual work-up yielded 2.0 g (35%) of the 1-ethanol, b.p. 121 - 122°/80 mmHg, n_D^{25} 1.4485, possessing a strong, camphor-like odor. Analysis found: C, 59.66; H, 12.49. $C_8H_{20}OSi$ calcd.: C, 59.93; H, 12.57%.

2-Triethylsilylethanol

This compound was obtained in ca. 20% yield in the following sequence.

Trichloro(methyl)silane was photochlorinated to yield trichloro(chloromethyl)silane in 56% yield; the latter compound with three equivalents of ethylmagnesium bromide gave chloromethyl(triethyl)silane in 89% yield; and, finally, the Grignard reagent of the latter compound with gaseous formaldehyde gave the 2-ethanol.

A better procedure involved the hydrosilation of vinyl acetate. Thus, a mixture of 34.4 g (0.4 mol) of vinyl acetate and 1.0 g of ionol was added dropwise over a period of 24 h to 54.0 g (0.4 mol) of trichlorosilane containing 4 drops of 10% chloroplatinic acid in 2-propanol. Subsequent distillation provided 49 g (56%) of the 2-trichlorosilylethyl acetate, b.p. 80 - 82°/8 mmHg.

The foregoing acetate (49 g, 0.22 mol) was slowly added to the Grignard reagent formed from 1.8 mol of ethyl bromide and 2 g-atom of magnesium turnings in 800 ml of ethyl ether. After 48 h at reflux and the usual work-up, 20.2 g (57%) of the 2-triethylsilylethanol was obtained as a fruity-smelling liquid, b.p. 110 - 113°/10 mmHg, n_D^{25} 1.4510. Analysis found: C, 59.71; H, 12.71. $C_8H_{20}OSi$ calcd.: C, 59.93; H, 12.57%.

Hydralumination procedures

The apparatus consisted of a three-necked, round-bottomed flask equipped with magnetic stirring and provided with a sampling port, a reflux condenser connected to the nitrogen line and a pressure-equalized addition funnel.

Three procedural modifications were employed. (A) the hydrocarbon, solvent and hydride were mixed at once, and the resulting mixture brought promptly to the stated temperature; (B) the hydride in solution was added dropwise to the hydrocarbon dissolved in the same solvent; and (C) the hydrocarbon was added dropwise to a solution of the hydride.

Carbonation of (1-acenaphthyl)diisobutylaluminum

Hydralumination of 2.2 g (0.014 mol) of acenaphthylene by 2.5 g (0.018 mol) of diisobutylaluminum hydride in 50 ml of heptane, after 12 h at reflux, had gone 70% to completion, as shown by hydrolysis of an aliquot and NMR spectral analysis. Gaseous, dry carbon dioxide was introduced into the mixture at room temperature, until heat was no longer noticed. Usual work-up under basic conditions yielded 0.78 g (35%) of acenaphthene. Acidification of the alkaline layer gave a precipitate that was collected and washed repeatedly with hot water. Recrystallization of the residue gave 1.25 g (65%) of 3-acenaphthenoic acid, m.p. 255 - 256° (lit 255 - 256°); infrared band at 1650 - 1700 cm^{-1} indicative of an α,β-unsaturated acid. This acid was converted into its methyl ester by the method of Edwards and Petrov [29], m.p. 70 - 71°. Its NMR spectrum in $CDCl_3$ showed absorptions at 3.1 - 3.8 (4H), 3.88 (3H) and 7.0 - 8.0 (5H) ppm.

Oxygenation of diisobutyl(1- and 2-triethylsilylethyl)aluminums

After the addition of diisobutylaluminum hydride to triethyl(vinyl)silane had gone to completion, the reaction mixture was diluted with 100 ml of hexane, benzene or octane, depending upon the temperature desired for the terminal heating period in the oxygenation. The solution was cooled in an ice bath and then one of two procedures was followed: (A) dry air was passed over the surface of the stirred solution, until an exotherm had ceased; then oxygenation was continued while heating in a bath; and (B) a mixture of dry oxygen and nitrogen was bubbled into the mixture by way of an immersed capillary tube; the oxygen content was varied from a trace up to pure oxygen; then heating was applied, as before.

Reductive dimerization of 1,1-diphenylallene and of 1,1-diphenyl-1,3-butadiene

Initial attempts to hydraluminate 1,1-diphenylallene by heating 11.4 mmol of each of the reagents together in 60 ml of heptane for 17 h at 45° resulted only in traces of allene and a large amount of polymer. However, in another run the allene dissolved in 25 ml of heptane was added dropwise to the hydride dissolved in 25 ml of heptane at 70 - 75°. Usual work-up allowed 0.15 g (7%) of a colorless solid, m.p. 144 - 146°, to be separated from the polymer. Spectral data follow: *(a)* UV in cyclohexane, λ_{max} 252 nm; *(b)* IR in CCl_4, 1385 cm^{-1} (CH_3); *(c)* NMR in $CDCl_3$ (ppm, δ-scale): 0.40, t, CH_3; 2.12, q, CH_2; 2.91, d, $C\underline{H}_2{-}CH$; 5.73, t, $C\underline{H}{-}CH_2$ and 7.21, m, 20H; *(d)* MS at 70 eV (*m/e* and relative intensity); no peak beyond 197: prominent peaks at 196(16), 195(100), 194(6), 193(26), 178(6), 167(6), 117(24), 115(18) and 91(37). Analysis found: C, 92.45; H, 7.01. Mol. wt. (Rast), 400. $C_{30}H_{28}$(388.5) calcd.: C, 92.74; H, 7.26%. Based upon these data, the solid is established as being 1,1,4,4-tetraphenyl-1-hexene.

From the gummy distillation residues remaining after distilling the monohydralumination products of 1,1-diphenyl-1,3-butadiene, there were isolated by crystallization from benzene, at least two different crystalline solids (total isolated yield ca. 5%): (i) m.p. 128 - 129°; mol. wt. (Rast), 38$\bar{0}$; UV (c-C_6H_{12}), λ_{max} 248 nm; and (ii) m.p. 139 - 139.5°; mol. wt. (Rast), 35$\bar{0}$; UV (c-C_6H_{12}), λ_{max} 258 nm. The NMR and mass spectra of the two compounds are similar: compound (i) has the following NMR absorptions: 1.00, d, CH_3; 1.91, m, CH; 6.81, d, CH; and 7.10, m, 10H; MS at 70 eV: no peaks beyond 209: prominent peaks at 209(3), 208(17), 207(100), 129(31), 119(8), 117(8), 105(17) and 91(13). Compound (ii) had similar NMR and mass spectra; the latter had different mass intensities: 209(4), 208(20), 207(100), 129(31), 119(4), 117(0), 105(7) and 91(16). Analysis found for compound (i): C, 92.78; H, 7.40; for compound (ii): C, 92.41; H, 7.43. $C_{32}H_{30}$ calcd.: C, 92.71; H, 7.29%. Based upon these data, these compounds are considered to be *meso* and *d,l* isomers of 3,4-dimethyl-1,1,6,6-tetraphenyl-1-5-hexadiene.

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