cyclopentene, 54664-61-8; *trans*-1,4-diacetoxy-2-methyl-2-cyclohexene, 92489-95-7; *cis*-1,4-diacetoxy-2-methyl-2-cyclohexene, 59055-07-1; *trans*-1,4-diacetoxy-1-methyl-2-cyclohexene, 92489-96-8; 1β,4β-diacetoxy-5α-carbomethoxy-2-cyclohexene, 92490-01-2; 1α,4β-diacetoxy-6α-methoxy-2-cycloheptene, 92490-03-4; (*Z*)-1,4-diacetoxy-2-methyl-2-butene, 59055-00-4; (*E*)-1,4-diacetoxy-2-methyl-2-butene, 59054-99-8; (*E*)-1,4-diacetoxy-2-butene, 1576-98-3; (*E*)-1,4-diacetoxy-2-pentene, 92490-06-7; 2(*E*),4(*E*)-hexadiene, 5194-51-4; 2(*E*),4(*Z*)-hexadiene, 5194-50-3; (*E*)-1,3-pentadiene, 2004-70-8; (*Z*)-1,4-diacetoxy-2-butene, 25260-60-0.

Kinetic Control and Locoselectivity in the Electrophilic Cleavage of Allylic Aluminum Compounds: Reactions of Acenaphthenylaluminum Reagents with Carbonyl Substrates[1]

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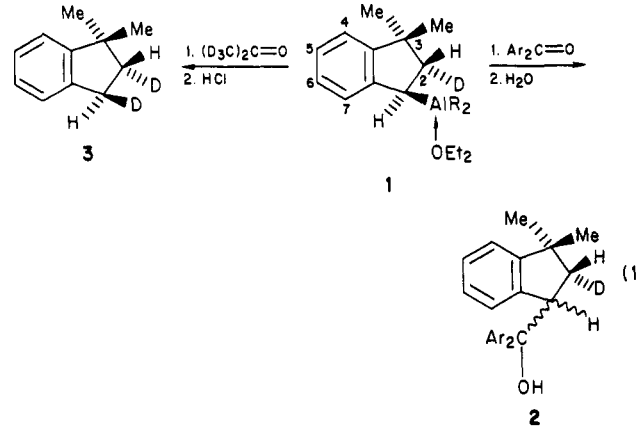
The benzylic reagent 1-acenaphthenyldiisobutylaluminum, which is formed by the addition of diisobutylaluminum hydride to acenaphthylene, exhibits a ^1H NMR spectrum at 25 °C consistent with a C_1–Al bond. At 110 °C the carbon–aluminum bond undergoes configurational inversion, as evidenced by the magnetic equivalence of the cis and trans C_2 protons. At −78 °C this aluminum compound reacts with ketones to give, upon hydrolysis, 65–75% of 3-(α-hydroxy-disubstituted methyl)-1,3-dihydroacenaphthylenes, which undergo acid-catalyzed isomerization to 3-(α-hydroxy-disubstituted methyl)acenaphthenes and which dissociate into acenaphthene and the ketone upon contact with Pd. On the other hand, the same reagents at 80–100 °C lead to the formation of 75–85% of 1-(α-hydroxy-disubstituted methyl)acenaphthenes. Similar reactions with acyl chlorides (RCOCl, where R = Me, Et, Ph) and with Me_3SiCl lead to 3-acylacenaphthenes and 1-(trimethylsilyl)acenaphthene, respectively. The stereochemically defined adduct of acenaphthylene and diisobutylaluminum deuteride, (*cis*-2-deuterio-1-acenaphthenyl)diisobutylaluminum diethyl etherate, is found to react with 9-fluorenone at 65 °C to yield a 1:1 mixture of *cis*- and *trans*-2-deuterio-1-acenaphthenylcarbinols. Similarly, treatment of the same aluminum reagent with O_2 gives a 1:1 mixture of *cis*- and *trans*-2-deuterio-1-acenaphthenols. The magnetically shielded C_8 or ortho proton in the original aluminum adduct offers a valuable monitor of the extent of complexation at the C_1–Al bond. The present findings demonstrate that electrophilic attack at the ortho position (leading to C_3 substitution) is the kinetically controlled process, while rearrangement to C_1 is thermodynamically determined.

The interaction of aluminum alkyls with carbonyl compounds raises an array of interesting mechanistic questions, since modest changes in the structure of the reactants or in experimental conditions can lead to varying amounts of 1,2-carbalumination,[2] conjugate or 1,4-carbalumination,[3] enol–salt formation,[4] or reduction by aluminum hydride transfer.[5] By employing aluminum alkyls having carbon–aluminum bonds of known configuration, previous work has provided stereochemical insight into two of these processes, namely, 1,2-carbalumination and enol–salt formation.[6] Thus, diisobutyl((1*R*,2*S*)-2-deuterio-3,3-dimethyl-1-indanyl)aluminum diethyl etherate[7] (1) was shown to insert the ketone 9-fluorenone with loss of configuration at the 1-indanyl position (2), but this aluminum reagent caused enolate formation with acetone with retention of configuration at the same indanyl site (3) (eq 1).



With benzylic aluminum compounds, such as 1, an additional reaction pathway with carbonyl substrates becomes competitive: orthoalkylation via allylic rearrangement. For example, the reaction of 1 with CO_2 leads principally to the indan-7-carboxylic acid.[8] In order to evaluate the factors determining the competition between normal 1,2-carbalumination and carbalumination with allylic rearrangement, therefore, we have examined the reactivity of 1-acenaphthenyldiisobutylaluminum (4) to-

(1) Part 40 of the series "Organometallic Compounds of Group III". Part 39: *J. Organomet. Chem.* **1983**, *250*, 63. Part 22 of the series Rearrangements of Organometallic Compounds.

(2) Lehmkul, H.; Ziegler, K. "Methoden der Organischen Chemie" (Houben-Weyl); Mueller, E., Ed.; Georg Hieme Verlag: Stuttgart, 1970; Vol. XIII-4, pp 224–236.

(3) (a) Gilman, H.; Marple, K. E. *Recl. Trav. Chim. Pays-Bas* **1936**, *55*, 133. (b) Kabalka, G. W.; Daley, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 4428.

(4) (a) Ziegler, K.; Schneider, K.; Schneider, J. *Liebigs Ann. Chem.* **1959**, *623*, 9. (b) Pasynkiewicz, S.; Sliwa, E. *J. Organomet. Chem.* **1965**, *3*, 121.

(5) (a) Meerwein, H.; Hinz, G.; Majert, H.; Soenke, H. *J. Prakt. Chem.* **1936**, *147*, 226. (b) Haubenstock, H.; Davidson, E. B. *J. Org. Chem.* **1963**, *28*, 2772. (c) Ashby, E. C.; Yu, S. H., *J. Org. Chem.* **1970**, *35*, 1034. (d) Giacomelli, G.; Menicagli, R.; Lardicci, L. *J. Org. Chem.* **1973**, *38*, 2370.

(6) Eisch, J. J.; Fichter, K. C. *J. Am. Chem. Soc.* **1975**, *97*, 4772.

(7) The configuration of the sample of 1 actually studied was racemic, that is, a 1:1 mixture of (1*R*,2*S*)- and (1*S*,2*R*)-1.

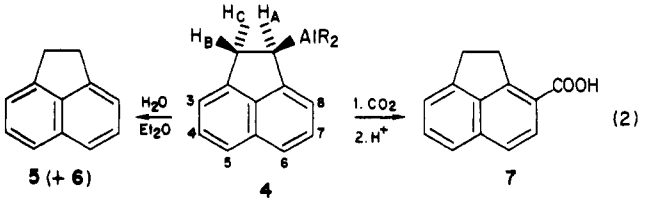
(8) Eisch, J. J. In Wilkinson, G.; "Comprehensive Organometallic Chemistry"; Stone, F. G. A.; Ebel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. I, p 574.

0022-3263/84/1949-4631$01.50/0

Table I. Effect of Added Lewis Bases on the SAR-OAR Proton Ratio of 1-Acenaphthenyldiisobutylaluminum (1.9 M)

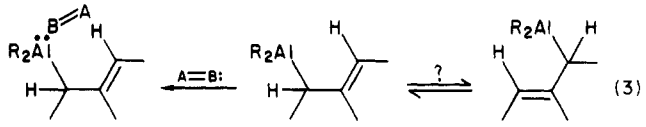
added donor	temp, °C	ratio SAR	ratio OAR
none	38	1.0	5.0
Et_2O, 0.26 equiv	38	1.0	8.5
Et_2O, 0.82 equiv	38	1.0	27.2
N-methylpyrrolidine, 0.26 equiv	38	1.0	8.8
N-methylpyrrolidine, 0.40 equiv	70	1.0	13.1
N-methylpyrrolidine, 0.80 equiv	38	1.0	39.0

ward carbonyl derivatives. Previous studies had shown that hydrolysis of **4** in ethyl ether solution gave a 9:1 ratio of acenaphthene (**5**) and 1,3-dihydroacenaphththylene (**6**) while treatment with CO_2 led exclusively to acenaphthene-3-carboxylic acid (**7**) (eq 2).[9]



5 (+ 6) 4 7 (2)

In the present work we wished to learn: (a) whether benzylic structure **4a** itself would rearrange to its 3-aluminio isomer (**4b**) at high temperatures or in more strongly basic solvents (cf. eq 3); (b) which experimental conditions

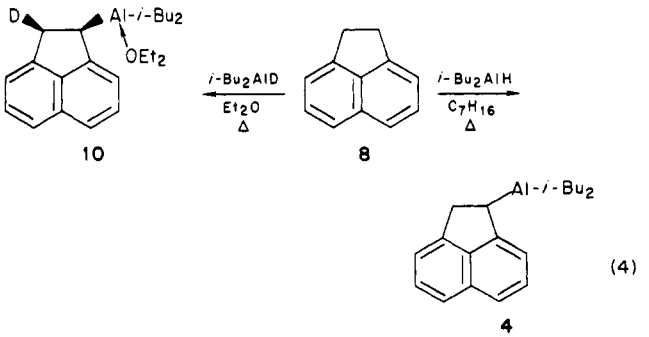


4c **4a** **4b** (3)

favored allylic rearrangement with carbonyl substrates; and (c) what role possible complexation of **4a** with the carbonyl substrate A=B might play in directing the course of the carbalumination reaction (**4c**).

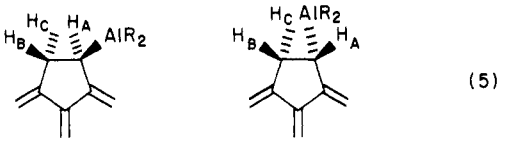
Results

Preparation of 1-Acenaphthenyldiisobutylaluminum (4). Hydralumination of acenaphthylene (**8**) with diisobutylaluminum hydride (**9**) in heptane at 80 °C gave essentially a quantitative yield of **4**. By use of ethereal media, diisobutylaluminum deuteride could be added to **8** and other cyclic olefins[10] under conditions where the initial syn adduct **10** was stable to isomerization (eq 4).



10 **8** **4** (4)

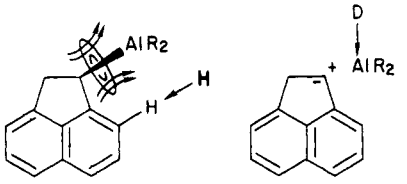
Structure of 1-Acenaphthenyldiisobutylaluminum (4). The proton NMR spectrum of the hydralumination product of acenaphthylene (**8**), measured at 37 °C in toluene-d_8, is in general accord with that expected for **4** but it displays some interesting features. When the sample's spectrum is recorded at 112 °C, the methylene bridge signals are sharpened into a triplet (J = 7 Hz), a doublet (J = 7 Hz), and a doublet (J = 4 Hz). The multiplicities of H_A, H_B, and H_C at 112 °C show that H_B and H_C have become equivalent by some process of C–Al bond inversion (**4d** ⇌ **4e**).[10,11]



4d **4e** (5)

The aromatic proton at 6.85 ppm, which is shielded relative to the aromatic protons at 7.2–7.45 ppm, is assigned to H_8. Confidence in this assignment was gained by hydraluminating acenaphthylene-*1,5-d*$_2$ (72% deuterated at C_5) with *i*-Bu_2AlH. The resulting deuterated analogue of **4** displayed an ^1H NMR spectrum whose shielded aromatic area at 6.85 ppm was in a 1:4 ratio to the other aromatic protons (SAR:OAR). Therefore, the shielded proton cannot be H_5 or H_6.

The observed SAR:OAR ratio in undeuterated **4** was somewhat dependent upon the concentration of **4** (OAR increasing as the concentration decreased) and upon the presence of excess R_3Al, R_2AlD, or R_2AlCl (OAR increasing in their presence). However, the addition of Lewis bases, such as diethyl ether or *N*-methylpyrrolidine, caused a pronounced decrease in the proportion of shielded aromatic protons (SAR) (Table I). The shielding of H_8 in donor-free **4** and its deshielding with coordinating ligands (R_3Al or D:) can be accounted for in terms of the magnetic anisotropy of the C–Al bond. For **4** in hydrocarbon media, the induced magnetic field of the C–Al bond shields H_8 (**4f**). Complexation of any ligand, such as R_3Al or a Lewis



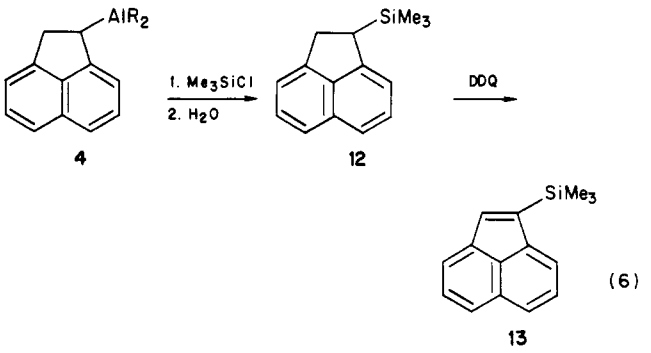
4f **4g**

base D, increases the ionic character of the C–Al bond and thereby converts the magnetic shielding of **4f** into the well-precedented deshielding observed for the ortho protons of benzylic anions (**4g**).[12]

Electrophilic Character of 1-Acenaphthenyldiisobutylaluminum (4) toward Chlorotrimethylsilane (11). The aluminum reagent reacted with **11** at 25 °C to give almost a quantitative yield of 1-(trimethylsilyl)-acenaphthene (**12**), whose identity was further corroborated by dehydrogenation with DDQ to produce 1-(trimethylsilyl)acenaphthylene (**13**) (eq 6). By contrast, **4** dissolved in THF failed to give any silyl derivative **12** when treated with Me_3SiCl at 25 °C.

Reactions of 1-Acenaphthenyldiisobutylaluminum (4) with Carbonyl Derivatives. (a) Acetone at 25 °C. Interaction at room temperature gave a 70:30 mixture of 3-(2-hydroxy-2-propyl)-1,3-dihydroacenaphthylene (**14**) and acenaphthene (**5**). In chloroform solution **14** rearranged to 3-(2-hydroxy-2-propyl)acenaphthene (**15**), and acid-catalyzed dehydration produced 3-(2-propenyl)-acenaphthene (**16**). Reduction of **16** by *i*-Bu_2AlH and

(9) Eisch, J. J.; Husk, G. R. *J. Organomet. Chem.* **1974**, *64*, 41.
(10) Eisch, J. J.; Fichter, K. C. *J. Organomet. Chem.* **1983**, *250*, 63.
(11) Eisch, J. J.; Fichter, K. C. *J. Am. Chem. Soc.* **1974**, *96*, 6815.
(12) Sandel, V. R.; Freedman, H. H. *J. Am. Chem. Soc.* **1963**, *85*, 2328.

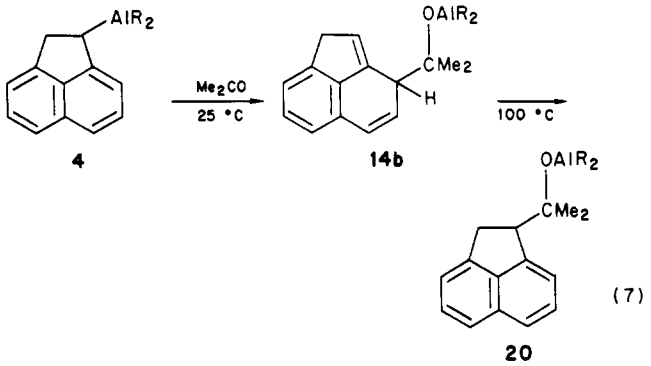


(6)

subsequent hydrolysis gave 3-(2-propyl)acenaphthene (**17**), which was shown to be distinguishable from the known 5-(2-propyl)acenaphthene (Scheme I).

By allowing **4** to react with acetone-d_6 under comparable conditions and by then isolating the 30% of acenaphthene formed prior to hydrolysis (namely, by subliming **5** from the unhydrolyzed reaction mixture), it was found that **5a** was 86.5% monodeuterated. Also, under the thermal condition of sublimation, **14a** rearranged to **17a** (cf. infra). Furthermore, an oxidative degradation of this acenaphthene gave a naphthalic anhydride (**18**) essentially devoid of deuterium. This result demonstrates that the deuterated **5a** had the preponderance of its deuterium at the benzylic positions. Consequently, **4** had reacted with the carbonyl group of acetone with allylic rearrangement but had formed the acetone enolate via proton abstraction without allylic rearrangement (Scheme II).

(b) Acetone at 100 °C. When **4** and acetone were allowed to react, first at −78 °C and eventually at temperatures up to 100 °C, the principal product finally isolated was 1-(2-hydroxy-2-propyl)acenaphthene (**19**). This outcome clearly shows that the kinetically favored product is **15**, arising from aluminum intermediate **14b**. However, at higher temperatures **14b** rearranges to give the thermodynamically favored product **20**, whose hydrolysis leads to **19** (eq 7).



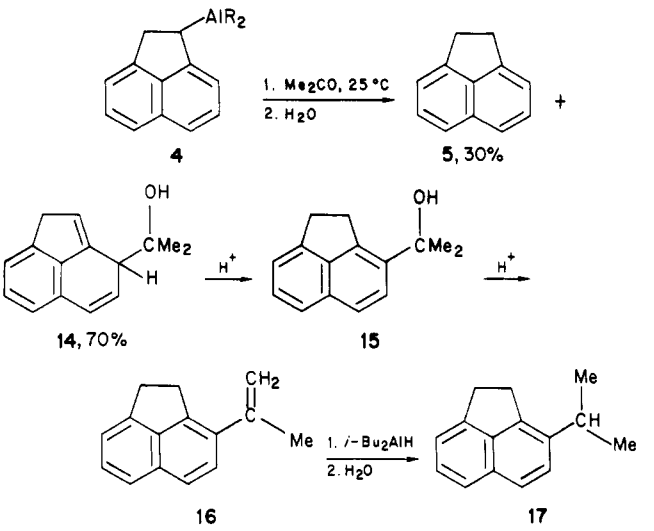
(7)

(c) Acetone at −78 °C with the *n*-Butylaluminate of 4. In contrast with the 70% yield of **14** or **19** obtained from **4** and acetone, the *n*-butyllithium adduct of **4** gave, at most, 10% of **14**; 90% of the acenaphthenyl groups did not add to the carbonyl group of acetone.

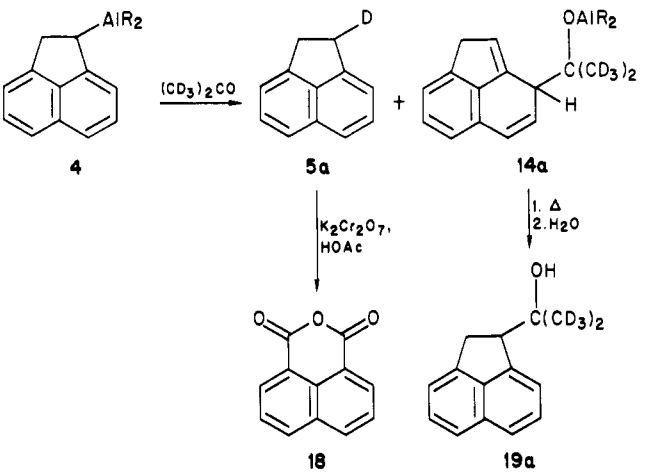
(d) Other Aliphatic Ketones. Both 3-pentanone and cyclopentanone displayed a pattern of reaction similar to that of acetone: in the temperature range of −50 °C to +25 °C, 70–75% of 3-(hydroxydialkyl)acenaphthene products; and the tendency to yield 1-(hydroxydialkyl)acenaphthenes at temperatures above 80 °C.

(e) Reactions of Propiophenone (21). This ketone reacted smoothly with **4** at −78 °C to give, upon hydrolysis at this temperature, 69% of 3-(1-hydroxy-1-phenyl-1-propyl)-1,3-dihydroacenaphthylene (**22**), which slowly isomerized to 3-(1-hydroxy-1-phenyl-1-propyl)-

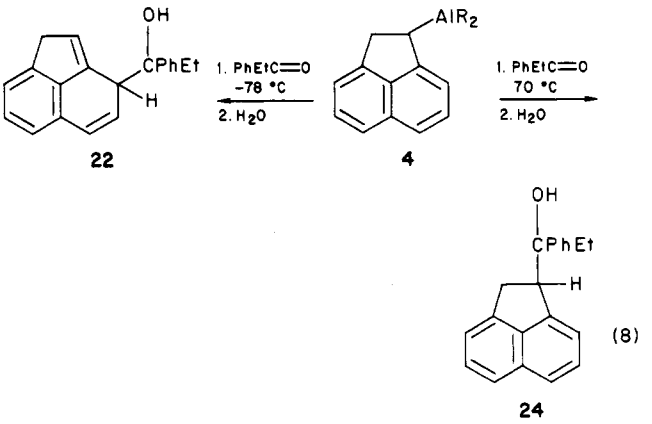
Scheme I



Scheme II



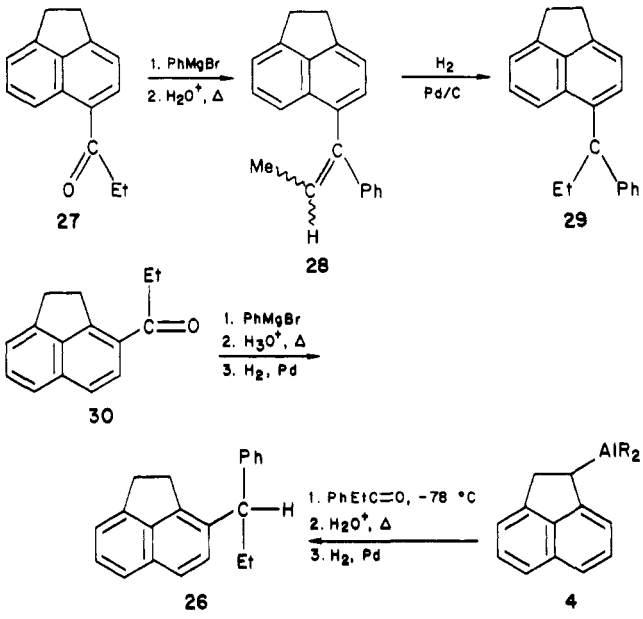
acenaphthene (**23**). The interaction of **21** and **4** at 70 °C, on the other hand, led to 80% of 1-(1-hydroxy-1-phenyl-1-propyl)acenaphthene (**24**) (eq 8).



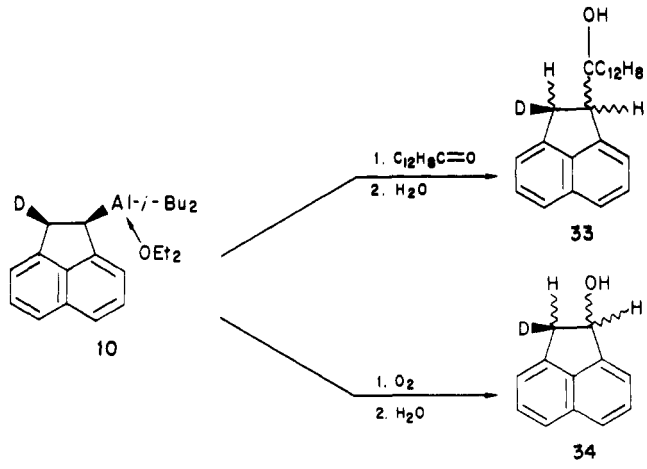
(8)

The structure of **23** as being a 3-substituted rather than a 5-substituted acenaphthene was verified in the following unambiguous manner: Compound **23** was dehydrated to **25** and this in turn catalytically hydrogenated to the 1-phenyl-1-propylacenaphthene (**26**). Thereupon, authentic 5-(1-phenyl-1-propyl)acenaphthene (**29**) was prepared by adding phenyl Grignard reagent to 5-propionylacenaphthene (**27**), dehydrating the alcohol to yield an *E,Z* mixture of 5-(1-phenyl-1-propenyl)acenaphthene (**28**) and then reducing **28** to provide **29**. In a parallel fashion, authentic 3-(1-phenyl-1-propyl)acenaphthene (**26**) was

Scheme III



Scheme IV



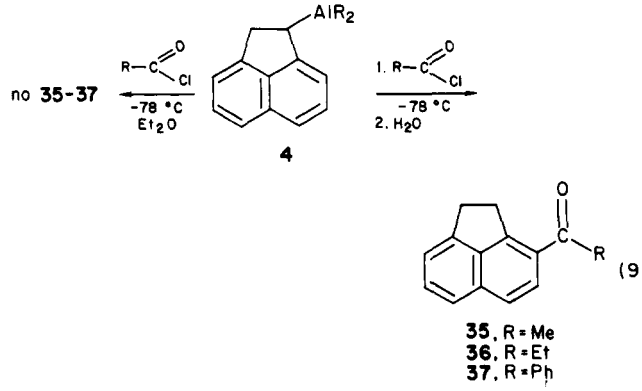
synthesized by adding phenyl Grignard reagent to 3-propionylacenaphthene (**30**), dehydrating the alcohol to an *E,Z* mixture of 3-(1-phenyl-1-propenyl)acenaphthene (**31**), and thereafter reducing **31** to produce **26** (Scheme III). Compounds **23** and **26** were demonstrably different.

As with the reaction of **4** with acetone at −78 °C, the *n*-butyllithium adduct of **4** reacts with **21** to give essentially no **23** but only dihydroacenaphthylenes.

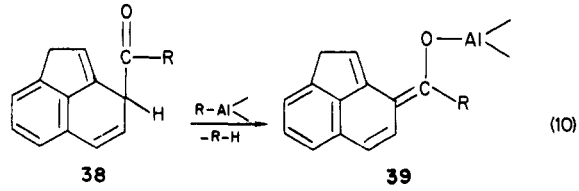
(f) Reactions with Fluorenone (32). The reactions of this ketone with **4**, at −78 °C and at +25 °C, respectively, were analogous to those of other ketones. The lower temperature favored the 3-substituted acenaphthylene in a kinetic process; the higher temperature produced the 1-substituted acenaphthene.

A further point of interest, however, was the stereochemistry with which the 2-deuterated, stereochemically defined etherate **10** reacted with ketone **32** at 25–50 °C. The isolated 9-(2-deuterio-1-acenaphthenyl)-9-fluorenol (**33**) obtained after hydrolysis was shown by ^1H NMR spectroscopy to be a 1:1 mixture of cis and trans isomers. This indicates that ketone insertion into the benzylic carbon–aluminum bond of **10** occurs in a nonconcerted, stepwise manner, so that there is no retention of configuration. In a similar result, oxidation of **10** with O_2 led to a 1:1 mixture of *cis*- and *trans*-1-acenaphthenol (**34**), again signaling the loss of C–Al bond configuration in the course of reaction (Scheme IV).

(g) Reactions wtih Acyl Chlorides. Acetyl, propionyl, and benzoyl chlorides reacted readily with **4**, even at −78 °C, to produce 3-acylacenaphthenes (**35**, **36** and **37**, respectively). In a manner reminiscent of the reaction of Me_2SiCl with **4** (section 2, Experimental Section), however, the presence of ether prevented the formation of **35–37** at −78 °C (eq 9). In the presence of Et_2O, higher temperatures were required to obtain 3-substituted products, but such derivatives were then 3-(1-hydroxyalkyl)-acenaphthenes, rather than the 3-acylacenaphthenes. Apparently, in the presence of ether, **4** reduces acyl chlorides to aldehydes, which then react with acenaphthenylaluminum compounds in the manner of ketones (cf. Scheme I).



Finally, the reaction products of **4** with acyl chlorides did not exhibit the temperature dependence observed with ketones. This difference may stem from the ease with which the initial product **38** can undergo enolate salt formation to **39** and prevent facile loss of the 3-acyl group (eq 10).



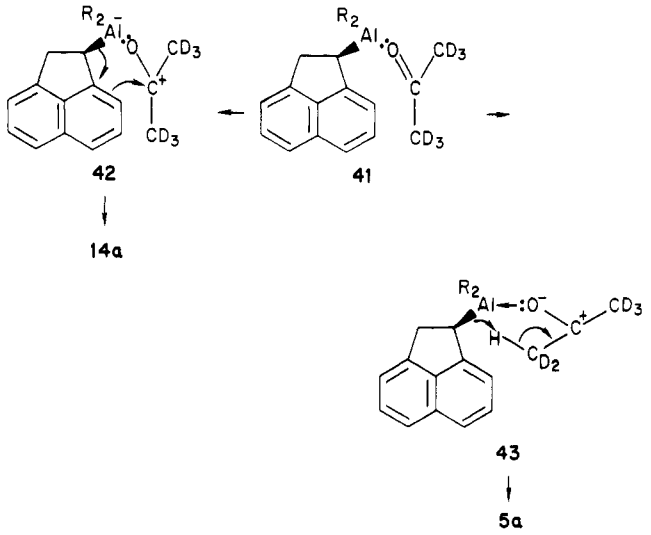
Discussion

Structural Aspects. From the NMR spectral properties of **4**, it is clear that at 25 °C the carbon–aluminum bond is localized at C_1 and that it undergoes rapid configurational inversion only above 100 °C. As with other highly branched aluminum alkyls,[13] **4** would be expected to be largely monomeric except in very concentrated solutions.[14] The shielding of the C_8 proton in **4** furnishes a useful probe for the polarity of the acenaphthenyl–aluminum bond. As was noted earlier, Lewis bases markedly reduce such shielding because they enhance the benzylic anionic character of C_1 (**4g**) and thus bring about a magnetic deshielding of the C_8 proton.[15]

Reactivity of 1-Acenaphthenyldiisobutylaluminum (4). The observation that in hydrocarbon solution **4** reacts readily with Me_3SiCl at 25 °C and with ketones and acyl chlorides even at −78 °C contrasts sharply with the failure of the corresponding reactions in ether solution. Indeed, even converting **4** into the lithium aluminate, LiAl(*n*-Bu)(*i*-Bu)$_2$($C_{12}H_9$), with *n*-butyllithium, a process expected to enhance the reactivity of the acenaphthenyl–aluminum

(13) Hoffmann, E. G. *Liebigs Ann. Chem.* **1960**, 629, 104.
(14) Smith, M. B. *J. Organomet. Chem.* **1970**, 22, 273.
(15) Chambers, D. B.; Coates, G. E.; Glockling, F.; Weston, M. *J. Chem. Soc.* **1969**, 1712.

Scheme V



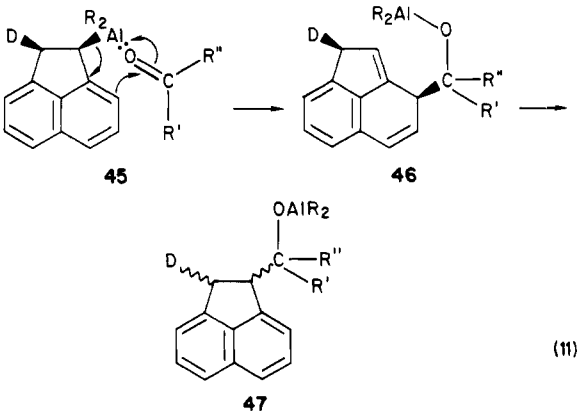
bond,[17] did not promote the carbalumination of acetone or propiophenone at −78 °C. These findings demonstrate the importance of complexation between triccordinate **4** and the organic substrate for successful reaction. The presence of ether or *n*-butyllithium forms a tetracoordinate substrate, **4**·OEt_2 or Li(*n*-Bu·**4**), that cannot easily complex with Me_3SiCl or R_2CO and hence is unreactive. Previous studies have shown that complexation between organoaluminum reagents and carbonyl substrates precedes the actual carbalumination,[18-20] but the present work underscores the essential role of such complexation.

The reaction of **4** at −78 °C with enolizable ketones, such as acetone and propiophenone, involved the competition between carbalumination with allylic rearrangement and enolate salt formation (**14a** vs. **5a** in Scheme II). The ratio of rates for these kinetically controlled processes was found to be $k_C:k_E$ = 7:3. As the reaction with acetone-d_6 revealed, enolate salt formation did not involve allylic rearrangement, for the deuteron abstracted from the acetone was preponderantly at the C_1 site of acenaphthene formed (**5a** in Scheme II). Both the rearrangement involved in forming **14a** and the lack of one in forming **5a** can be reconciled by the dual rearrangements possible for complex **41**, both of which processes can be depicted as evolving through concerted, six-membered transition states **42** and **43** (Scheme V). The transition state depicted in **43** implies a retention of configuration at the C_1–Al bond, an expectation actually realized in the reactions of benzyl–aluminum bonds (eq 1).[6]

The carbalumination of **4** with CO_2, ketones, and acyl chlorides occurred most readily at C_8. Hence, this reaction is kinetically controlled and exhibits a high locoselectivity.[21] The facile attack at C_8 is nicely accommodated by the six-membered transition state depicted in **42**. Coordination of the ketone on aluminum should enhance the benzylic anionic character of C_1 (cf. **4g** and **42**) and the electron density at C_8, leading to ready attack by the carbonyl electrophile.

However, the ease with which the 3-substituted product in ketone reactions rearranges to the 1-substituted acenaphthene shows how labile intermediates like **14a** are. Furthermore, this conversion proves that 1-substitution is thermodynamically favored. The failure of 3-acylacenaphthenes to rearrange to 1-acyl isomers probably is due to the irreversible enolate salt formation shown in eq 10.

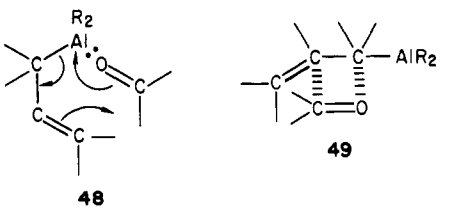
The readiness with which ketones attack **4** first at C_8 and then in slower step yield C_1-substituted products explains why the stereochemically defined aluminum reagent **10** reacted nonstereoselectively with 9-fluorenone at 25 °C (Scheme IV). The stereoisomeric products **33** might actually have been the rearrangement products of the kinetically controlled product 9-(1,3-dihydro-3-acenaphthenyl)-9-fluorenol (**44**). This latter intermediate could be detected by conducting the reaction at −78 °C. The loss in configuration at C_1 in converting **4** and fluorenone into **33**, therefore, could have occurred either in the formation of the aluminum salt of **44** itself or in its isomerization to **33**. From the stereochemical implications of transition state **42** (**45**), however, it is likely that **14a** (i.e., **46**) is formed stereoselectively, putting the 3-substituent syn to the benzylic deuteron (eq 11). On the other hand,



(11)

the observed lability of intermediates like **14** and **14a** (i.e., **46**) make it more probable that nonstereoselective C–C bond dissociation occurs during the conversion of **46** into **47**. Whether **46** is converted into **47** by a heterolytic or a homolytic cleavage of the C_3–$CR_2OAlR'R''$ bond cannot be decided. Either bond cleavage would yield a 1:1 mixture of *cis*- and *trans*-**33**. It should be noted that an unequivocally homolytic process, the reaction of **10** with O_2,[22] also yields a 1:1 mixture of *cis*- and *trans*-1-acenaphthenols (**34**, Scheme IV).

Since the attack of carbonyl substrates occurs more rapidly at the C_8 site of **4**, rather than at C_1, it is appealing to suggest that six-membered transition state is of lower energy than a four-membered configuration (**48** vs. **49**). A



lower energy for **48** may be attributed to its resembling the transition state of an allowed [3,3]-sigmatropic rearrangement. Similarly, a higher energy for **49** may be ascribed to its resembling a disallowed $[_\sigma 2_2 + {}_\pi 2_s]$ interaction.[23]

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Finally, the reactions of acenaphthenylaluminum reagents open up some novel preparative methods permitting ready access to both 1- and 3-substituted acenaphthenes. These methods form a satisfying complement to Friedel–Crafts alkylations and acylations, which yield 5- and 5,6-substituted derivatives.

Experimental Section

General Techniques. All organometallic reactions were conducted under an atmosphere of dry, deoxygenated nitrogen.[24,25] Techniques followed in the preparation, handling, and analysis of organoaluminum alkyls and hydrides have already been described.[24-29]

The spectral samples were prepared by published techniques[28] and measured as previously recorded.[10]

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 Prep-kromatic 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, MI, and deuterium analyses were done by Dr. Josef Nemuth of Urbana, IL, by the falling drop method.[30]

Preparation and Purification of Reagents and Products. Aluminum Compounds. Commercial diisobutylaluminum hydride (*i*-Bu_2AlH, Texas Alkyls) was fractionally distilled through a 15-cm Vigreux column and was analyzed by the isoquinoline titration procedure.[25] Diisobutylaluminum deuteride was synthesized by a published procedure.[25,28] Ethanolysis and mass spectral analysis of the evolved hydrogen gas showed it to be >97% isotopically pure. Tribenzylaluminum was prepared from aluminum metal and dibenzylmercury[31] (Orgmet) according to a published procedure.

Acenaphthylene and acenaphthene samples were purified by sublimation and then recrystallized from methanol.

1,5-Dihydroacenaphthylene and 1,5-dihydroacenaphthylene-*1,5-d_2* were prepared by adaptation of a published method.[32] By ^1H NMR spectroscopy the product wwas about 95% pure (CCl_4): δ 3.25 (s, acenaphthene impurity), 3.35 (m, H at C_1), 3.57 (m, H at C_5), 5.81 (m, H at C_2), 5.88 (d of d, H at C_4, $J_{3,4}$ = 10 Hz, $J_{4,5}$ = 3.5 Hz), and 6.45 (d of d, H of C_3, $J_{3,5}$ = 2.5 Hz).

1,3-Dihydroacenaphthylene, admixed with about an equimolar amount of acenaphthene, was obtained by the protodealumination of 1-acenaphthenyldiisobutylaluminum.[10]

Acenaphthylene-*1,5-d_2* was prepared by treating 2.0 g (13 mmol) of 1,5-dihydroacenaphthylene-*1,5-d_2* dissolved in 50 mL of benzene with 3.18 g (14 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in a portionwise manner. The reaction mixture was filtered to removed the hydroquinone and the filtrate was chromatographed on neutral alumina. The first yellow band eluted with benzene amounted to 750 mg; sublimation and recrystallization from benzene gave the acenaphthylene; mp 80–90 °C. Anal. Calcd for $C_{12}H_6D_2$: D, 25.00. Found: D, 16.15.

The deuterium content at C_5 was determined by successive reduction to the acenaphthene by *i*-Bu_2AlH (cf. infra) and then oxidation to the 1,8-naphthalic anhydride.[33] Anal. Calcd for $C_{12}H_5DO_3$: D, 16.65. Found: D, 12.10. Thus, one C_5 position is 72% deuterated.

Organic and Inorganic Substrates. Nickel(II) acetylacetonate (Alfa) was allowed to crystallize from toluene. Acetone, acetyl chloride, chlorotrimethylsilane, benzophenone, benzoyl chloride, cyclopentanone, 9-fluorenone, propiophenone, and propionyl chloride were obtained from commercial sources and were carefully distilled or recrystallized under anhydrous conditions before use. The acetone-d_6 obtained from Merck, Sharpe & Dohme was 99.5% isotopically pure.

The gases O_2, CO_2 and N_2 were passed through successive drying columns of granular P_2O_5 (Baker) and the Linde molecular sieves (4A).

Hydralumination Procedures. 1-Acenaphthenyldiisobutylaluminum (4) from Acenaphthylene. A solution of 1.52 g (10 mmol) of acenaphthylene and 1.9 mL (10.5 mmol) of *i*-Bu_2AlH in 20 mL of heptane was heated for 40 h at 80 °C. Protolysis of this aluminum adduct with methanol at −100 °C gave 98% of acenaphthene and only 2% of 1,3-dihydroacenaphthylene.

(a) Cleavage with Chlorotrimethylsilane. (1) In Heptane. A 13-mmol portion of **4** in 25 mL of heptane was added dropwise to a solution of 10 mL (15 mmol) of Me_3SiCl in 20 mL of heptane. The solution was stirred for 48 h at 25 °C, diluted with heptane, and then hydrolyzed by the slow addition of 1 N aqueous HCl. The separated organic layer was washed with aqueous $NaHCO_3$ and then dried over solid anhydrous $MgSO_4$. Solvent removal and distillation yielded a pale yellow liquid, 2.41 g (82%), bp 97–99 °C (0.5 mm), which by NMR spectroscopy was shown to be 1-(trimethylsilyl)acenaphthene (**12**) containing 5% acenaphthene. This product was purified by recrystallizing it twice from methanol at −78 °C (solid CO_2–acetone) to give a product: mp 4–6 °C; ^1H NMR (CCl_4, δ downfield from Me_3Si group as 0) 2.84 (d of d, H_1, J_{trans} = 3.0 Hz, J_{cis} = 8.5 Hz), 3.22 (d of d, H_2 cis to Me_3Si, J_{gem} = 18.0 Hz), 3.50 (d of d, H_2 trans to Me_3Si), and 6.9–7.7 (m, 5 H). Anal. Calcd for $C_{15}H_{18}Si$: C, 79.58; H, 8.01. Found: C, 79.69; H, 7.93.

Compound **12** was further characterized by heating 540 mg (2.4 mmol) of it with 540 mg (24 mmol) of DDQ in 5 mL of benzene for 45 min. Solvent removal and column chromatographic separation on neutral alumina (Brockmann Activity I) with petroleum ether yielded 32 mg (59%) of 1-(trimethylsilyl)acenaphthylene (**13**) as the first yellow band to be eluted; ^1H NMR (CCl_4, δ downfield from Me_3Si group as 0) 6.75, H_2 (s, vinylic H), and 6.9–7.3 (m, 6 H). Anal. Calcd for $C_{15}H_{16}Si$: C, 80.30; H, 7.19. Found: C, 80.11; H, 7.35.

(2) In Tetrahydrofuran. A 7-mmol portion of **4** in 15 mL of heptane was added dropwise to a solution of 5 mL (40 mmol) of Me_3SiCl in 20 mL of anhydrous THF. After a 24-h stirring period at 25 °C, usual hydrolysis gave an organic layer that by NMR spectral analysis contained only acenaphthene and 1,3-dehydroacenaphthylene in a 1:1 ratio and unreacted Me_3SiCl. No **12** was detected.

(b) Cleavage with Acetone at 25 °C. A 10-mmol portion of acetone of **4** in 10 mL of heptane was treated dropwise with 5 mL of acetone (68 mmol, dried over P_2O_5). After 15 min the reaction solution was hydrolyzed with 1.2 N aqueous HCl. Usual workup gave 2.1, g of crude product, whose ^1H NMR spectrum showed the presence of 70% of 3-(2-hydroxy-2-propyl)-1,3-dihydroacenaphthylene (**14**) [(CCl_4) 1.03 (s, 3 H) and 1.18 (s, 3 H), 2.72 (s, OH), 3.52 (br s, H_3), 5.81 (1 H, d of d, H_4, $J_{3,4}$ = 4.2 Hz, $J_{4,5}$ = 11 Hz), 6.17 (1 H, m, H_2), 6.45 (1 H, d of d, H_5, $J_{3,5}$ = 2.4 Hz)] and 30% of acenapthene (signal at 3.21 ppm). When the NMR spectrum was remeasured in $CDCl_3$ solution, the signals at 1.03, 1.18, 2.72, 5.81, 6.17, and 6.45 ppm had almost disappeared and new strong singlets appeared at 1.47 (6 H) and 1.84 ppm (1 H); also a new multiplet had grown in at 3.24 ppm. These signals would accord with the rearrangement of **14** into 3-(2-hydroxy-2-propyl)acenaphthene (**15**).

This product was heated at reflux with 100 mg of *p*-toluenesulfonic acid in 30 mL of benzene for 60 min. The solution was washed with aqueous NaOH, dried over anhydrous $MgSO_4$, and then stripped of solvent. Fractional distillation gave 1.2 g (62%)

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of an oil, bp 104–110 °C (0.14 mm), that was mostly pure 3-(2-propenyl)acenaphthene (**16**). Recrystallizations from MeOH gave a colorless solid: mp 50–50.5 °C; ^{1}H NMR (CCl_4) 2.14 (s, 3 H), 3.25 (br s, 4 H), 5.13 (d of d, 2 H, C=CH_2), 7.0–7.45 ppm (m, 5 H). Anal. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.59; H, 7.50.

The mother liquors from recrystallizing **16** were freed of solvent and the ^{1}H NMR spectrum was recorded in $CDCl_3$. The strong singlets of 1.98 and 2.10 ppm and the multiplets centered at 3.14 and 3.50 ppm matched those of 1-(2-hydroxy-2-propyl)-acenaphthene (**19**, cf. infra).

(c) Cleavage with Acetone-d_6 at 25 °C. A 10-mmol portion of **4** in 5 mL of heptane was treated with 10 g of acetone-d_6 (99.5% deuterated) at 25 °C. Usual hydrolysis and ^{1}H NMR spectral analysis showed the presence of 70% of **14** (as d_6 derivative) and 30% acenaphthene. From an identical reaction on the same scale, the unhydrolyzed mixture was transferred to a sublimator under nitrogen. The solvent was stripped off and the residue sublimed at 70 °C in vacuo. The sublimed acenaphthene was recrystallized from MeOH to yield crystals, mp 92.5–93.8 °C. Anal. Calcd for $C_{12}H_{10}D$: D, 10.0. Found: D, 8.65. The sublimation residue in CCl_4 upon hydrolysis showed the presence of >60% of acenaphthene and <40% of **19a** (d_6). No sign of **14** (d_6) was evident.

This acenaphthene was oxidized with $K_2Cr_2O_7$ and glacial acetic acid to naphthalic anhydride. The sublimed anhydride was analyzed for deuterium: Less than 5% deuterium was found.

(d) Cleavage with Acetone at 100 °C. A 7.5-mmol portion of **4** in 10 mL of heptane was treated with 10 g of acetone at −78 °C and then allowed to reach 25 °C. The solvent and excess acetone were removed at 80 °C in vacuo and then 10 mL of toluene was added. Heating at 100 °C for 50 h and usual hydrolysis gave 1.15 g of crude oil, which was separated by column chromatography on silica with hexane to yield 300 mg of an oil whose ^{1}H NMR spectrum showed that 1-(2-hydroxy-2-propyl)acenaphthene (**19**) was the preponderant component: ($CDCl_3$) 1.98 (s, 3 H), 2.10 (s, 3 H), 3.14 (m, 1 H), 3.25 (m, 2 H), and 7.0–7.6 ppm (m, Ar). The doublet of doublets centered at 5.42 ppm (J = 7.0 and 2.5 Hz) may be due to some dehydration to 1-(2-propenyl)-acenaphthene.

(e) Cleavage of the *n*-Butyllithium Adduct of 4 by Acetone at −78 °C. A 10-mmol portion of **4** in 10 mL of heptane was diluted with 25 mL of anhydrous ethyl ether and then treated with 10 mmol of the lithium reagent in hexane. The aluminate complex was cooled to −78 °C and then treated with 6 mL of acetone. A prompt reaction and the appearance of a yellow color were observed. After 15 min the mixture was protolyzed with MeOH and worked up. By ^{1}H NMR spectroscopy 81% of acenaphthene, 9% of 1,3-dihydroacenaphthylene and 10% of **14** were formed.

(f) Reduction of 3-(2-Propenyl)acenaphthene (16). A solution of 193 mg of **16** and 2 mL of *i*-Bu_2AlH in 5 mL of heptane was heated at reflux for 20 h. Usual hydrolysis and workup gave essentially pure 3-(2-propyl)acenaphthene (**17**). Collection by GLPC gave on oil displaying a sharp iR band at 815 cm[21]: ^{1}H NMR (CCl_4) 1.24 (d, 6 H, J = 7 Hz), 3.11 (septet, 1 H, partly hidden, J = 7 Hz), 3.18 (s, 4 H), and 6.95–7.5 ppm (m, 6 H). The oil was heated with a benzene solution of 1,3,5-trinitrobenzene and then cooled to deposit orange needles. Recrystallization from MeOH gave a melting point of 119.5–121 °C (melting point depressed by admixture with 1,3,5-trinitrobenzene). This melting point differs from that of the 5-(2-propyl)acenaphthene complex (lit.[34] mp 89–90 °C. Anal. Calcd for $C_{21}H_{19}N_3O_6$: C, 61.61; H, 4.68. Found: C, 61.60; H, 4.78.

(g) Cleavage with Other Aliphatic Ketones. 3-Pentanone gave principally the 3-(3-hydroxy-3-pentyl)-1,3-dihydroacenaphthylene (75%) with possibly some 1-(3-hydroxy-3-pentyl)acenaphthene when the reaction was conducted at 80 °C (^{1}H NMR analysis of the products).

Similarly, cyclopentanone gave 64% of 3-(1-hydroxy-1-cyclopentyl)-1,3-dihydroacenaphthylene from the reaction with **4** at −50 °C.

(h) Cleavage with 9-Fluorenone. A 10-mmol portion of **4** in 20 mL of heptane was treated at 25 °C with 9-fluorenone (either 10- or 20-mmol portions). The resulting orange suspensions were stirred at 25 °C for 18–24 h; in one case, a heating period of 6 h at 60 °C was then employed. Hydrolysis of the reaction mixture with 1.2 N aqueous HCl and column chromatography of the organic products on silica gel with a series of eluting solvents, alkane–benzene, gave the following fractions (1 equiv of 9-fluorenone). Fraction 1: acenaphthene with some acenaphthylene (300 mg, 20%). Fraction 2: cream-colored solid, (160 mg, 5%), mp 191–192 °C (from acetone); ^{1}H NMR ($CDCl_3$) 3.40 (d of d, 1 H, J = 18.0 Hz and J = 4.0 Hz), 4.00 (d of d, 1 H, J = 18.0 Hz and J = 9.0 Hz), 4.9 (d of d, J = 4.0 Hz and J = 9.0 Hz) and 7.0–7.8 ppm (m, 14); mass spectrum, m/e (70 eV) (relative abundance) 334 (3), 333 (5), 332 (28), 331 (100), 330 (43), 329 (59), 328 (6). The data can fit the resulting structure being *x*-(1-acenaphthenyl)-9-fluorenone (product B). Fraction 3: colorless solid (1.95 g, 58%); mp 172–174 °C (from MeOH); ^{1}H NMR (C_6D_6 at 60 °C, M in capillary) 1.68 (s, OH), 2.30 (d of d, H_2 cis to 9-hydroxyfluorenyl, J_{gem} = 18 Hz, J_{trans} = 4.0 Hz), 2.77 (d of d, H_2 trans to 9-hydroxyfluorenyl, J_{cis} = 8.5 Hz), 4.36 (d of d, H_1), 6.25–7.75 (m, 14H); mass spectrum, m/e (70 eV) (relative abundance), 334 (1.2), 318 (10), 317 (27), 316 (89), 315 (100), 314 (27), 313 (50), 312 (4.8). Anal. Calcd for $C_{25}H_{18}O$: C, 89.79; H, 5.42. Found: C, 89.85; H, 5.63. The data permit this compound to be assigned the structure of 9-(1-acenaphthenyl)-9-fluorenol (**33**). Fraction 4: 9-fluorenol (620 mg, 34%); mp 153–155 °C.

When 2 equiv of 9-fluorenone and a 6-heating period were employed, the recovered acenaphthene decreased to 6% and product B to 0.6%, while product **33** rose to 76% and 9-fluorenol to 53%.

When a 10-mmol portion of **4** in 10 mL of heptane was treated with 1 equiv of 9-fluorenone in ethyl ether at −78 °C and the resulting mixture treated after 60 min with methanol, the ^{1}H NMR spectrum of the product revealed the presence of 65% of 9-(1,3-dihydro-3-acenaphthylenyl)-9-fluorenol: ^{1}H NMR (CCl_4) 4.37 (br s, OH), 5,48 (m, H_2), 5.57 (d of d, H_4, $J_{3,4}$ = 4.0 Hz, $J_{4,5}$ = 11 Hz), 6.18 ppm (d of d, H_5, $J_{3,5}$ = 2.5 Hz).

(i) Cleavage with Propiophenone at −78 °C. A 10-mmol portion of **4** in 10 mL of heptane at −78 °C was treated with 1 equiv of the ketone in 25 mL of ether. After 60 min the mixture was hydrolyzed at −78 °C with 1.2 N methanolic HCl. An ^{1}H NMR spectral analysis showed the presence of 69% of 3-(1-hydroxy-1-phenyl-1-propyl)-1,3-dihydroacenaphthylene (**22**) ((CCl_4) 0.65 (t, 3 H), 1.77 (d of q, 2 H), 2.0 (s, OH), 3.90 (br s, H_3), 5,46 (m, H_2), 5.67 (d of d, $J_{3,4}$ = 4.2 Hz, $J_{4,5}$ = 10 Hz), 6.50 ppm (d of d, $J_{3,5}$ = 2.5 Hz)). This crude product upon standing rearranged to 3-(1-hydroxy-1-phenyl-1-propyl)acenaphthene (**23**), as evidenced by the disappearance of the NMR signals at 5.46, 5.67, and 6.50 ppm; new signals appeared at 0.70 (t), 3.35 (d of q), and 3.1 ppm.

In an identical reaction, the crude product was treated with 100 mg of *p*-toluenesulfonic acid in MeOH at 25 °C for 20 h, in order to promote the formation of **23**. Column chromatography on silica gel gave 45% of **23** upon elution with a benzene–petroleum ether pair (1:2). This compound was dehydrated by reflux in benzene with *p*-TsOH to yield an *E,Z* mixture of 3-(1-phenyl-1-propenyl)acenaphthene (**25**) (^{1}H NMR: doublets at 1.65 and 1.88 ppm). After chromatographic purification **25** was hydrogenated in benzene with a 30% palladium-on-charcoal catalyst and at 35 lbs psi of hydrogen for 48 h. The 3-(1-phenyl-1-propyl)acenaphthene (**26**) displayed ^{1}H NMR signals at (CCl_4) 1.90 (t, 3 H), 2.05 (q), 3.12 (s, 4 H), and 3.88 ppm (t, 1 H). Anal. Calcd: C, 92.60; H, 7.40. Found: C, 92.35; H, 7.58.

(j) Cleavage with Propiophenone at 70 °C. A reaction identical with that in section i was run, except that the ketone in ether solution was added at 25 °C and the resultant mixture heated at 70 °C for 22 h. Usual hydrolysis and NMR spectral examination of the crude product showed the absence of signals ascribable to either 3-(1-hydroxy-1-phenyl-1-propyl)-1,3-dihydroacenaphthylene or 3-(1-hydroxy-1-phenyl-1-propyl)-acenaphthene. Approximately 80% of the product was 1-(1-hydroxy-1-phenyl-1-propyl)acenaphthene (**24**, cf. infra); in addition, 10% acenaphthene and 10% 1-phenyl-1-propanol were present.

Column chromatography on silica gel and elution with a benzene–petroleum ether gradient gave 1.65 g of **24**, which upon recrystallization from hexane melted at 120.5–123 °C: ^{1}H NMR

(34) Cairns, J. F.; Hickenbottom, W. T. *J. Chem. Soc.* **1962**, 870.

($CDCl_3$) 0.66 (t, 3 H, J = 7.5 Hz), 1.20 (s, OH), 2.08 (m, 2 H), 3.01 (d, H_2 trans to $HOCPhCH_2CH_3$, J_{cis} = 9.0 Hz), 3.12 (d, H_2 cis to $HOCPhCH_2CH_3$, J_{trans} = 3.0 Hz), 4.06 (d of d, H_1), and 6.95–7.65 ppm (, Ar). Anal. Calcd for $C_{21}H_{20}O$: C, 87.49; H, 6.96. Found: C, 87.17; H, 6.92.

(k) Cleavage of the *n*-Butyllithium Adduct of 4 by Propiophenone at −78 °C. A 10-mmol portion of 4 in 10 mL of heptane was diluted with 10 mL of ether and then 10 mmol of *n*-butyllithium added. After cooling to −78 °C, 1 equiv of the ketone was introduced. An orange color developed during the 15-min reaction period. Usual hydrolysis at −78 °C with methanol and 1.2 N aqueous HCl and workup revealed that only traces of **22** were formed. Greater than 95% of the $C_{12}H_{10}$ was present as acenaphthene and <5% as the 1,3-dihydroisomer. Some of the ketone had been reduced to 1-phenyl-1-propanol.

(l) Cleavage of the 3-(1-Hydroxy-1-phenyl-1-propyl)-1,3-dihydroacenaphthylene Product. In an attempt to aromatize **22** to the 3-substituted acenaphthene, a reaction mixture obtained as in section i was dissolved in CCl_4 and stirred with 200 mg of 30% palladium on charcoal at 25 °C for 24 h. The ^1H NMR analysis showed that **22** had been almost completely converted into acenaphthene and propiophenone.

(m) Cleavage with Acetyl Chloride. A 10-mmol portion of **4** in 10 mL of heptane was treated at −78 °C with 1 equiv of acetyl chloride. After 15 min the usual workup gave 2.2 g of crude product that was chromatographed on silica gel. Elution with benzene–petroleum ether gave 850 mg of product (44%). Recrystallization from acetone gave colorless crystals of 3-acetylacenaphthene: mp 104.5–106 °C; ^1H NMR ($CDCl_3$) 2.60 (s, 3 H), 3.3 (m, 2 H), 3.66 (m, 2 H), and 7.2–7.9 ppm (m, 5 H). Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.35; H, 6.01. It should be noted that 5-acetylacenaphthene is said to melt at 75 °C.[35]

When a comparable reaction was run in the presence of 20 mL of ether, no acetyl derivative could be found.

(n) Cleavage with Benzoyl Chloride. A reaction comparable to that of section m with benzoyl chloride gave 720 mg of product. Recrystallization from acetone gave pure 3-benzoylacenaphthene: mp 92.5–93 °C; ^1H NMR (CCl_4) 3.21 (m, 2 H), 3.44 (m, 2 H), 7.05–7.7 ppm (m, 10 H). Anal. Calcd for $C_{19}H_{14}O$: C, 88.34; H, 5.46. Found: C, 88.14; H, 5.47. It should noted that 5-benzoylacenaphthene melts at 100.5–101.8 °C.[36]

(o) Cleavage with Propionyl Chloride. A reaction comparable to that in section m was conducted, except that 1 equiv of propionyl chloride in 20 mL of ether was added at −78 °C. Since no visible change was observed at −78 °C, the mixture was warmed to 25 °C and held there for 2 h. Usual workup and CC on silica gel gave 825 mg of a product that ^1H NMR analysis showed to be 3-(1-hydroxy-1-propyl)acenaphthene: ^1H NMR (CCl_4) 0.74 (q, 3 H), 1.45 (m, 2 H), 1.77 (s, OH), 2.98 (m, 4 H), 4.43 (t, OH) , and 6.95–7.45 ppm (, Ar). This crude product was oxidized with the Jones reagent[37] and the crude product was chromatographed and recrystallized from acetone to yield 3-propionylacenaphthene (**36**): mp 121–122 °C; ^1H NMR ($CDCl_3$) 1.26 (t, 3 H), 3.07 (q, 2 H), 3.43 (m, 2 H), 2.74 (m, 2 H), and 7.2–8.0 (m, Ar). Anal. Calcd for $C_{15}H_{16}O$: C, 85.68; H, 6.71. Found: C, 85.53; H, 6.95.

Structure Verification. (a) Synthesis of 3-(1-Phenyl-1-propyl)acenaphthene. To 20 mmol of phenylmagnesium bromide in 15 mL of ether was added 362 mg of **36**. After 2 h at 25 °C usual hydrolysis gave a crude product that by NMR analysis was principally **23**. This product was dehydrated by reflux in benzene solution containing *p*-toluenesulfonic acid and the 3-(1-phenyl-1-propenyl)acenaphthene was separated by column chromatography on silica gel. Its NMR agreed with that reported in section i. This olefin was hydrogenated over 30% palladium on charcoal at 25 °C and at 30 psi of hydrogen. The ^1H NMR spectrum of the resulting product was identical with that given in section i for 3-(1-phenyl-1-propyl)acenaphthene (**26**).

(b) Synthesis of 5-(1-Phenyl-1-propyl)acenaphthene. A solution of 15.4 g (100 mmol) of acenaphthene and 100 mmol of propionyl chloride in 100 mL of CS_2 was treated with 15 g of freshly sublimed $AlCl_3$ at 25 °C. After 5 h the mixture was poured into ice water. The separated organic layer was dried over $MgSO_4$, the solvent was evaporated, and the residue was extracted into benzene. Column chromatography on silica gel with a benzene–petroleum ether gradient gave 72% of 5-propionylacenaphthene (**27**): mp 69–70 °C (from acetone); ^1H NMR ($CDCl_3$) 1.22 (t, 3 H), 3.03 (q, 2 H), 3.24 (s, 4 H), 7.12 (d, H_3), 7.22 (d, H_8), 7.51 (t, H_7), 7.9 (d, H_4), and 8.62 ppm (d, H_6).

The reaction mixture of 2.1 g (10 mmol) of **27** and excess phenyl magnesium bromide in ether was hydrolyzed with dilute aqueous HCl and the product taken up in benzene. The benzene solution was refluxed with *p*-toluenesulfonic acid to yield an *E,Z* mixture of 5-(1-phenyl-1-propenyl)acenaphthene. Column chromatography gave the pure isomeric mixture: ^1H NMR (CCl_4) 1.52 and 1.86 (two d), 3.05 (m), 5.90 and 6.28 (two q) and 6.9–7.4 ppm (m).

This hydrocarbon was hydrogenated over 30% palladium on charcoal, as in section i, to give 5-(1-phenyl-1-propyl)acenaphthene (**29**); ^1H NMR (CCl_4) 0.90 (t, 3 H), 2.1 (q, 2 H), 3.04 (s, 4 H), 4.39 (t, 1 H) and 6.9–7.6 ppm (m). This spectrum is unmistakably different from that of 3-(1-phenyl-1-propyl)acenaphthene.

(c) Synthesis of 5-(1-Hydroxy-1-phenyl-1-propyl)-acenaphthene (29a). As in the preceding section, acenaphthene was treated with benzoyl chloride and $AlCl_3$ in CS_2 solution. By recrystallization of the crude product from hexane, 16.5 g (64%) of 5-benzoylacenaphthene was obtained: mp 100–102 °C; ^1H NMR ($CDCl_3$) 3.30 (s, 4 H) and 7.1–8.2 ppm (m, 10 H).

Treatment of 1.5 g of the ketone with 1.8 equiv of ethyllithium in ether, followed by workup with aqueous HCl, gave **29a** admixed with 5-(1-hydroxy-1-phenylmethyl)acenaphthene. Column chromatography on silica gel gave the pure 5-(1-hydroxy-1-phenyl-1-propyl)acenaphthene: mp 109–110 °C (heptane); ^1H NMR (CCl_4) 0.74 (t, 3 H), 2.00 (s, OH), 2.23 (m, 2 H), 3.16 (s, 4 H), and 6.60–7.60 ppm (m, 10 H). Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.55; H, 6.95.

Admixed with 1-(1-hydroxy-1-phenyl-1-propyl)acenaphthene, the pair melted at 90–98 °C. Furthermore, its NMR spectrum is distinctly different than that of 3-(1-hydroxy-1-phenyl-1-propyl)acenaphthene.

Deuterioalumination of Acenaphthylene. (a) Cleavage with 9-Fluorenone. The diethyl etherate of *cis*-2-deuterio-1-acenaphthenyldiisobutylaluminum (**10**) was formed as a colorless solid by heating 1.52 g (10 mmol) of **8** and 1.0 mL (10.6 mmol) of *i*-Bu_2AlH in 10 mL of ethyl ether over a 10-day period at 60 °C. The reaction mixture was cooled to 25 °C, diluted with 50 mL of ether, and then treated with 1.80 g (10 mmol) of 9-fluorenone in 15 mL of benzene. After a reaction time of 3.5 h at 65 °C and 15 h at 25 °C, the reaction was terminated with 1.2 N aqueous HCl. Column chromatographic separation as described in section h permitted the isolation of 9-(2-deuterio-1-acenaphthenyl)-9-fluorenol (**33**): mp 172–174 °C; ^1H NMR (C_6D_6 at 60 °C, ^2H decoupled with 11-μA irradiation at 3633 Hz) 1.68 (s, OH), 2.30 (d, 0.5 H, H_2 cis to 9-hydroxyfluorenyl, J_{trans} = 4.0 Hz), 2.77 (br d, 0.5 H, H_2 trans to 9-hydroxyfluorenyl, J_{cis} = 8.5 Hz), 4.36 (br d, H_1) and 6.25–7.75 ppm (m). These data show that **33** was formed as a 1:1-mixture of cis and trans isomers.

(b) Cleavage with Oxygen. A 10-mmol portion of **4**, which was prepared as in section a, was diluted with 50 mL of ethyl ether and 50 mL of benzene and then dry oxygen gas (previously passed over solid P_2O_5 and Linde molecular sieve (4A)) was bubbled through the solution for 60 min at temperatures between 25 and 50 °C. Usual hydrolysis and column chromatography on silica gel gave upon elution with benzene–chloroform a 620-mg fraction that was essentially pure acenaphthenol. Recrystallization from benzene gave colorless crystals: mp 144.5–145 °C; ^1H NMR ($CDCl_3$ at 60 °C, ^2H decoupled) 2.56 (s, OH), 3.69 (d, 0.5 H, H cis to OH, J_{trans} = 2.5 Hz), 4.24 (d, 0.5 H, H trans to OH, J_{cis} = 6.7 Hz), 6.16 (m, H geminal to OH) and 7.7–8.3 ppm (m). These data show the alcohol is a 1:1 cis:trans mixture of 2-deuterio-1-acenaphthenol.

^1H NMR Spectral Studies of 1-Acenaphthenyldiisobutylaluminum. (a) Temperature Dependence in Toluene-d_8. A solution of 1.14 g (7.5 mmol) of **8** in 2 mL of toluene-d_8 was allowed to react with 1.42 mL (8.0 mmol) of *i*-Bu_2AlH for 1.9 days at 80 °C. The cooled adduct solution (4.0 mL) was sampled into four 0.5-mL portions. The spectrum of one portion was recorded successively at 37 °C, at 95 °C, and at 112 °C. The spectrum at 37 °C exhibited signals at 0.28 (d, 4 H, CH_2Al), 1.05

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(d, 12 H, CH_3 of *i*-Bu), 1.2-2.3 (m, 2 H, CH of *i*-Bu), 2.5-3.0 (featureless m, 1 H, benzylic CHAl), 3.15-3.65 (featureless m, 2 H, benzylic CH_2), 6.6-7.1 (br, featureless signal, 1.0 H, H_3), and at 7.2 (br m) and at 7.45 ppm (br d) (total of 4.7-5.0 H. Trace signals of dissolved isobutene were detected at 1.67 and 4.78 ppm. As this spectrum was recorded at successively higher temperatures, the signals due to **4** sharpened very markedly: at 112 °C, the benzylic signals between 2.5-3.0 and 3.15-3.65 ppm resolved into a triplet and doublet, respectively (J = 7 Hz), the broad signal at 6.6-7.1 became a doublet at 6.88 (J = 4 Hz), and the signal at 7.2 ppm became a four-line multiplet. The ratio of the signal at 6.88 vs. the other aromatic signals was 1.0:4.85.

(b) Effect of Added *i*-Bu_2AlR. Each of the other three portions of **4** prepared above were admixed either with 0.98 equiv of *i*-Bu_2AlD, 0.86 equiv of *i*-Bu_2AlCl, or 0.55 equiv of *i*-Bu_3Al. The ^1H NMR spectra were recorded and the ratio of the shielded aromatic resonance at 6.88 ppm (SAR) to the other aromatic signals (OAR) was determined.

(c) Effect of Added Lewis Bases. Another portion of **4** was prepared as in section a. The ratio of all aromatic resonances to the isobutyl resonances revealed an excess of 0.22 equivalence of *i*-Bu_2AlH. This solution was apportioned among several samples that were treated with various amounts of ethyl ether or *N*-methylpyrrolidine. The amount of donor added was ascertained by noting how the ratio of aromatic area to the area between 1.0 and 5.0 ppm changed upon adding the donor aliquot. The resulting ratios of SAR to OAR are given in Table I.

(d) Effect of 5-Deuteration of Acenaphthylene and Concentration of 4-d_2. A sample of acenaphthylene-*1,5*-d_2, which was 72% deuterated at C_5 (0.269 g, 1.7 mmol) was hydraluminated in toluene-d_8 as in section a (0.35 mL of *i*-Bu_2AlH in 0.5 mL of toluene). The ^1H NMR spectra of the resulting sample and of various samples made by dilution with toluene-d_8 were recorded. The relative positions and areas of the SAR and OAR were noted.

^1H NMR Spectra of Other Benzylic Aluminum Systems. The spectrum of tribenzylaluminum in mesitylene solution showed a ten-line multiplet for the benzyl group downfield from the mesitylene's aromatic singlet. The two upfield (ortho CH) lines sharpened to a clean doublet between 100 °C and 149 °C (6.80 ppm, J = 4 Hz) and shifted downfield from the mesitylene signal by 5 Hz.

Diisobutyl(1,1-dimethyl-3-indanyl)aluminum in toluene-d_8[6b] was examined by ^1H NMR spectroscopy between 37 °C and 97 °C. The aromatic region consisted of a singlet at 6.8 ppm (~3,5 H) and a broad singlet at 6.95 ppm (~0.5 H), and these resonances did not vary with temperature. It should be noted that in the ^1H NMR spectrum of 1,1-dimethylindan the aromatic protons display a singlet at 6.99 ppm.

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Enantiomers of the Biologically Active Components of the Insect Attractant Trimedlure

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The biologically most active components of a synthetic lure that is used to attract male Mediterranean fruit flies are the *tert*-butyl esters of *cis*-4-(and *trans*-5-)chloro-*trans*-2-methylcyclohexanecarboxylic acids (**1-A** and **1-C**). These compounds have been synthesized enantiomerically pure (≥99.6% ee) from resolved *trans*-6-methyl-3-cyclohexenecarboxylic acid. Configurations were assigned on the basis of literature analogy, proton chemical shift data, and high-pressure liquid chromatographic elution orders of selected diastereomeric adducts of the acids.

The best tool currently available for monitoring infestations of Mediterranean fruit fly, *Ceratitis capitata* (Wiedemann), is a synthetic attractant mixture known as trimedlure **1** (Scheme I). Discovered in a screening program conducted by the U.S. Department of Agriculture during the sixties,[1] its commercial synthesis involves a Diels-Alder reaction between butadiene and crotonic acid that produces primarily *trans*-6-methyl-3-cyclohexenecarboxylic acid (**2**) generally less than 5% of the cis isomer). Hydrogen chloride addition to the double bond produces a mixture of monochlorides **3** in which axially oriented chlorine predominates at both positions 4 and 5 and in which the methyl and carboxyl substituents are equatorial.[2] Esterification of the acid mixture with isobutylene and acid produces the mixture of *tert*-butyl esters referred to as trimedlure. The designations of the individual isomers in Scheme I are those of the authors who made the original assignments and refer to gas chromatographic elution orders.[2] The most attractive isomers

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