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KINETIC AND STEREOCHEMICAL FACTORS IN THE HYDRALUMINATION OF ALKENES AND THE CONFIGURATIONAL STABILITY OF THE RESULTING CARBON–ALUMINUM BOND *

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Summary

A series of cyclic olefins was subjected to hydralumination by diisobutylaluminum hydride, in order to determine the stereochemistry, the regiochemistry and the influence of structure on reactivity. The reactivity gradation observed was: acenaphthylene > 1,1-dimethyl-3-trimethylsilylindene > 1-methylacenaphthylene > 1,1-dimethylindene > 1-phenylacenaphthylene ≫ 1,1-dimethyl-3-phenylindene. By working in donor solvents it was demonstrated that *cis*-hydralumination is the kinetically controlled mode of addition. The reactivity for 3-substituted-1,1-dimethylindenes reflected polar effects, whereas that for 1-substituted acenaphthylenes responded to steric effects. The regiochemistry of hydralumination was generally determined by steric factors, except for the case of the silylindene. The isomerization of the hydralumination adduct could occur either by carbon–aluminum bond inversion or by dehydralumination. The former process took place readily in the absence of Lewis bases, but the latter process required elevated temperatures and protracted times. The stable *cis*-hydralumination adducts could be protodealuminated with retention of configuration at the C–Al bond, although acenaphthenyl systems gave significant amounts of 1,3-dihydroacenaphthylenes. The nature of these unusual hydrolysis products was elucidated by deuterium labeling, ^{1}H NMR and chemical degradation studies. A complete series of C_2- and C_3-deuterated-1,1-dimethylindenes was synthesized unambiguously in order to permit these foregoing studies.

The configurational stability of these organoaluminum compounds toward heat, neutral Lewis bases and carbanions was evaluated. These observations, together with

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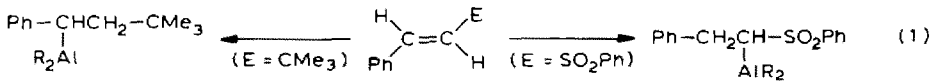
the temperature-dependent ^1H NMR spectrum of 1-acenaphthenyl(diisobutyl)aluminum, lend some insight into the pathways of carbon–aluminum bond inversion.

Introduction

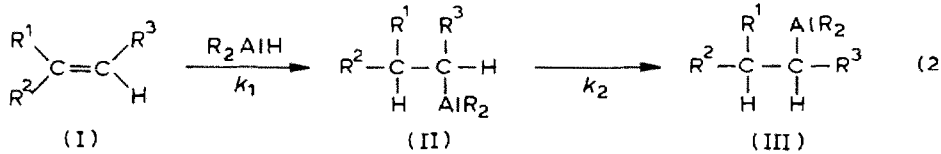
The addition of aluminum hydrides to olefinic bonds ranks as the most versatile route to alkylaluminum compounds [1,2]. The regiochemistry of such hydraluminations is determined by an interplay of polar and steric factors, as exemplified by the response of β-substituted styrenes toward dialkylaluminum hydrides, R_2AlH (eq. 1, R = i-C_4H_9) [3,4]:



(1)

In addition to the regiochemical course, the stereochemistry of these additions would be important for generating alkyl carbon–aluminum bonds of known configuration.

Although stereospecific *cis*- [5,9] and *trans*- [8,10–11] hydraluminations of alkynes have been demonstrated, the stereochemical course for the hydralumination of alkenes has been obscured by the isomerization of the initial adduct (II) formed from a prochiral olefin (I) (eq. 2):



(2)

Proton NMR studies have shown that, in hydrocarbon solvents, the alkyl carbon–aluminum bond undergoes inversion at moderate temperatures with a rate (k_2) comparable to that of hydralumination (k_1) [12,13]. In order to determine the stereochemistry of the hydralumination step, k_1 had to be made much larger than k_2. Experimentally, this requirement could be fulfilled by choosing strained, more reactive cyclic olefins [14] and by adding to the hydralumination medium solvents that are known to retard C–Al inversion processes [13,14].

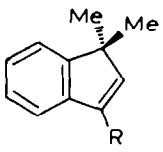
We report here our findings concerning both the stereochemistry of the hydralumination of alkenes, and the factors that determine the configurational stability of the resulting saturated carbon–aluminum bond. It will be seen that the availability of the resulting stereochemically defined alkylaluminum compounds enables one to study the stereochemistry of insertion and substitution reactions at sp^3-C–Al centers [14,15].

Results

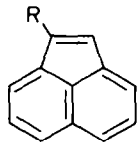
Hydralumination

(a) Relative rates. In order to determine the stereochemistry of hydralumination more readily, cyclic olefin substrates were appealing. Since cyclopentene has been

shown to be much more reactive than cyclohexene in hydralumination (pseudo first-order $t_{1/2}$ in excess Et_2AlH: 200:1180 min) [16], suitably substituted indenes (IV–VI) and acenaphthylenes (VII–IX) were chosen for a detailed study. By



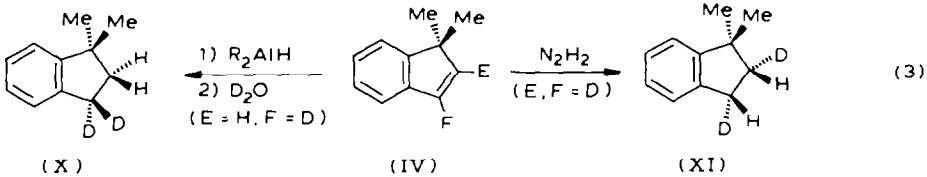
(IV, R = H;
V, R = Me_3Si;
VI, R = Ph)



(VII, R = H;
VIII, R = Me;
IX, R = Ph)

comparison of the temperature and time required to achieve hydralumination and, in some cases, by measuring relative rates by pairwise competition experiments, the following gradation in reactivity was established: acenaphthylene (VII) > 1,1-dimethyl-3-trimethylsilylindene (V) > 1-methylacenaphthylene (VIII) > 1,1-dimethylindene (IV) > 1-phenylacenaphthylene (IX) ≫ 1,1-dimethyl-3-phenylindene (VI). The role of the polar effect of R on the indene reactivity is seen in the sequence: V > IV ≫ VI, whereas steric hindrance by R governs the reactivity of the acenaphthylenes: VII > VIII ≫ IX.

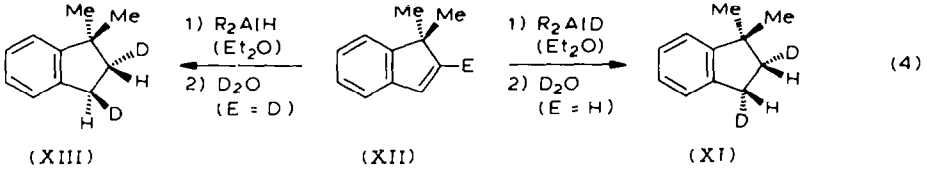
(b) Stereochemistry. For determining the stereochemistry and the possible reversible elimination of R_2AlH during the hydralumination of indene, various specifically deuterated indans (eq. 3, X, XI) were prepared by regiospecific hydraluminations of deuterated indenes or by the diimide reduction of indenes (cf. eq. 3 for the illustrative preparations of 3,3-dideuterated indans and *cis*-2,3-dideuterated indans):



(X) (IV) (XI) (3)

In analogous ways, the following indans were prepared: compounds deuterated at 2-d_1, 3-d_1, 2,2-d_2, 2,2,3-d_3, 2,3,3-d_3 and 2,2,3,3-d_4. Their structures were verified by ^{1}H NMR and differing IR spectra, as well as by elemental deuterium analyses.

The stereochemistry of hydralumination was shown to be stereospecifically *cis* in two concordant ways: the hydralumination of 1,1-dimethylindene-2-d_1 (XII, E = D) in ethyl ether, followed by deuterolytic work-up (XIII); and the deuteroalumination of 1,1-dimethylindene (XII, E = H) in ethyl ether, followed by deuterolytic work-up (XI) (eq. 4). Although the ether solvent strongly retarded the hydralumination, it retarded C–Al bond inversion even more markedly ($k_1 \gg k_2$).

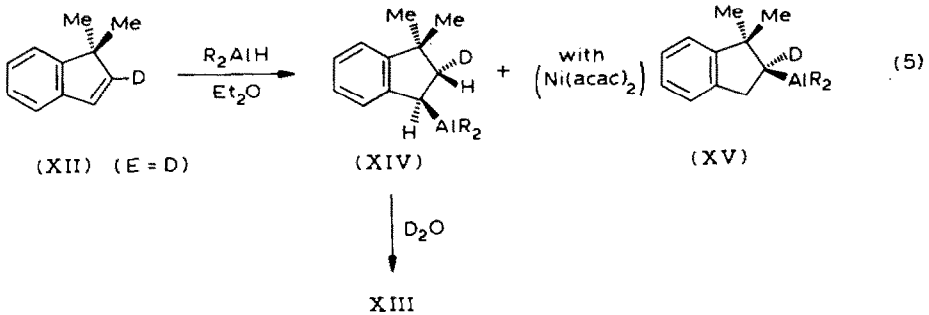


(XIII) (XII) (XI) (4)

Compound XI was shown to be a 2,3-d_2 isomer having an IR spectrum identical with that of the isomer from the diimide reaction (eq. 3). Compound XIII was shown by ^{1}H NMR spectroscopy to be a 2,3-d_2 isomer that had a different IR spectrum from that of XI.

Because of complexities in the protolysis step, the stereochemistry for the hydralumination of acenaphthylene itself could not be determined. But 1-methylacenaphthylene (VIII) and 1,1-dimethyl-3-trimethylsilylindene (V) were shown also to undergo *cis*-hydralumination exclusively. Partial isomerization was encountered with the less reactive 1-phenylacenaphthylene (IX), which yielded a 2/1 mixture of the *cis*/*trans*-aluminum adduct.

(c) Regiochemistry. Regardless of whether the hydralumination of IV was conducted in heptane (relatively rapid) or in ethyl ether, the addition occurred regiospecifically to place the aluminum exclusively on C(3) (XIV), as revealed by the isolation of 1,1-dimethylindane-2,3-d_2 (XIII) upon deuterolysis (eq. 5).



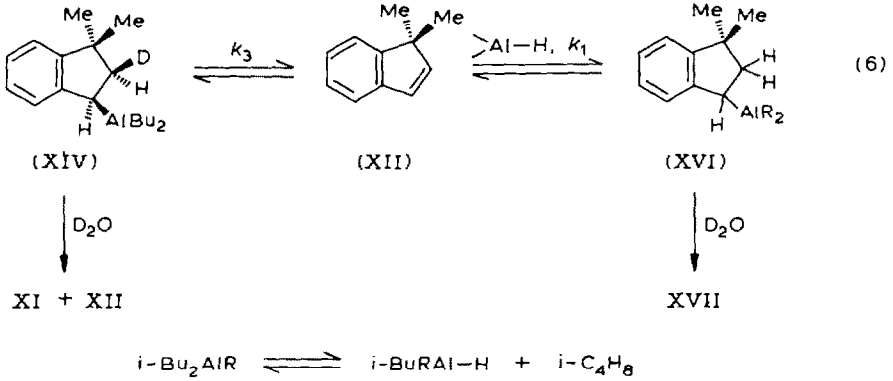
However, the nickel-catalyzed hydralumination [17] of 1,1-dimethylindene-2-d_1 was still stereospecific, for work-up with D_2O still gave XIII. But at short conversions ($\sim$ 50%), up to 26% of the dideuterated indan was the 2,2-d_2 isomer. This indicates that XV builds up in the early stages of the reaction and that XV eventually isomerizes to XIV.

On the other hand, acenaphthylenes VIII and IX underwent regiospecific hydralumination to place the aluminum at C(2), but this mode of addition was not influenced by nickel salts.

(d) Isomerization of the 1,1-dimethyl-3-indanyl(diisobutyl)aluminum. With authentic samples of both *cis*- and *trans*-1,1-dimethylindan-2,3-d_2 now in hand (XI and XIII) it could be shown that the hydralumination of 1,1-dimethylindene-2-d_1 in heptane at 60°C, followed by deuterolytic work-up, gave a 50/50 mixture of XI and XIII. Thus, in the absence of ether, the initially formed XIV (eq. 5) rapidly undergoes C–Al bond inversion.

Another type of isomerization, one involving reversible Al–H elimination, occurred upon protracted heating of such aluminum adducts over 80°C. Thus, heating indene XII (E = H) with diisobutylaluminum deuteride for short periods gave upon deuterolysis only the expected 50/50 mixture of *cis*- and *trans*-2,3-dideuterated indans, XI and XIII. Longer heating (> 4 days), however, gave a 52/48 mixture of 2,3-dideuterated indan (XI, XIII) and 3-deuterated indan (XVII). Clearly, initially formed adduct XIV had undergone Al–D elimination and the regenerated XII had readded an Al–H bond, which arose thermally from the loss of isobutene from an

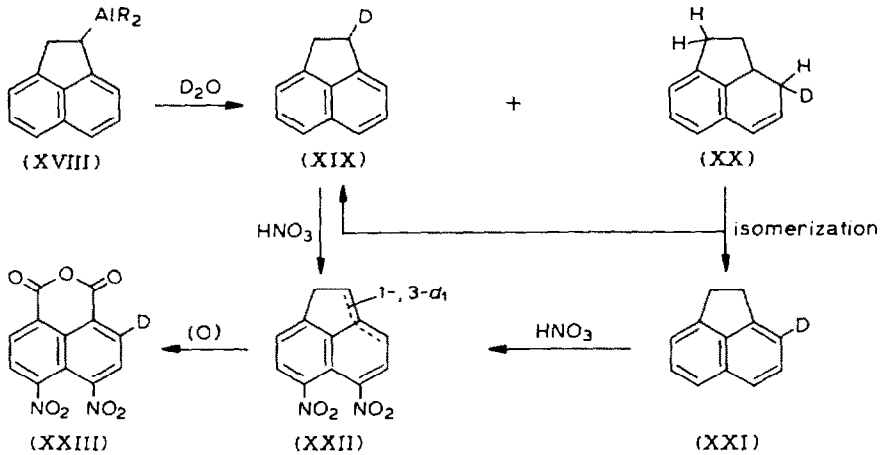
isobutyl group [18] (eq. 6):



(6)

$$i\text{-}Bu_2AlR \rightleftharpoons i\text{-}BuRAl\text{—}H + i\text{-}C_4H_8$$

(e) Protodealumination. Treatment of the hydralumination adducts from the indene system (IV–VI) with H_2O or D_2O delivered a hydrogen to the benzylic carbon almost exclusively (cf. section c). The adducts from the acenaphthylenes (VII–IX), however, gave significant amounts (5–50%) of 1,3-dihydroacenaphthylenes, in addition to the expected acenaphthenes. The formation of the 1,3-dihydro, rather than the 1,5-dihydro isomer, was verified by comparison with an authentic sample of the 1,5-dihydro isomer [19] and by the chemical degradation depicted in Scheme 1.



SCHEME 1

Deuterolysis of the 1-acenaphthenyl(diisobutyl)aluminum (XVIII) * led to a mixture of deuterated isomers, XIX and XX. Preparative GLC on Chromosorb W caused isomerization to a mixture of 1- and 3-deuterioacenaphthenes, XIX and XXI, containing 88% d_1. Replacement of the 5- and 6-hydrogens by nitro groups caused no loss of deuterium (XXII, 88% d_1), and thus no deuteron was at these positions in XIX and XXI. Oxidation of XXII to 1,8-naphthalic anhydride (XXIII) caused the

* The structure of the initial adduct as having only the 1-acenaphthenyl group (XVIII) could be independently verified by direct ^1H NMR examination and proton integration (cf. infra).

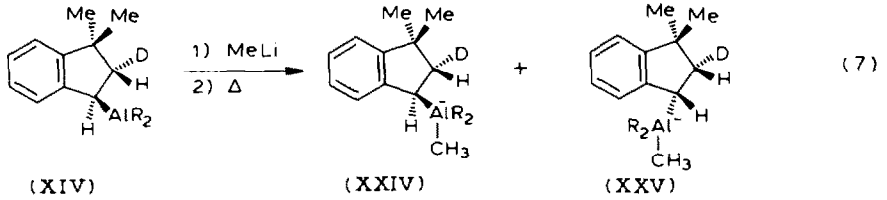
loss of 74% of deuterium (XXIII, 14.4% d_1). Thus, a mixture containing ~ 14% of XXI was formed by isomerization. This value agrees well with the 31% of XX measured by ^{1}H NMR analysis of the hydrolysis. Non-concerted, acid-catalyzed isomerization of XX to yield XIX and XXI would leave about 15% of deuterium at C(3) [20]. The ^{1}H NMR spectral absorptions in XX could be assigned by a combination of deuteroaluminations of VII, followed by either protolytic or deuterolytic work-up. Unfortunately, the stereochemistry of the deuterons in the 1,3-dihydroacenaphthylene-1,3-d_2 obtained in this manner could not be ascertained. Hence, protolysis did not provide a way of determining the stereochemistry of hydralumination for acenaphthylene itself.

Configurational stability

(a) Thermal effect. The hydralumination adduct of indene IV in heptane undergoes C–Al bond inversion at 60–80°C at a rate comparable to that of its formation ($k_2 \simeq k_1$ in eq. 2). Change in the C–Al bond configuration by an elimination-readdition of R_2AlH is much slower (eq. 6, $k_3 \ll k_1$). It is noteworthy, therefore, that both the 3-trimethylsilylindene (V) and the 3-phenylindene (VI) undergo a stereospecific *cis*-hydralumination in heptane under these same conditions. Although k_1 for V is larger than that of IV (relative k_1 (V)/k_1 (IV) = 1.5/1.0), k_1 for VI is much smaller. Thus, the effect of the 3-substituent is to make k_2 smaller relative to k_1.

(b) Lewis bases. In ethyl ether solution the hydralumination of the parent indene IV is markedly retarded relative to that in heptane (after 72 h at 50°C, complete conversion in heptane, but none in ether). In *N*-methylpyrrolidine even slower hydralumination was observed. But in both donor solvents the hydralumination that did occur was stereospecifically *cis* ($k_1 \gg k_2$). But in a weaker donor medium, such as anisole, the reaction was again markedly retarded and the hydralumination adduct underwent equilibration to a 1/1 *cis/trans* mixture (k_1(small) $\simeq k_2$) *.

(c) Aluminate complex formation. The hydralumination adduct of 1,1-dimethylindene-2-d_1 (XIV) in ether was treated with methyllithium and heated to 60°C. Subsequent deuterolysis gave a 1/1 mixture of *cis*- and *trans*-2,3-dideuteroindans (XI and XIII).



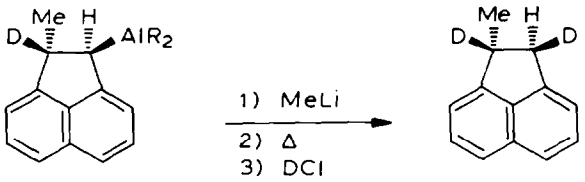
(XIV) (XXIV) (XXV) (7)

Accordingly, aluminate formation brought about isomerization to a mixture of XXIV and XXV (eq. 7). In a similar manner, the *cis*-deuteroalumination adduct of 1,1-dimethyl-3-trisilylindene in heptane was complexed with methyllithium and the resultant complex deuterolyzed. Again, a 1/1 mixture of the *cis*- and *trans*-1,1-dimethyl-3-trimethylsilylindans-2,3-d_2 resulted.

In contrast, the *cis*-deuteroalumination adduct of 1-methylacenaphthylene

* A strongly competitive cleavage of the anisole to $PhOAlR_2$ also took place.

(XXVI) underwent complexation with methyllithium and subsequent deuterolysis without loss of configuration (eq. 8, XXVII):



(XXVI) (XXVII) (8)

(d) ^1H NMR spectrum of 1-acenaphthenyl(diisobutyl)aluminum (XVIII). The ^1H NMR spectrum of XVIII was measured on a solution that was 1.9 molar in toluene-d_8 and that had a sealed capillary of tetramethylsilane as an external standard. At 37°C the spectrum exhibited acenaphthyl resonances at 2.75 and 3.43 ppm as broad, featureless benzylic signals in a 1H/2H ratio, as well as a one-proton shoulder between 6.4–7.1 ppm and a 4.5-proton, broad multiplet at 7.1–7.7 ppm. At higher temperatures (90–115°C) the resonances sharpened pronouncedly: the benzylic signals at 2.75 and 3.43 ppm became a triplet and a doublet, respectively, reminiscent of an A_2X pattern ($J \simeq 5$ Hz); the shoulder at 6.4–7.1 ppm became a broad doublet at 6.91 ppm; and the rest of the aromatic protons became a seven-line multiplet.

Discussion

Hydralumination

Previous kinetic studies uniformly conclude that the slow step in hydralumination involves the attack of tricoordinate monomeric R_2AlH on the alkyne or alkene [11,21,22]. The retarding effect of Lewis bases arises from their complexing with the R_2AlH and thus making it less available for reaction. The enthalpy of complexation (ΔH_c) will be incorporated into the observed activation energy for hydralumination, $\Delta E^{\ddagger}_{HA}$ (eq. 9). Since ΔH_c is greater for amines than for ethers [23], it is understanda-

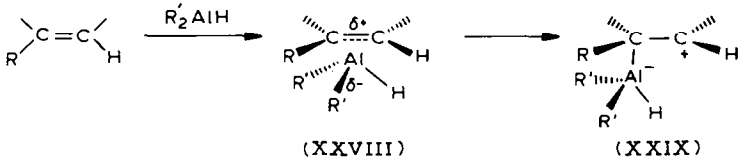
$$R_2AlH + :D \rightleftharpoons R_2AlH{:}D \qquad -\Delta H_c \tag{9}$$

ble that *N*-methylpyrrolidine retards the Al–H bond addition more markedly than ethyl ether. Not only can donors coordinate with monomeric R_2AlH, but also the products of hydralumination, namely R_2AlR' (e.g., II) form complexes with R_2AlH and thus retard the reaction [21,24] *.

From a study of relative reactivities [25] and observed small R_2AlH/R_2AlD isotope effects [21], the transition state in hydralumination is considered to resemble a π-complex (XXVIII). In this light the observed relative reactivities of the indenes IV–VI are understandable. If one invokes Taft polar substituent constants, σ^*, to

* Kinetic studies based both on initial rates and on a complete reaction analysis show rate laws of the form, $v = k[R_2AlH]^{1/3}$[hydrocarbon] and exhibit autoinhibition [21,24]. Rate studies claiming half-order dependence on hydride, $[R_2AlH]^{1/2}$, have not taken such $R_2AlH \cdot R_2AlR'$ complexation into account [22].

assess inductive electron release into the 2,3-π-bond of indenes IV–VI (eq. 10), the reactivity trend is rationalized; $\sigma^{\star}_{Me_3Si} = -0.73 > \sigma^{\star}_{H} = +0.49 > \sigma^{\star}_{Ph} = +0.60$ (eq. 10) [25,26]:



(XXVIII) (XXIX) (10)

Collapse of XXVIII, possibly through a high-energy σ-complex intermediate (XXIX), then yields the observed *cis*-adduct. For the acenaphthylenes, the relative reactivities, R = H > Me ≫ Ph, do not follow $\sigma^{\star}$ ($\sigma^{\star}_{Me} = 0.0$), but do follow various criteria for steric demands of R [26,27]. The interaction between R and R′ in XXVIII is determinant here.

The regiochemistry of Al–H addition observed with the acenaphthylenes and 1,1-dimethylindene is that expected from steric considerations, namely linking the R_2Al group at the more spatially accessible carbon. With the 3-trimethylsilylindene (V), however, one must invoke a hyperconjugative effect by silicon (XXIX, R = Me_3Si) that would stabilize positive charge build-up in the transition state [28].

Stability of the resulting diisobutyl(alkyl)aluminum compounds

In their reaction with proton sources, these compounds generally undergo protodealumination with retention of configuration. In this respect, aluminum compounds resemble many other organometallics that undergo electrophilic substitution (S_E2) by front-side or flank attack [29]. The protolysis of the acenaphthenylaluminum products is remarkable in producing so much of the *ortho*-protonated product. Although one might assume that such allylic S_E2' substitution occurs with *syn*-addition or retention of configuration, the stereochemistry remains to be proved *.

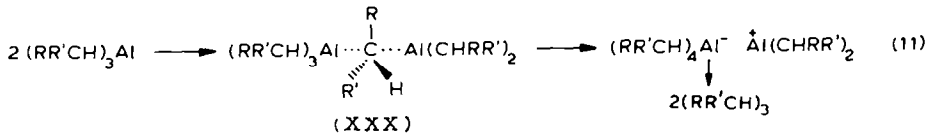
The reversible character of these hydraluminations at 90–100°C is clear from the behavior of the indanylaluminum system (XIV, eq. 6), but such elimination-readdition of $R_2AlH(D)$ is so slow so as not to play a role in hydraluminations conducted under 60 h. Accordingly, the isomerizations observed involve only C–Al bond inversions, and not R_2AlH-elimination.

Carbon–aluminum bond inversion

From the retarding effect of Lewis bases on inversion, it is evident that tricoordinate R_3Al undergoes inversion more rapidly than $R_3Al{:}D$. But such tricoordination is not sufficient. Of the 1,1-dimethylindanylaluminum systems, only the 3-protio inverts to 60°C. The corresponding 3-trimethylsilyl- and 3-phenylindanylaluminum compounds do not. In previous studies of C–M bond inversions, mechanistic interpretations of two types have been advanced: (i) ionic dissociation into M^+ and carbanions, followed by carbanion inversion, as has been advanced for lithium alkyls [12,30]; and ii) an associative S_En process ($n \geq 2$), whereby an electrophilic R_mM attacks a second R_mM from the back side (eq. 11, for $(RR'CH)_3Al$)), which has

* The interesting experimental variables favoring such allylic protodemetallation will be reported in a subsequent article.

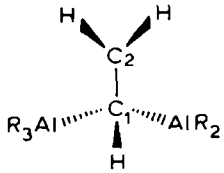
been suggested for magnesium alkyls [13,31–34]. That Lewis bases, such as Et_2O and $(CH_2)_4NMe$, retard C–Al bond inversion argues against the ionic dissociation mechanism for the neutral aluminum alkyl, for solvation of M^+ should promote



(11)

dissociation. On the other hand, the retarding effect of 3-trimethylsilyl or 3-phenyl group on inversion of the indanylaluminum argues strongly for an associative S_E2 process, since the back-side attack in these systems should be sterically hindered (XXX). Moreover, were ionization to a 3-indanyl carbanion necessary for inversion (mechanism 1), both Me_3Si and phenyl groups should have promoted inversion, for both groups stabilize carbanions on α-carbons [35].

In addition, the temperature-dependent ^1H NMR spectrum of 1-acenaphthenyl(diisobutyl)aluminum offers evidence for an S_E2 inversion at the carbon–aluminum bond. That the benzylic grouping, CH_2–CH–AlR_2, of XVIII appears as an A_2X pattern at 115°C speaks for a rapid exchange process that makes the diastereotopic CH_2 protons equivalent. Precisely the exchange depicted in eq. 11 and in XXXI would achieve this equivalency. Although it is not likely that such bulky $R_2R'Al$ are significantly associated at equilibrium [36], it should be noted that such dimerization involves front-side bridging of R groups, rather than the back-side bridging upon which XXXI depends *.



(XXXI)

Finally, although a heterolytic C–Al bond dissociation (mechanism (i)) is not acceptable for C–Al bond inversion in neutral $R_2R'Al$, such dissociation does fit the ready inversion observed with lithium tetraorganoaluminates, $LiAlR_2R'Me$. Here the ease with which even the 1,1-dimethyl-3-trimethylsilylindanylaluminate group undergoes inversion speaks for the dissociation of the most stable carbanion from $AlR_2R'Me^-$, namely the benzylically stabilized indanyl, its inversion and its recombination with R_2MeAl. In the one case where no inversion was observed, namely the aluminate of XXVI (eq. 8), it appears that the β-methyl group assures that the carbanion complexes or protonates only from the side *trans* to the bulky methyl group.

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* At elevated temperatures it is quite possible that a small amount of 1-acenaphthenyl (diisobutyl)aluminum dissociates into alkene and R_2AlH. Such a hydride would be much less sterically demanding for approaching the back side of the C–Al bond (cf. XXX and XXXI) and effecting inversion.

Experimental

General techniques. All organometallic reactions were conducted under an atmosphere of dry deoxygenated nitrogen [11,12]. Techniques followed in the preparation, handling and analysis of organoaluminum alkyls and hydrides have already been described [11,21,24,25,37]. All solvents employed with organometallic compounds were dried and distilled under an atmosphere of nitrogen, with the use of these drying agents: $LiAlH_4$ for ethers and hydrocarbon; BaO for pyridine and *N*-methylpyrrolidine, CaH_2 for triethylamine; CaO for t-butyl alcohol; and activated Mg for methyl and isopropyl alcohols [38].

The spectral samples were prepared by published techniques [37] and measured by the following instruments: ^1H NMR with Varian A-60 or HA-100D models equipped with a Varian V-6040 temperature controller and, for the HA-100D model, with a Hewlett-Packard HP-205AG audiofrequency generator for spin decoupling (external audiofrequency being passed through NMR Specialties Heteronuclear Spin Decoupler HD-60B with an FK-3 modification kit to irradiate at 15 MHz and to observe at 100 MHz). IR with a Perkin–Elmer 457 model equipped with KBr plate cells for neat liquids and NaCl solution cells; mass spectra at the Mass Spectral Facility at Cornell University, where a Perkin–Elmer model 270 was used and either an AEI-902 or a CEC-21-103A was employed.

Chromatographic analyses were performed on an F&M, dual-column programmed-temperature gas chromatograph, model 720, using the following columns: A, 25% SE-30 on 60–80 mesh Chromosorb W; and B, 10% silicone gum rubber on 60–80 mesh Chromosorb W. Preparative separations were effected with a Nester-Faust Prepkromatic 850. Column chromatographic purifications were done on 60–200 mesh silica gel (Baker) and, for some, an automatic fraction collector, Instrumentation Specialties, model 720-004-01, was used.

Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan and deuterium analyses were done by Dr. Josef Nemuth of Urbana, Illinois, by the falling-drop method [39].

Preparation and purification of reagents and products

Aluminum compounds. Commercial diisobutylaluminum hydride (Texas Alkyls) was degassed for several hours at 70–80°C and then fractionally distilled through a 15-cm Vigreux column. The final product was analyzed by the isoquinoline titration procedure [2]. Diisobutylaluminum deuteride was synthesized by a published procedure [21]. Ethanolysis and mass spectral analysis of the evolved hydrogen gas showed it to be > 97% isotopically pure.

Hydrocarbons

1,1-Dimethylindene. 3,3-Dimethyl-1-indanone was prepared from neophyl chloride by a known route [40]. A solution of 46.4 g (290 mmol) of this ketone in 75 ml of ethyl ether was added to a stirred suspension of 6.0 g (150 mmol) of $LiAlH_4$ in 250 ml of ethyl ether at a rate sufficient to cause gentle reflux. The gray mixture was heated at reflux for 24 h and then cautiously hydrolyzed by a sequence of 6 ml H_2O, 6 ml of 15% aqueous NaOH and 18 ml of H_2O (Steinhardt technique, ref. 41). After 1 h of stirring, the ether layer was separated, dried with $MgSO_4$ and evaporated to give 3,3-dimethyl-1-indanol as a spectrally pure oil (97%), ^1H NMR spectrum

($CDCl_3$) δ 1.12 (s, 3H), 1.30 (s, 3H), 1.72 (d of d, H_2 *cis* to OH, J_{gem} 13, J_{trans} 6.5 Hz), 2.19 (d of d, H_2 *trans* to OH, J_{cis} 6.7 Hz), 4.36 (br s, OH), 5.07 (br q, H_1) and 6.8–7.35 (m, 4H).

In a 100-ml flask fitted with a short-path distillation head was heated a mixture of 45.4 g (280 mmol) of this indanol and 200 mg of *p*-toluenesulfonic acid. Over the range of 80–100°C dehydration occurred and the hydrocarbon/water mixture was distilled off. The crude indene was dried with $MgSO_4$ and redistilled to give 84% of 1,1-dimethylindene, b.p. 72–75°C at 7.0 mmHg. Spectral data: ^1H NMR (CCl_4): δ 1.23 (s, 6H), 6.18 (d, H_2, $J_{2,3}$ 5.6 Hz), 6.47 (d, H_3) and 6.94–7.26 (m, 4H); IR (neat, cm^{-1}): 3060m, 3020m, 3008m, 2960s, 2927m, 2895m, 2865m, 1467s, 1459s, 1450m, 1440m, 1358m, 1310, 1278, 1201, 1178, 1152, 1140, 1119, 1083, 1068, 1020, 941, 935, 891, 868, 789s, 754s, 733m, 605m, 596m, 473, 440.

Anal. Found: C, 91.55; H, 8.42. $C_{11}H_{12}$ calcd.: C, 91.70; H, 8.30%.

1,1-Dimethylindene-3-d$_1$. A stirred, ice-cooled solution of 3.21 g (20 mmol) of 3,3-dimethyl-1-indanone in 20 ml of heptane was treated with 4.4 ml (24.5 mmol) of i-Bu_2AlD. After 12 h of stirring, hydrolysis according to Steinhardt and usual work-up (cf. supra) gave 2.82 g (77%) of spectrally pure 3,3-dimethyl-1-indanol-d_1 (^1H NMR spectrum lacked a signal at 5.07 ppm).

Dehydration of this alcohol with *p*-toluenesulfonic acid gave a 65% yield of 1,1-dimethylindene-3-d_1, whose ^1H NMR spectrum lacked the signal at 6.47 ppm.

1,1-Dimethylindene-2-d$_1$. A solution of 25 g (156 mmol) of 3,3-dimethyl-1-indanone in 30 ml of petroleum ether was stirred rapidly with 10 ml of D_2O and 20 drops of a 40% solution of NaOD in D_2O for 48 h. The suspension was acidified with a 37% solution of DCl in D_2O. After 5 min the organic layer was separated and dried over $MgSO_4$. This treatment was carried out four times on the same sample, whereupon the ^1H NMR spectrum of the neat ketone (3,3-dimethyl-1-indanone-2,2-d_2) had only a faint absorption at 2.50 ppm ($CO–CH_2$).

Reduction of this ketone and dehydration of the resulting indanol (cf. supra) gave up to an 84% yield of 1,1-dimethylindene-2-d_1, whose ^1H NMR spectrum had no signal at 6.18 ppm.

Anal. Found: D, 8.30. $C_{11}H_{11}D$ calcd.: D, 8.33%.

1,1-Dimethylindene-2,3-d$_2$. This compound was prepared by reducing 3,3-dimethyl-1-indanone-2,2-d_2 with $LiAlD_4$ and dehydrating the indanol-d_3 with *p*-toluenesulfonic acid. The resulting hydrocarbon was obtained in 72% yield and displayed no olefinic absorption at 6.18 or 6.47 ppm in its ^1H NMR spectrum.

Anal. Found: D, 16.40. $C_{11}H_{10}D_2$ calcd.: 16.66%.

cis-1,1-Dimethylindan-2,3-d$_2$. A mixture of 730 mg (5 mmol) of 1,1-dimethylindene-2,3-d_2, 25 ml of MeOH and 15 g (77 mmol) of dipotassium azodicarboxylate (Aldrich: supplier of the precursor azodicarbonamide) was heated to 50–55°C while a solution of 25 ml of glacial acetic acid in 15 ml of MeOH was added dropwise over a 22-h period. The mixture was admixed with 50 ml of water and the resultant extracted with 2 × 50 ml portions of pentane. Drying of the organic extracts with $MgSO_4$ and subsequent removal of solvent provided 680 mg (92%) of *cis*-1,1-dimethylindan-2,3-d_2. A sample collected by GLC gave the following IR spectrum: (neat, cm^{-1}) 2185m, 2173m, 2135m, 1317m, 1308m, 1299m, 1289m, 1285, 1178, 1155, 1143, 1113, 1080, 1026m, 939, 759s, 724s, 711m, 578m, 552, 463 and 441m.

Anal. Found: D, 14.05. $C_{11}H_{12}D_2$ calcd.: 14.30%.

1,1-Dimethyl-3-trimethylsilylindene. A solution of 38.6 g (170 mmol, ~ 95% pure,

cf. infra) of 1,1-dimethyl-3-trimethylsilylindan in 500 ml of CCl_4 was heated at 70°C with stirring, while 33.8 g (190 mmol) of *N*-bromosuccinimide were added in portions over 30 min. Subsequent heating at 85°C for 4 h brought about dehydrobromination. The suspension was cooled to 5°C and the succinimide filtered off. The filtrate was concentrated by rotary evaporation and 100 ml of MeOH then added. Chilling the solution in a solid CO_2-acetone bath gave a precipitation of the indene. Reconcentration of the mother liquor and recooling yielded another crop of the indene. The combined crops of the indene were washed with 100 ml of 50% aqueous MeOH and then recrystallized from MeOH to yield 15.5 g (40%) of 1,1-dimethyl-3-trimethylsilylindene m.p. 49–50°C: ^{1}H NMR (CCl_4): δ 0.29 (s, 9), 1.25 (s, 6), 6.48 (s, H_2) and 6.92–7.42 (m, 4H).

Anal. Found: C, 77.86; H, 9.44. $C_{14}H_{20}Si$ calcd.: C, 77.70; H, 9.32%.

Retreatment of the residual product in the mother liquor (after removal of MeOH) with *N*-bromosuccinimide in CCl_4 provided ~ 10 g of additional product.

Acenaphthylene and acenaphthene. These commercial samples were sublimed and the sublimates recrystallized from methanol. By ^{1}H NMR spectroscopy and TLC both samples were free of the other hydrocarbon.

1-Methylacenaphthylene and 1-methylacenaphthylene-2-d_1. The undeuterated hydrocarbon was prepared from acenaphthenone [42], b.p. 141–142.5°C at 5.8 mmHg; ^{1}H NMR (CCl_4): δ 2.22 (s, 3H, *J* 1.9 Hz), 6.49 (q, H) and 7.1–7.7 (m, 6H).

The deuterated hydrocarbon was prepared from acenaphthenone-2,2-d_2 by the same method. The deuterated ketone was prepared by heating acenaphthenone with 5 ml of acetic acid-O-d_1 and 15 ml of D_2O and repeating the treatment with fresh deuterated reagents thrice. By its ^{1}H NMR spectrum the product was 91%-d_2 and 9%-d_1.

Hydralumination

General procedure

The hydralumination of the olefinic substrates was conducted in a 100-ml, round-bottom flask having an elongated center neck to accommodate a cold-finger condenser in its ground joint. An angular side neck on the flask, about 1.0 cm O.D., was provided with a septum. The flask was purged with dry nitrogen and charged with the olefin and the solvent. The diisobutylaluminum hydride or deuteride was introduced through the septum via a gastight syringe. The reaction mixture was stirred magnetically while maintained at the desired temperature in an oil bath. After reaction aliquots were withdrawn by syringe and protolyzed in one of three ways: (i) dilution with degassed solvent and cautions addition of water or 1*N* HCl; (ii) direct injection of the aliquot into a hydrolyzing agent; and (iii) extended treatment with dilute acid, over 1–4 h, for hydrolysis (required especially for acenaphthenylaluminum adducts). Usual separation of the organic layer, drying of this layer over $MgSO_4$ and solvent removal ensued.

1,1-Dimethylindene substrates

(a) 1,1-Dimethylindene with diisobutylaluminum hydride. Heating a solution of 1.54 g (10.7 mmol) of the indene with 1.97 ml (11.3 mmol) of the hydride in 20 ml of heptane for 48 h at 80°C gave, upon hydrolysis, only 1,1-dimethylindan. By distillation 1.30 g (81%) of the pure product could be isolated, b.p. 180–182°C at 760

mmHg. ^{1}H NMR spectrum (CCl_4): δ 1.20 (s, 6H), 1.83 (t, 2H, $J_{2,3}$ 7.2 Hz), 2.80 (t, benzylic 2H) and 6.99 (s, 4H); IR (neat, cm^{-1}) 1319, 1310m, 1292, 1268, 1213, 1157, 1109m, 1080, 1023m, 932, 759s, 728s, 705, 588m, 562, 471, 453m.

An identical reaction, but with a deuterolytic work-up, yielded 1,1-dimethylindan-3-d_1: ^{1}H NMR (CCl_4, ^{2}H decoupled): δ, 1.20 (s, 6H), 1.85 (d of t, CH_2, $J_{2,3}$(H,H) 7.2, $J_{2,3}$(H,D) 1.2 Hz), 2.79 (t of t, benzylic H, $J_{3,3}$(H,D) 2.5 Hz) and 6.99 (s, 4H; IR (neat, cm^{-1}): 2182, 2135, 1312m, 1295, 1260, 1211, 1168, 1133, 1108, 1074, 1012, 935, 786, 761s, 749s, 735s, 721, 712, 692, 678, 583m, 560, 464, 441m.

(b) 1,1-Dimethylindene with diisobutylaluminum deuteride. Treatment of the indene (777 mg, 5.4 mmol) with 1.0 ml (5.6 mmol) of the deuteride in 10 ml of heptane for 4.7 d at 80°C, followed by work-up with D_2O, gave 1,1-dimethylindan, which contained various deuterated components. The amount of indan undeuterated at C(2) was estimated by taking the difference in signal areas at 1.83 and 2.80 ppm in the ^{1}H NMR spectrum over the area at 2.80 ppm, namely 0.384–0.796 or 48%. On this basis, the product was a 52/48 mixture of *cis*- and *trans*-1,1-dimethylindan-2,3-d_2 (cf. infra) and 1,1-dimethylindan-3-d_1

(c) 1,1-Dimethylindene with diisobutylaluminum deuteride with Lewis bases. After 72 h at 50°C, a solution of 1.56 g (10.9 mmol) of the indene and 6.8 ml (38.2 mmol) of the deuteride in 10 ml of ethyl ether was sampled for hydrolysis, and no indan had formed. About 4 ml of ether were evaporated from the original reaction solution, which then was heated at 80°C for a further 8 d. Work-up with D_2O and GLC analysis showed that an 85/15 mixture of starting indene and deuterated 1,1-dimethylindan were present. Preparative GLC separation of the indan and IR comparison identified this compound as pure *cis*-1,1-dimethylindan-2,3-d_2. Furthermore, its NMR spectrum verified it to be dideuterated (CS_2, ^{2}H decoupled): δ 1.20 (s, 6H), 1.83 (d, H_2, J 7.5 Hz), 2.80 (d, benzylic H) and 6.99 (s, 4H).

Heating a solution of 1.02 g (7.0 mmol) of the indene and 4.2 ml (23.6 mmol) of the deuteride in 2.7 ml (30.3 mmol) of *N*-methylpyrrolidine at 60°C for 36 d and work-up with D_2O gave 56% conversion to the indan. Again, GLC separation of the indan and spectral comparison proved it to be pure *cis*-1,1-dimethylindan-2,3-d_2.

Heating a solution of 978 mg (6.8 mmol) of the indene and 4.0 ml (22.5 mmol) of the deuteride in 4.0 ml (37 mmol) of anisole at 60°C and periodic sampling gave the following deuterolysis products, indan and phenol, in ratios of moles: 0.8 d, 0.48/3.2 mmol; 2.0 d, 0.75/4.8; 6.0 d (15% conversion to the indan), 1.02/5.7. The 6-d sample was separated by preparative GLC and the indan was identified as an equimolar mixture of *cis*- and *trans*-1,1-dimethylindan-2,3-d_2 (cf. infra for the synthesis and IR data for the *trans*-isomer, under the heading: 1,1-Dimethylindene-2-d_1, with diisobutylaluminum hydride).

Hydrolysis of the remaining reaction mixture after 8 d at 60°C gave 40% of pure phenol and 15% of pure 1,1-dimethylindan-2-d_1. This indan gave the expected proton ratios in its ^{1}H NMR spectrum and the following characteristic IR bands (neat, cm^{-1}): 2191m, 2160, 1319, 1300, 1294, 1286, 1260, 1240, 1184, 1150, 1109m, 1081m, 1023m, 763s, 745s, 585, 558, 465, 453m.

(d) 1,1-Dimethylindene-2-d_1 with diisobutylaluminum hydride. A solution of 816 mg (5.6 mmol) of the indene and 1.2 ml (6.74 mmol) of the hydride in 10 ml of heptane was heated at 80°C for 60 h and then deuterolyzed. A 96% conversion to an equimolar mixture of *cis*- and *trans*-1,1-dimethylindan-2,3-d_2 was realized, as confirmed by IR and NMR spectroscopy and by deuterium analysis.

Anal. Found: D, 13.70. $C_{11}H_{12}D_2$: calcd.: D, 14.30% (Analysis corresponds to 95.6% $C_{11}H_{12}D_2$ and 4.9% $C_{11}H_{14}$). A check experiment conducted for 12 d at 55°C showed the 5% of recovered olefin still contained 97% $C_{11}H_{11}D$. Thus, no large amount of undeuterated indene was produced by elimination of i-Bu_2AlD in these cases. Also, the recovered 1,1-dimethylindan-2-d_1 contained 7.14% D (calcd. 7.14%).

A solution of 1.40 g (10.1 mmol) of the indene and 6.5 ml (36.6 mmol) of the hydride in 7 ml of ethyl ether was heated for 11 days at 55°C. Treatment of one portion with D_2O and work-up gave 49% of the indan that proved to be pure *trans*-1,1-dimethylindan-2,3-d_2 by NMR and IR spectroscopy. ^1H NMR (CS_2, ^2H decoupled); δ 1.20 (s, 6H), 1.83 (d, 1H, J 7.2 Hz), 2.80 (d) and 6.99 (s, 4H). IR (neat, cm^{-1}): 2187, 2167, 1308, 1291, 1273, 1106, 1079, 1022m, 761s, 736m, 729s, 710m, 666, 576, 546, 456, 438.

Anal. Found: D, 14.40. $C_{11}H_{12}D_2$ calcd.: D, 14.30%. Treatment of the rest of the reaction mixture with H_2O and GLC separation of the starting olefin and indan gave the following deuterium analyses:

1,1-Dimethylindene-2-d_1: Anal. Found: D, 8.20. $C_{11}H_{11}D$ calcd.: D, 8.32%.

1,1-Dimethylindan-2-d_1: Anal. Found: D, 7.16. $C_{12}H_{13}D$ calcd.: D, 7.14%.

Thus, no reversible elimination of i-$Bu_2AlH(D)$ took place.

(e) 1,1-Dimethylindene-2-d_1 with diisobutylaluminum deuteride. A solution of 1.0 g (6.9 mmol) of the indene and 4 ml of the deuteride in 5 ml of heptane and 3 ml of ethyl ether is heated for 7 d at 50°C. Hydrolysis gave 65% of 1,1-dimethylindan-2,2-d_2, which was separated by GLC. IR (neat, cm^{-1}): 2214, 2132, 2095, 1318, 1289, 1268, 1247, 1190, 1116, 1081m, 1058, 1021m, 763s, 745m, 738s, 580m, 550, 461m, 450m.

Anal. Found: D, 13.05. $C_{11}H_{12}D_2$ calcd.: D, 14.30% (Analysis corresponds to 91.2% d_2).

(f) 1,1-Dimethylindene-3-d_1 with diisobutylaluminum hydride. Treatment of 1.02 g (7.0 mmol) of the indene with 2.5 ml of the hydride in 5 ml of heptane for 60 h at 55°C and deuterolytic work-up gave pure 1,1-dimethylindan-3,3-d_3. The ^1H NMR spectrum lacked the benzylic protons at 2.80 ppm; IR (neat, cm^{-1}): 2222, 2200m, 2180, 2129, 2118m, 2102, 2080, 1307m, 1177m, 1153, 1140, 1119m, 1087m, 1078m, 1046, 1023, 940m, 938, 776, 762s, 725s, 713s, 670, 646, 596, 581m, 557, 456, 443m.

(g) 1,1-Dimethylindene-3-d_1 with diisobutylaluminum deuteride. Treatment of 917 mg (6.33 mmol) of the indene with 1.65 ml (9.2 mmol) of the deuteride in 10 ml of heptane and 1 ml of ether for 48 h at 80°C and hydrolysis of an aliquot showed a 33% conversion to indan. By IR analysis this product was a 30/70 mixture of *cis*- and *trans*-1,1-dimethylindan-2,3-d_2.

A further 72-h heating of the remaining reaction mixture and subsequent hydrolysis now yielded an 85% conversion to an equimolar mixture of the *cis*- and *trans*-dideuterated indans.

(h) 1,1-Dimethylindene-2,3-d_2 with diisobutylaluminum hydride. A solution of 1.49 g (10.2 mmol) of the indene and 6.5 ml of the hydride in 7.5 ml of ethyl ether was heated for 14 d at 60°C. Hydrolysis of half the solution and spectral analysis revealed an 89% conversion to pure *cis*-dimethylindan-2,3-d_2. Deuterolysis of the remaining reaction mixture gave pure 1,1-dimethylindan-2,3,3-d_3; IR (neat, cm^{-1}): 2201m, 2178, 2163, 2130, 2118, 1312, 1300m, 1287, 1152, 1118, 1090, 1021m, 938, 760s, 741m, 710s, 617, 575, 547m, 450, 431.

(i) 1,1-Dimethylindene-2,3-d_2 with diisobutylaluminum deuteride. The hydride in

part (h) was replaced by 6.5 ml of the deuteride and the reaction conducted as before. Deuterolytic work-up of a portion provided 1,1-dimethylindan-2,2,3,3-d_4; IR (neat, cm^{-1}): 2215m, 2175, 2143, 2126, 2100, 1309, 1300, 1282, 1268, 1182, 1153, 1131, 1104, 1091, 1067, 1030, 1018, 939, 888, 782, 761s, 742m, 711s, 619, 571, 542, 450, 430.

Hydrolysis of the remaining reaction solution gave pure 1,1-dimethylindan-2,2,3-d_3; IR (neat, cm^{-1}): 2218m, 2192, 2165, 2100, 1313, 1295m, 1269, 1235, 1189, 1180, 1152, 1119, 1084, 1060, 1025m, 963, 950, 938, 840, 803, 781, 762s, 742m, 736, 725s, 711m, 619, 575m, 548, 458, 440.

1,1-Dimethyl-3-trimethylsilylindene

(a) With diisobutylaluminum hydride. Heating 948 mg (4.39 mmol) of the indene and 2.5 ml (14.1 mmol) of the hydride in 5 ml of heptane for 4.7 d at 60°C, followed by deuterolysis at 60°C with 2 ml of D_2O and 1 ml of DCl (37% in D_2O), gave 85% of the indan. By ^1H NMR spectroscopy, this proved to be exclusively 1,1-dimethyl-3-trimethylsilylindan-3-d_1 (CCl_4, ^2H-decoupled): δ in ppm downfield from Me_3Si lock signal, 0.84 (s, 3H), 1.02 (s, 3H), 1.45 (d, H_2 *cis* to Me_3Si, J_{gem} 13.0 Hz), 1.72 (d, H_2 *trans* to Me_3Si), 6.4–7.1 (m, 4H).

(b) With diisobutylaluminum deuteride. A similar reaction of the indene with the deuteride was carried out. Deuterolysis of a portion after 2.5 days showed a 75% conversion to *cis*-1,1-dimethyl-3-trimethylsilylindan-2,3-d_2. In the ^1H NMR spectrum the signal of 1.72 ppm had disappeared.

Treatment of the remaining reaction mixture with HCl gave *trans*-1,1-dimethyl-3-trimethylsilylindan-2-d_1, whose ^1H NMR spectrum lacked the signal at 1.72 ppm, but displayed a benzylic doublet at 2.25 ppm (J_{trans} 10.5 Hz).

Acenaphthylene

(a) Reaction with diisobutylaluminum hydride. Heating a yellow solution of 1.52 g (10 mmol) of acenaphthylene and 1.9 ml (10.7 mmol) of the hydride in 25 ml of heptane for 48 h at 75–80°C gave an almost colorless adduct in 90–100% yield. The product was diluted with deoxygenated heptane and then added dropwise to water at 25°C. The organic layer consisted preponderantly of acenaphthene (73%) and 1,3-dihydroacenaphthylene (27%); ^1H NMR (CCl_4, resonances of the 1,3-dihydro component only): δ 3.16 (m, 2H at C(1)), 3.45 (m, 2H at C(3)), 5.63 (d of t, H at C(4), $J_{3,4}$ 3.8, $J_{4,5}$ 10.0 Hz), 5.83 (m, H at C(2)), 6.29 (d of t, C(5), $J_{3,5}$ 2.3 Hz) and 6.66–7.65 (m, 3H).

A similar hydralumination in heptane conducted on a 20 mmol-scale, followed by treatment with D_2O, gave a mixture of acenaphthene-1-d_1 and 1,3-dihydroacenaphthylene-3-d_1. The latter compound had a ^1H NMR spectrum having doublets of doublets at 5.63 and 6.29 ppm.

When ethyl ether was used as the solvent for hydraluminating acenaphthylene at 60°C, almost 20 d were required for a complete run. The precipitation of colorless 1-acenaphthenyl(diisobutyl)aluminum diethyl etherate occurred during this period.

The percent of 1,3-dihydroacenaphthylene in the crude product was determined by ^1H NMR integration and use of the formula:

$$\%1,3\text{-}H_2\text{-}C_{12}H_8 = \frac{(2)\ (\text{area of } 5.6\text{–}6.35 \text{ region})(100)}{(\text{area of } 5.6\text{–}7.7 \text{ region})}$$

The formula gives the percentage of dihydro product relative to acenaphthene and any derivative (oligomer) having six protons between 6.35–7.7 ppm.

(b) Reaction with diisobutylaluminum deuteride. A 20 mmole-scale reaction with the deuteride was conducted as in part (a). One portion was treated with H_2O to yield a mixture of acenaphthene-1-d_1 and 1,3-dihydroacenaphthylene-1-d_1. The ^1H NMR spectrum of the latter component had a 1-proton signal at 3.16 and a 2-proton signal at 3.45 ppm. The above formula for the percentage of the 1,3-dihydro component could be applied to the 1-d_1 and 3-d_1 isomers as well, since deuterium occurred only in the methylene groups.

A similar reaction with the deuteride was worked up with D_2O to yield acenaphthene-1,2-d_2 and 1,3-dihydroacenaphthylene-1,3-d_3. The latter's ^1H NMR spectrum had 1-proton signals at 3.16 and 3.45 ppm.

(c) Isomerization of 1,3-dihydroacenaphthylenes. Attempts to isolate this isomer by recrystallization, GLC or column chromatography on silica gel led to isomerization to acenaphthene. Intentional isomerization could be achieved as follows: a 27/73 mixture of 1,3-dihydroacenaphthylene-1,3-d_2 and acenaphthene-1,2-d_2 (300 mg) was dissolved in 15 ml of benzene and treated with 2 ml of MeOH and 20 mg of *p*-toluenesulfonic acid-O-d_1 for 15 min. After water extraction and drying over $CaCO_3$ the product exhibited no olefinic protons in its ^1H NMR spectrum. Column chromatography on alumina gave pure acenaphthene, m.p. 92–94°C; mass spectrum (PE-270, 70 eV, 30°C probe and 190°C ion source): *m/e* (%) 157 (13.2), 156 (86.5), 155 (100), 154 (67.7), 153 (32.6). This corresponds to 98% $C_{12}H_8D_2$ and 2% $C_{12}H_7D_3$.

(d) Chemical evidence for the 1,3-dihydroacenaphthylene structure. Treatment of 1-acenaphthenyl(diisobutyl)aluminum in heptane at 0°C with D_2O gave a mixture containing 31.3% of 1,3-dihydroacenaphthene-3-d_1 and acenaphthene-d_1 and preparative GLC was used to isomerize the mixture to deuterated acenaphthene, m.p. 92–94°C, from aqueous methanol (1/4).

Anal. Found: C, 92.78; D, 8.82. $C_{12}H_9D$ calcd.: C, 92.93; D, 10.00% (88% d_1).

This deuterated acenaphthene was converted to its 5,6-dinitro derivative m.p. 213.5–214.3°C, by a known method [43].

Anal. Found: D, 11.00. $C_{12}H_7DN_2O_4$ calcd.: D, 12.50% (88% d_1).

Oxidation of the deuterated acenaphthene by a known procedure [44] gave 1,8-naphthalic anhydride, m.p. 269–270°C.

Anal. Found: C, 72.57; D, 2.40. $C_{12}H_5DO_3$ calcd.: C, 72.67; D, 16.68% (14.4% d_1).

1-Methylacenaphthylene

(a) Reaction with diisobutylaluminum deuteride. Heating 1.18 g (7.06 mmol) of the acenaphthylene and 3.5 ml (19.5 mmol) of the deuteride in 5 ml of heptane for 10 d at 80°C and then deuterolyzing with 37% DCl in D_2O gave a pale yellow liquid, which was ~ 90% of reduced product (GLC) and contained ~ 40% of 1,3-dihydro-1-methylacenaphthylene-1,3-d_2 and ~ 60% of *cis*-1-methylacenaphthene-1,2-d_2. About 30% of these two isomers had protons at C(1), as was shown by methyl doublet signals at 1.13 (1,3-dihydro) and 1.25 (1,2-dihydro) ppm and by the methine signal (HCMe) at C(1) at 3.4 ppm (1-methylacenaphthene-2,2-d_2). ^1H NMR (CCl_4, ^2H-decoupled with 9 μamps irradiation at 3669 Hz): (a) *cis*-1-methylacenaphthene-1,2-d_2: δ 1.24 (s, CH_3), 2.69 (s, H_2 *cis* to CH_3) and 6.8–7.45 (m, aromatic H); (b)

1,3-dihydro-1-methylacenaphthylene-1,3-d_2: 1.12 (s, CH_3), 3.21 (m, H_3), 5.53 (d of d, H_4, $J_{3,4}$ 3.8, $J_{4,5}$ 10.0 Hz), 5.69 (d, H_2, $J_{2,3}$ 3.0 Hz), 6.22 (d of d, H_5, $J_{3,5}$ 2.2 Hz) and 6.6–7.5 (m, aromatic).

(b) Diisobutylaluminum deuteride in ethyl ether. Reaction of 1.13 g (6.79 mmol) of the hydrocarbon with 6.5 ml (36.2 mmol) of the deuteride in 7.5 ml of ethyl ether at 85°C for 8 d gave an almost colorless solution. Hydrolysis of one portion yielded a mixture of 80% of 1-methylacenaphthene-1-d_1 (^{1}H NMR: CH_3 group as a singlet at 1.25; 2.69 (s, H_2 *cis* to CH_3, J 17.5 Hz), 3.38 (d, H_2 *trans* to CH_3) and 20% of some unknown having a slightly longer GLC retention time (NMR signals at 4.91, 5.35 and 5.65 ppm).

Deuterolysis of another portion gave a product that by ^{1}H NMR analysis was principally *cis*-1-methylacenaphthene-1,2-d_2 containing ~ 10% of 1,3-dihydro-1-methylacenaphthylene-1,3-d_2 and the same unknown cited above.

Finally, the remaining reaction solution was freed of ether in vacuo and then heated at 85°C for 4 d. Diluting a portion with heptane and adding D_2O gave a 55/45 mixture of the 1,2- and 1,3-dihydro-d_2 isomers. Diluting another portion with THF and adding D_2O gave a 90/10 mixture of the 1,2- and 1,3-dihydro compounds.

(c) 1-Methylacenaphthylene-2-d_1 with diisobutylaluminum hydride. A solution of 197 mg (1.2 mmol) of the hydrocarbon and 168 mg of the hydride in 0.4 ml of toluene-d_8 was heated at 80°C for 4 d. Hydrolysis of one-half the mixture and ^{1}H NMR analysis showed the presence of 13% of the starting hydrocarbon (2.19 (s, CH_3)), 24% of 1,3-dihydro-1-methylacenaphthylene-2-d_1 (1.12 (d, CH_3, J 7.5 Hz), 5.56 (d of t, H_4), 5.74 (m, H_2) and 6.20 (d of t, H_5) and 63% of *cis*-1-methylacenaphthene-2-d_1 (1.24 (d, CH_3) and 3.2 (m, H_2 *trans* to CH_3 and other benzylic protons); N.B.: no signal at 2.69 ppm (H_2 *cis* to CH_3)).

Treatment of the other half of the reaction mixture with 20% DCl in D_2O gave 14% of unreacted olefin, 41% of 1-methylacenaphthene-2,2-d_2 and 45% of 1,3-dihydro-1-methylacenaphthylene-2,3-d_2, ^{1}H NMR (CCl_4): 1.12 (d, CH_3, J 7.5 Hz), 3.2–3.9 (br, m, benzylic H), 5.56 (d of d, H_4, $J_{3,4}$ 4.0, $J_{4,5}$ 9.8 Hz), 6.20 (d of d, H_5, $J_{3,5}$ 2.3 Hz) and 6.55–7.0 (m, aromatic).

Hydrolysis of alkyllithium adducts of aluminum compounds

(a) cis-1,1-Dimethyl-3-indanyl(diisobutyl)aluminum with methyllithium. A solution of 1.50 g (10.2 mmol) of 1,1-dimethylindene-2,3-d_2 and 6.5 ml (36.6 mmol) of diisobutylaluminum hydride was heated for 16 d at 60°C. Hydrolysis of an aliquot and combined GLC and IR analysis showed an 89% conversion to pure *cis*-1,1-dimethylindan-2,3-d_2.

The remaining aluminum adduct was treated with 2 equivalents of methyllithium in ether. After 2 d at 60°C hydrolytic work-up gave an equimolar mixture of *cis*- and *trans*-1,1-dimethylindans-2,3-d_2.

(b) cis-2-Deuterio-1,1-dimethyltrimethylsilyl(diisobutyl)aluminum with methyllithium. The aluminum adduct was prepared from the 3-silylindene and diisobutylaluminum deuteride (cf. supra). An excess of an ethereal solution of methyllithium was added and the mixture maintained at 60°C for 18 h. Deuterolysis with 37% DCl in D_2O gave an equimolar mixture of *cis*- and *trans*-1,1-dimethyl-3-trimethylsilylindan-2,3-d_2 (^{1}H NMR 1.06 and 1.26 ppm signals for Me_3Si groups).

(c) 1-Acenaphthenyl(diisobutyl)aluminum with n-butyllithium. A solution of 10 mmol of the aluminum compound in 20 ml of heptane was treated with one

equivalent of n-butyllithium in hexane. Hydrolysis of the yellow suspension gave only acenaphthene.

(d) trans-2-Deuterio-2-methyl-1-acenaphthenyl(diisobutyl)aluminum with methyllithium. The aluminum adduct was prepared by heating 5 mmol of 1-methylacenaphthylene with 5.5 ml (30 mmol) of diisobutylaluminum deuteride in 6 ml of ether at 85°C for 8 d. The solution was diluted with 30 ml of heptane and then 14 mmol of methyllithium in ether were added dropwise. A white precipitate and flashes of orange color developed during the addition. Heating the pale orange mixture for 2 d at 80°C and work-up with 37% DCl in D_2O gave > 90% of *cis*-1-methylacenaphthene-1,2-d_2 and < 10% of 1,3-dihydro-1-methylacenaphthylene-1,3-d_2. No sign of the *trans*-1,2-d_2 isomer was seen.

Relative olefin reactivities in hydralumination

A qualitative ranking of olefin reactivity toward diisobutylaluminum hydride in heptane at 85°C could be made by noting the conversion to adduct in a given period (olefin, % adduct, days): acenaphthylene, > 95%, 1.5; 1-methylacenaphthylene, 87%, 3.0; 1-phenylacenaphthylene, 50%, 7.8; 1,1-dimethyl-3-phenylindene, 0%, 3.0; phenanthrene, 0%, 4.5.

By pairwise competition experiments with hydride at 75°C, the relative rates were: 1,1-dimethyl-3-trimethylsilylindene, 1.5; 1-methylacenaphthylene, 1.1; and 1,1-dimethylindene, 1.0.

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References

1 H. Lehmkuhl, K. Ziegler and H.G. Gellert in E. Müller (Ed.), Houben-Weyl, Methoden der Organischen Chemie, Vol. XIII/4, Georg Thieme, Stuttgart, 1970, pp. 23–46.
2 J.J. Eisch in G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Vol. I, Pergamon Press, Oxford, 1982, Ch. 6.
3 J.J. Eisch and R. Amtmann, J. Org. Chem., 37 (1972) 3410.
4 J.J. Eisch and L.E. Hallenbeck, unpublished studies.
5 G. Wilke and H. Müller, Justus Liebigs Ann. Chem., 629 (1960) 222.
6 J.J. Eisch and W.C. Kaska, J. Amer. Chem. Soc., 88 (1966) 2213.
7 J.J. Eisch and M.W. Foxton, J. Organometal. Chem., 11 (1968) P50.
8 J.J. Eisch and M.W. Foxton, J. Org. Chem., 36 (1971) 3520.
9 J.J. Eisch, H. Gopal and S.-G. Rhee, J. Org. Chem., 40 (1975) 2064.
10 G. Zweifel and R.B. Steele, J. Amer. Chem. Soc., 89 (1967) 5085.
11 J.J. Eisch and S.-G. Rhee, J. Amer. Chem. Soc., 97 (1975) 4673.
12 G. Fraenkel, D.T. Dix and M. Carlson, Tetrahedron Lett., (1968) 579.
13 M. Witanowski and J.D. Roberts, J. Amer. Chem. Soc., 88 (1966) 737.
14 J.J. Eisch and K.C. Fichter, J. Amer. Chem. Soc., 96 (1974) 6815.
15 J.J. Eisch and K.C. Fichter, J. Amer. Chem. Soc., 97 (1975) 4772.
16 K. Ziegler, H.G. Gellert, H. Martin, K. Nagel and J. Schneider, Justus Liebigs Ann. Chem., 589 (1954) 91.
17 J.J. Eisch and M.W. Foxton, J. Organometal. Chem., 12 (1968) P33.

18 K. Ziegler, H. Martin and F. Krupp, Justus Liebigs Ann. Chem., 629 (1960) 14.
19 V.R. Sandel and H.H. Freedman, J. Amer. Chem. Soc., 85 (1963) 2328.
20 W.J. Bailey and R.A. Baylouny, J. Org. Chem. 27 (1962) 3476.
21 J.J. Eisch and S.-G. Rhee, J. Amer. Chem. Soc., 96 (1974) 7276.
22 J.N. Hay, G.R. Jones and J.C. Robb, J. Organometal. Chem., 15 (1968) 295.
23 E. Bonitz, Chem. Ber., 88 (1955) 742.
24 J.J. Eisch and S.-G. Rhee, J. Organometal. Chem., 86 (1975) 143.
25 J.J. Eisch and S.-G. Rhee, Justus Liebigs Ann. Chem., (1975) 565.
26 R.W. Taft, Jr., in M.S. Newman (Ed.), Steric Effects in Organic Chemistry, Wiley, New York, N.Y., 1956, p. 586.
27 S. Winstein and N.J. Holness, J. Amer. Chem. Soc., 77 (1955) 5562.
28 N.A. Clinton, R.S. Brown and T.G. Traylor, J. Amer. Chem. Soc., 92 (1970) 5228.
29 F.R. Jensen and B. Rickborn, Electrophilic Substitution of Organomercurials, McGraw-Hill, New York, N.Y., 1968.
30 G. Köbrick, D. Merkel and K. Imkampe, Chem. Ber., 106 (1973) 2017.
31 G. Fraenkel, C.E. Cottrell and D.T. Dix, J. Amer. Chem. Soc., 93 (1971) 1704.
32 G. Fraenkel and D.T. Dix, J. Amer. Chem. Soc., 88 (1966) 979.
33 H.O. House, R.A. Latham and G.M. Whitesides, J. Org. Chem., 32 (1967) 2482.
34 E. Pechhold, D.G. Adams and G. Fraenkel, J. Org. Chem., 36 (1971) 1368.
35 J.J. Eisch and M.-R. Tsai, J. Organometal. Chem., 225 (1982) 5.
36 M.B. Smith, J. Organometal. Chem., 22 (1970) 273.
37 J.J. Eisch, Organometallic Syntheses, Vol. II, J.J. Eisch and R.B. King, (Eds.), Academic Press, New York, N.Y., 1981.
38 A. Vogel, A Textbook of Practical Organic Chemistry, Longmans, Green, London, 1948, p. 168.
39 A.S. Keston, D. Rittenberg and R. Schoenheimer, J. Biol. Chem., 122 (1938) 227.
40 L. Ames, E. Chaitman and F. Grant, J. Org. Chem., 26 (1961) 1299.
41 L. Fieser and M. Fieser, Reagents for Organic Synthesis, Vol. I, Wiley, New York, N.Y., 1967, p. 584.
42 R.B. Brown and D.L. Hammick, J. Chem. Soc., (1948) 1395.
43 I. Honda and M. Okayaki, J. Soc. Org. Syn. Chem., Japan, 7 (1950) 25.
44 Elsevier Encyclopedia of Organic Chemistry, F. Radt, (Ed.), Elseviers, Amsterdam, Vol. 12B, 1954, p. 4700.