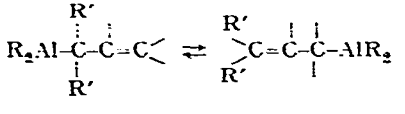
Allylic rearrangements in organoaluminum systems

The pioneering research of Ziegler and co-workers has demonstrated that aluminum alkyls and hydrides add to olefinic[1] and acetylenic[2] unsaturation with unexpected ease. Hence, if both a carbon–aluminum bond and carbon–carbon unsaturation were present in the same molecular unit, interesting *intramolecular* interactions of these functional groups might be expected[3]. The behavior of the relatively unexplored allylic aluminum system has been of particular interest, since such proposed interactions could cause interconversion of the allylic isomers*:

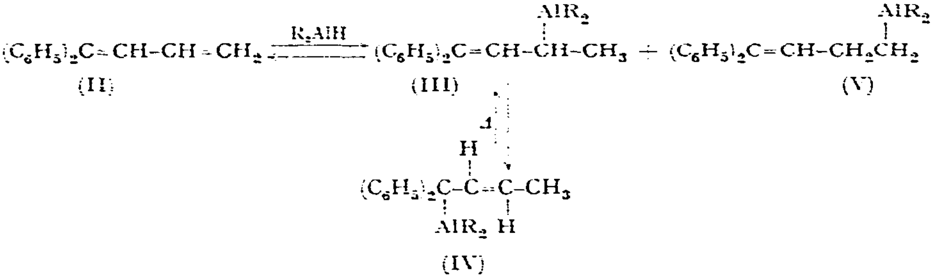


$$R_2Al\!-\!\underset{R'}{\overset{R'}{C}}\!-\!\overset{|}{C}\!=\!C\Big< \rightleftarrows \overset{R'}{\underset{R'}{\Big>}}C\!=\!\overset{|}{C}\!-\!\underset{|}{\overset{|}{C}}\!-\!AlR_2 \qquad (1)$$

(IA) (IB)

Previous studies of allylic Grignard reagents counseled the use of both physical and chemical means in detecting allylic rearrangements. Moreover, since unsolvated, simple allylaluminum compounds would be expected to be prone to polymerization[6], substituted allylic systems seemed more suitable for this investigation.

Therefore, we wish to report the preparation of model allylic aluminum systems and the observation of interesting rearrangements both in their formation and subsequent reactions. As a route to such allylic aluminum compounds, we have added diisobutylaluminum hydride (R_2AlH) to the following conjugated alkenes: 1,1-diphenylallene, 1,1-diphenyl-1,3-butadiene, and acenaphthylene (*e.g.*, eqn. 2). In addition, the behavior of 1,1-diphenylethylene toward R_2AlH was used to gain insight into prevailing steric factors in these reactions.



$$\underset{(II)}{(C_6H_5)_2C\!=\!CH\!-\!CH\!=\!CH_2} \xrightarrow{R_2AlH} \underset{(III)}{(C_6H_5)_2C\!=\!CH\!-\!\overset{AlR_2}{\overset{|}{CH}}\!-\!CH_3} + \underset{(V)}{(C_6H_5)_2C\!=\!CH\!-\!CH_2\overset{AlR_2}{\overset{|}{CH_2}}} \qquad (2)$$

$$(III) \rightleftarrows \underset{(IV)}{(C_6H_5)_2\underset{AlR_2}{\underset{|}{C}}\!-\!\overset{H}{\overset{|}{C}}\!=\!\underset{H}{\underset{|}{C}}\!-\!CH_3}$$

The organoaluminum adducts were treated with D_2O and the resulting hydrocarbons were analyzed by NMR spectroscopy (Table 1). The positions of the C–D bonds in the hydrocarbons would label reliably the positions of the C–Al bonds in the organoaluminum adducts, only if hydrolysis did not involve rearrangement.

To learn whether hydrolysis with D_2O does tag the positions of C–Al bonds reliably, the organoaluminum adduct mixture resulting from R_2AlH and 1,1-diphenyl-1,3-butadiene (eqn. 2) was examined directly by NMR spectroscopy. The

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* *Cf.* Gaudemar[4] for an infrared study of the sesquibromide mixture resulting from crotyl bromide and aluminum metal.

TABLE I

REACTION OF DIISOBUTYLALUMINUM HYDRIDE WITH CONJUGATED ALKENES

Alkene[a]	*Temp.* (*h*)	*Solvent*	*Products* (D_2O *or* H_2O *treatment*) %[b]
$(C_6H_5)_2C{=}CH_2$	110° (36)	neat	$(C_6H_5)_2CHCH_2D$, 100%
	165° (48)	neat[c]	$(C_6H_5)_2CHCH_2D$, 100%
$(C_6H_5)_2C{=}C{=}CH_2$	67° (15)	$C_7H_{16}(Et_2O)$[d]	$(C_6H_5)_2CDCH{=}CH_2$, 90% + $(C_6H_5)_2C{=}CHCH_2D$, 10%
$(C_6H_5)_2C{=}C{=}CH_2$	67° (16)	$C_7H_{16}(Et_3N)$[d]	$(C_6H_5)_2CDCH{=}CH_2$, 56% + $(C_6H_5)_2C{=}CHCH_2D$, 44%
$(C_6H_5)_2C{=}CHCH{=}CH_2$	108° (21)→145° (16)	C_7H_{16}	*trans*-$(C_6H_5)_2CH{-}CH{=}CH{-}CH_3$, 60% → 24% + $(C_6H_5)_2C{=}CHCH_2CH_3$, 40% → 76%
$(C_6H_5)_2C{=}CHCH{=}CH_2$	90° (7)	C_7H_{16}	*trans*-$(C_6H_5)CD{-}CH{=}CHCH_3$, 64% + $(C_6H_5)C{=}CHCH_2{-}CH_2D$, 36%
Acenaphthylene	90° (12)	C_7H_{16}	1-deuterioacenaphthene, 89%[e]

[a] Equivalent quantities of R_2AlH and alkene (0.01–0.03 mole) were employed. [b] Yields are based upon volatile products. Small amounts (*ca.* 5%) of residue were obtained in most cases. [c] After 24 h nickel acetylacetonate was added to promote hydride elimination and product equilibration. [d] Amounts of ether or amine equivalent to R_2AlH were added. [e] The remainder was acenaphthylene.

phenyl proton signal of the adducts at $\delta = 7.17$ was taken as a standard of 10.0 protons. The vinyl protons in the region, $\delta = 5.7$–6.5, were counted in reference to this standard*. The observed vinyl count H_r was 1.5 ± 0.05. Treatment of the same aluminum adducts with D_2O and subsequent NMR analysis revealed only *trans*-1-deuterio-1,1-diphenyl-2-butene (64%) and 4-deuterio-1,1-diphenyl-1-butene (36%). If these hydrocarbons reflect accurately the composition of the organoaluminum adducts, [only (IV) and (V)] the expected value of H_r would be 1.6 [$= 0.64 \times 2$ vinyl protons for (IV) $+ 0.36 \times 1$ vinyl proton for (V)]. If only (III) and (V) were present in the aluminum adduct [(III) undergoing complete allylic rearrangement upon hydrolysis], H_r should be 1.0. If (III), (IV) and (V) were all present, H_r could range between 1.0 and 1.6. Because of the close agreement between the observed H_r and the H_r expected for hydrolysis without rearrangement, and because of the absence of any deuteriated hydrocarbon corresponding to (III), we conclude that (IV) is the predominating, if not the sole, allylic isomer present. Therefore, hydrolysis with D_2O does appear to label C–Al bonds reliably in this case.

Now inspection of the hydrolysis data in Table 1 for the aluminum adducts reveals several important points. First, 1,1-diphenylethylene yields only 2-deuterio-1,1-diphenylethane under short-contact or prolonged reaction times. Examination of Stuart–Briegleb models for such additions[8] shows that approach of the R_2Al group to C_1 would be severely impeded. Secondly, however, the principal product, at lower

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* The NMR spectrum of the adducts in heptane revealed a triplet centered at $\delta = 6.05$, $J = 8$ cps, and two partially resolved broad signals at $\delta = 6.3$ and 6.4, each having a suggestion of hyperfine splitting. The signal at $\delta = 6.4$ appeared to be a doublet, $J = 2$ cps, and that at $\delta = 6.3$ seemed to be a higher multiplet. Since the NMR spectrum of 1,1-diphenyl-1-butene has its vinyl triplet at $\delta = 6.05$, the corresponding peak in the aluminum adducts' spectrum is assigned to (V). *trans*-1,1-Diphenyl-2-butene displays its vinyl proton multiplets between $\delta = 5.2$ and 6.2. In the aluminum adduct (IV) these vinyl protons are apparently deshielded and occur at $\delta = 6.3$ and 6.4.

temperatures, both with 1,1-diphenylallene and 1,1-diphenyl-1,3-butadiene, is the 1-deuterio-2-alkene. This predicates the preferred formation of the aluminum precursor, $(C_6H_5)_2C(AlR_2)CH{=}CHR$. As with 1,1-diphenylethylene, the direct addition of the R_2Al moiety at C_1 is most unfavorable. The most acceptable interpretation* is that addition of R_2AlH occurs to the C_2–C_3 bond of the allene and to the C_3–C_4 bond of the butadiene (in both orientations). Thereafter, the R_2Al group at C_3 rearranges to the 1-alumino-2-alkene (eqn. 2). Thirdly, the interconversion of the C_1 and C_3 allylaluminum isomers (eqn. 1, $R' = C_6H_5$) apparently is a function of donor solvent and temperature. The observation that the allylic isomeric composition obtained from 1,1-diphenylallene is dependent upon donor solvent suggests the more basic amine favors (IB) over (IA). The greater steric accessibility of the R_2Al group at C_3 to coordination by the amine may underlie this preference. Moreover, the observation that the adducts of R_2AlH and 1,1-diphenyl-1,3-butadiene are subject to thermal isomerization [(IV):(V) = 1.5 at 108° and 0.32 at 145°] strongly implicates a reverse reaction (eqn. 2), involving the sequence: (IV) → (III) → (II) → (V).

Finally, the allylic, 1-acenaphthenylaluminum system (VI), obtained from R_2AlH and acenaphthylene, has been found to undergo allylic rearrangements in certain reactions other than hydrolysis. Thus, treatment of (VI) with carbon dioxide and hydrolytic work-up gave exclusively the rearrangement product, acenaphthene-3-carboxylic acid, m. 255–256°, methyl ester, m. 70–71°.

This novel detection of discrete allylic aluminum isomers and the demonstration of their sensitivity to rearrangement has unusual significance for mechanistic and synthetic studies in organoaluminum chemistry. In particular, our further research on the isomerization rates and equilibria for allylic aluminum compounds should furnish quantitative information on the electronic and stereochemical aspects of carbon–metal bond formation.

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* The 1,2-addition of Al–H bonds to terminal C=C linkages is greatly favored over addition to internal C=C bonds (ref. 6, p. 217). Addition in a 1,4-fashion would demand the formation of the hydrolysis product, *cis*-1,1-diphenyl-2-butene, deuteriated at C_1 and/or C_4. The absence of such a hydrocarbon rules out 1,4-addition.

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