Convenient Synthesis of Perinaphthane via Chloroaluminum Hydride Reduction of Perinaphthanone[1]

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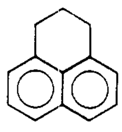
As part of a project involving the synthesis of ^{13}C labeled benzo[*a*]pyrenes we had need for pure perinaphthane (**1**) which has been prepared from perinaphthenone (**2**), perinaphthene (**3**), and perinaphthanone (**4**). Reduction of perinaphthenone (**2**) affords perinaphthane (**1**) via high-pressure hydrogenation over copper chromite in yields of 70–80%;[2,3] however, the success of these reductions is largely dependent on the ketone/catalyst ratio and the purity of **2** used. Hydrogenation of perinaphthene (**3**) is reported to give **1** in excellent yield;[4,5] however, the preparation of **3** from **2** proceeds in poor yield[4] and its synthesis from perinaphthanone (**4**) in two steps as well as other miscellaneous methods were unsuitable for our needs.[5] Perinaphthanone (**4**), which is available from 1-(chloromethyl)naphthalene,[6] has been converted to **1** via the Clemmensen method[3,6] in 12% yield or in 46% yield by hydrogenation over Pd/C in acetic acid at 2 atm.[7] Attempts to prepare perinaphthanone (**4**) from perinaphthenone (**2**) by the method of Dokunikhin[8] failed, the net result being that reported earlier by Fieser and Hershberg.[2] Reduction of **2** using 5% Pd/C in ethyl acetate at room temperature afforded mainly perinaphthanol (**5**).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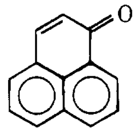
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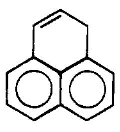
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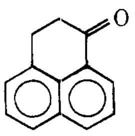
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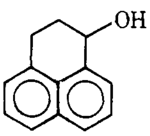
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We wish to report a highly successful synthesis of **1** from **4** via reduction with lithium aluminum hydride and aluminum chloride in ether.[9] Using a molar ratio of $LiAlH_4/AlCl_3$ of 0.5 in the reduction affords 91–97% yields of perinaphthane (**1**) of good quality in runs using from 1 to 20 g of **4**. The quality of the **4** used does not appear to be critical with respect to the yields of **1** obtained. The crude perinaphthane (**1**) was readily purified by column chromatography over silica gel to give material of equal of better quality than that obtained by high-pressure hydrogenation of perinaphthenone followed by fractional distillation.[2,3] We feel that the preparation of perinaphthane by the reduction of perinaphthanone with $LiAlH_4/AlCl_3$ in ether as described here is superior to other methods used for the preparation of **1**.

Experimental Section

Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The ^1H-NMR spectrum of **1** was measured on a Hitachi Perkin-Elmer Model R-24 spectrometer using Me_4Si as an internal standard, and the ^{13}C NMR was recorded on a Varian Model CFT-20 spectrometer. Reactions were monitored and product purity was checked by thin-layer chromatography on precoated silica gel plates (EM Laboratories 60F-254) using benzene as a developing solvent. The compounds and their approximate R_f values were as follows: **1** (0.64), **2** (0.05), **4** (0.15), **5** (0.19).

Perinaphthane (1). A 300-mL three-necked flask equipped with a condenser, addition funnel, and magnetic stirrer was flushed with dry N_2 and charged with $LiAlH_4$ (3.22 g, 84.8 mmol) and 50 mL of anhydrous ether. To this mixture was added over a 10–15-min period a solution of $AlCl_3$ (22.8 g, 171 mmol) in 80 mL of anhydrous ether (prepared by adding ether dropwise with stirring to the $AlCl_3$ in an Erlenmeyer flask equipped with a dropping funnel, reflux condenser, and drying tube). To this mixture a solution of 9.0 g (49.4 mmol) of perinaphthanone (**4**),[6] mp 76–80.5 °C, in 70 mL of anhydrous ether was added over a period of 45 min while sustaining a gentle reflux. The reaction mixture was refluxed for an additional 2 h, after which time 5 mL of ethyl acetate was added slowly to the cooled reaction mixture to destroy the excess $LiAlH_4$. The reaction mixture was poured over ice (600 mL), and the ether layer was washed with water and dried over anhydrous $MgSO_4$. Removal of the ether afforded a pale yellow solid, mp 60.5–65 °C, in quantitative yield. The crude product was taken up in cyclohexane and chromatographed over silica gel (EM Laboratories 230–400 mesh) in a 25 × 190 mm column. Elution with cyclohexane gave a slightly fluorescent colorless band which was collected in 125 mL of eluent. Removal of the cyclohexane afforded colorless **1** (7.61 g, 92%), mp 62.5–65 °C. One recrystallization from 60 mL of methanol yielded perinaphthane (**1**) as colorless plates (82% recovery), mp 66–67 °C (lit.[2] mp 65.4 °C). An additional colorless crop (10%, mp 64–65.5 °C) was obtained from the mother liquor. Since **1** is light sensitive, the chromatography and other purification steps were carried out in subdued light. The ^1H-NMR spectrum of **1** was identical to that reported by Shannon and Cox,[10] and the ^{13}C-NMR spectrum (CCl_4) matched that reported by Hunter and Stothers.[11]

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Registry No.—**1**, 479-58-3; **2**, 548-39-0; **3**, 203-80-5; **4**, 518-85-4.

References and Notes

(1) Supported in part by Grant No. CA-16871 from the National Cancer Institute, DHEW.
(2) L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **60**, 1658 (1938).
(3) I. K. Lewis and R. D. Topsom, *Aust. J. Chem.*, **18**, 923 (1965).
(4) G. Lock and G. Gergely, *Ber.*, **77B**, 461 (1944).
(5) V. Boekelheide and C. E. Larrabee, *J. Am. Chem. Soc.*, **72**, 1245 (1950).
(6) L. F. Fieser and M. D. Gates, *J. Am. Chem. Soc.*, **62**, 2335 (1940).
(7) C. Heidelberger and H. S. Rieke, *Cancer Res.*, **11**, 640 (1951).
(8) N. S. Dokunikhin, S. L. Solodar', and A. V. Reznichenko, *Zh. Org. Khim.*, **12**, 379 (1976).
(9) For references to mixed hydride reductions see: (a) E. C. Ashby and J. Prather, *J. Am. Chem. Soc.*, **88**, 729 (1966), and references therein; (b) J. Blackwell and W. J. Hickinbottom, *J. Chem. Soc.*, 1405 (1961); (c) J. H. Brewster and H. O. Bayer, *J. Org. Chem.*, **29**, 105 (1964), and references therein; (d) R. M. Pagni and C. R. Watson, *Tetrahedron*, **29**, 3807 (1973).
(10) R. L. Shannon and R. H. Cox, *Tetrahedron Lett.*, 1603 (1973).
(11) D. H. Hunter and J. B. Stothers, *Can. J. Chem.*, **51**, 2884 (1973).

Thermal Decomposition of Aluminum Alkoxides

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Numerous methods are available for the dehydration of alcohols, including the conventional approaches using acid catalysts, as well as a variety of more specialized thermal methods including the Hofmann elimination, amine oxide, xanthate, and acetate pyrolysis.[1] None are universally applicable and in fact often give poor yields or unmanageable

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Table I. Alkenes from the Thermal Decomposition of Aluminum Alkoxides

alcohol	registry no.	alkene (% yield)	registry no.
1-octanol	111-87-5	1-octene (70)	111-66-0
1-decanol	112-30-1	1-decene (89)	872-05-9
1-octadecanol	112-92-5	1-octadecene (75)	112-88-9
geraniol	106-24-1	myrcene (62)	123-35-3
farnesol[a]	4602-84-0	β-farnesenes (79)	18794-84-8
2-octanol	123-96-6	1-octene (43); 2-octene (37)	—; 111-67-1
cyclohexanol	108-93-0	cyclohexene (67)	110-83-8
isopulegol	89-79-2	$\Delta^{2,8}$-*p*-menthadiene (22); $\Delta^{3,8}$-*p*-menthadiene (44)	499-99-0; 586-67-4
menthol	2216-51-5	Δ^{2}-*p*-menthene (24); Δ^{3}-*p*-menthene (60)[b]	5256-65-5; 619-52-3
cholesterol	57-88-5	$\Delta^{3,5}$-cholestadiene (79)	747-90-0
linalool	78-70-6	myrcene (90)	
citronellol	106-22-9	citronellene (63)	2436-90-0

[a] The farnesol was a mixture containing a 60:40 ratio of $\Delta^{6,7}$ trans/cis alcohols. [b] $[\alpha]^{20}{}_{D}$ 68.4°.

Table II. Regioselectivity in Elimination Reactions

$CH_3CH_2CH(L)CH_3 \longrightarrow CH_3CH_2CH{=}CH_2 + CH_3CH{=}CHCH_3$

L =	rel % of products		ref
$-{}^{+}N(CH_3)_3\ OH^-$	67	33	7
$-N(\rightarrow O)(CH_3)_2$	95	5	7
-OAc	57	43	8
$-OCSSCH_3$[a]	52	48	9
-OH (Al_2O_3, 273 °C)	43	57	10
$-OAl(OR)_2$ (R = 2-butyl)	40	60	6

[a] 2-Octanol was used.

mixtures. We have been interested particularly in dehydrating a variety of terpenoid alcohols which are known to be especially sensitive to acid-catalyzed rearrangements.[2] In the course of such studies we have explored the thermal decomposition of aluminum alkoxides and report our results herewith.

Aluminum alkoxides are readily prepared by exchange reactions with aluminum isopropoxide and, with more difficulty, by direct reaction of the alcohols with amalgamated aluminum.[3] The products thus formed, while formally represented as simple stoichiometric replacements, in fact exist as more complex oligomeric forms.[4] For the purposes of this study, however, we have assumed the simpler monomeric form in our discussion.

Although there has been some interest in the properties of simpler alkoxides, especially aluminum triisopropoxide, surprisingly little work appears in the literature regarding the thermal decomposition of aluminates. Tishchenko reported that the thermal decomposition of several simple aluminates gave aldehydes, alkenes, and ethers.[5] More recently a preliminary publication reports that the thermal decomposition of the alkoxides derived from 2-butanol and 2-pentanol gives the same mixture of olefins as that obtained by catalytic dehydration over alumina, although the proportions of cis and trans isomers differed. Interestingly, the thermal decomposition of the alkoxides appeared to give cis/trans ratios close to the value expected at thermodynamic equilibrium.[6]

Preparative Use. Initially we investigated the dehydration of cyclohexanol in order to determine the optimum conditions for dehydration. It was found that a 1:1 ratio of aluminum triisopropoxide to cyclohexanol gave the best yields. The mixed alkoxide was prepared by initial distillation to remove the calculated amount of 2-propanol. Thus the product would have the approximate composition $ROAl\,[OCH(CH_3)_2]_2$. The results obtained are given in Table I.

From Table I it may be gathered that primary alcohols in particular may be dehydrated in excellent yield, and that secondary alcohols give moderate to good yields. Tertiary alcohols also dehydrate readily as expected.

Stability toward Isomerization. In order for a dehydration technique to be useful, there must be a minimum of isomerization, whether this be positional, geometric, or optical. Pines and co-workers have shown that unless alumina is carefully neutralized, considerable isomerization of the products from menthol results. We note in our method that the Δ^{2}- and Δ^{3}-*p*-menthenes are the sole products. However, prolonged heating over the residual alumina does cause isomerization.

In order to examine the stability of geometric isomers, we dehydrated a commercial mixture of farnesols consisting of a 60:40 mixture of the $\Delta^{6,7}$ trans/cis isomers. The stereochemistry of the $\Delta^{2,3}$ bond does not concern us here, since its stereochemistry is lost in the formation of β-farnesene. We observed that the $\Delta^{6,7}$ trans/cis ratio in the product β-farnesenes was 63:37, corresponding within experimental error to the original isomeric composition. We may therefore conclude that little isomerization occurred during this elimination. Similarly, isopulegol, geraniol, and cholesterol gave principally the expected olefins.

The reaction is not completely sterospecific. The *p*-menthene mixture is approximately 40% racemized. This is not surprising considering the temperatures needed for decomposition and the known catalytic action of alumina.

Regioselectivity. It is of interest to compare the new method of elimination with respect to regioselectivity. Table II gives information on elimination reactions commonly used. It appears that with the exception of the Hofmann that the eliminations essentially approach the statistical 60:40 ratio of 1- to 2-olefin. This is also true for our procedure applied to 2-octanol.

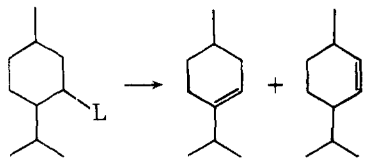
We attempted to influence the regioselectivity by substituting bulky groups for isopropoxy groups in the alkoxide according to the following equation:

$$ROAl[OCH(CH_3)_2]_2 + 2ArOH \rightleftarrows ROAl(OAr)_2 + 2(CH_3)_2CHOH$$

Phenols were chosen on the assumption that they would be less likely to cleave. Phenol, 2,6-dimethylphenol, and thymol were used. In no case was a significant change in the ratio of 1- to 2-olefin found. In addition, when more substituted alkoxides were used, such as the di-2-octyl or tri-2-octyl derivatives, no significant changes in the ratio were observed. We must conclude that the substituents are sterically too far removed to exert a significant influence on the choice of proton to be eliminated.

Stereochemistry and Mechanism of Elimination. The elimination reactions of menthol and its derivatives have received extensive study. Some of these results are presented in Table III. From Table III it may be concluded that, with the exception of the Hofmann and Cope eliminations and neutral or basic alumina catalysis, that Δ^{3}-*p*-menthene is the pre-

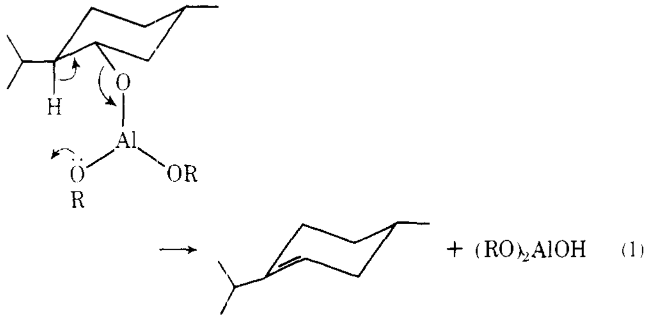
Table III. Elimination Reactions of Menthol and Its Derivatives



L	over-all yield, %	rel yields of products		ref
$-OB(OR)_2$	92	90	10	11
$-OH\ (H_3BO_3)$	82	87	13	11
$-OCSSCH_3$	51	75	25	12
-OAc	65	65	35	13
$-N(\rightarrow O)(CH_3)_2$	85	36	64	14
$-OH\ (Al_2O_3$, acidic)	94	53 (31 actual)	47 (27 actual) (36% Δ^1)	15
$-OH\ (Al_2O_3$, neutral)	98	20 (19 actual)	80 (75 actual) (<3% Δ^1)	15
$-OH\ (Al_2O_3$, basic)	95	18	78	15
$-{}^+N(CH_3)_3\ OH^-$	80		100	16
$-OAl(OR)_2$ (R = 2-propyl)	92	74	26	this work

ferred product. It should be noted that our results with aluminate esters are clearly different from those using alumina as catalyst, suggesting either a different mode of elimination when using solid alumina as catalyst or isomerization of the initially formed product under the reaction conditions used with alumina.

The xanthate and acetate eliminations are generally considered as cyclic cis eliminations. The high proportion of Δ^3-*p*-menthene formed by the thermal decomposition of the alkoxide suggests that a similar mechanism is operative. Presumably a nucleophilic oxygen removes the proton with concurrent cleavage of the C–O bond as pictured in eq 1.



Conclusion

The thermal decomposition of aluminum alkoxides represents a facile means for dehydration, especially for primary alcohols. The temperature threshold is well below that for comparable xanthate or acetate pyrolyses. Yields are better, although some isomerization occurs; even relatively sensitive alcohols such as the allylic terpenoid alcohols can be successfully dehydrated. The mechanism appears to be a standard concerted cis-1,2-elimination.

Experimental Section

Materials. Both freshly prepared and commercial aluminum triisopropoxide were, used with no significant difference. Analyses were performed using either a 5 ft × 1/8 in. × 10% SE-30 or a 10 ft × 1/8 in. × 10% TCEPE GLC column.

Preparation and Thermolysis of Aluminum Alkoxides. Aluminum isopropoxide (20.4 g, 0.1 mol) was combined with 0.1 mol of the appropriate alcohol, and the mixture was heated. The theoretical amount of 2-propanol was removed by simple distillation in the case of high-boiling alcohols, or by fractional distillation in case of the lower boiling alcohols. After removal of the 2-propanol, the temperature was gradually increased. Depending on the structure of the alcohol, decomposition commences in the range 200–270 °C. The distillate is washed with water, dried, and distilled.

In case of nondistillable olefins, the mixture is heated to 270 °C for 0.5 h, and the mixture is then cooled and extracted with ether. The ether layer is washed with water, dried, and evaporated. The residue is further purified by recrystallization or chromatography. Yields are given in Table II.

Product identification was made in the usual manner using infrared and NMR spectroscopy.

Analysis of Octenes. Since 1-octene and *trans*-2-octene could not be satisfactorily separated by GLC, analysis of the product mixture was made by quantitative IR using the bands at 11.0 and 10.3 μm, respectively.

Registry No.—Bis(isopropoxy)(1-octyloxy)aluminum, 69027-59-4; bis(isopropoxy)(1-decyloxy)aluminum, 69027-60-7; bis(isopropoxy)(1-octadecyloxy)aluminum, 69027-61-8; bis(isopropoxy)(geranyloxy)aluminum, 69027-62-9; bis(isopropoxy)(farnesyloxy)aluminum, 69027-63-0; bis(isopropoxy)(2-octyloxy)aluminum, 69027-64-1; bis(isopropoxy)(cyclohexyloxy)aluminum, 69027-65-2; bis(isopropoxy)(isopulegyloxy)aluminum, 69027-66-3; bis(isopropoxy)(menthyloxy)aluminum, 69027-67-4; bis(isopropoxy)(cholesteryloxy)aluminum, 69027-68-5; bis(isopropoxy)(linaloyloxy)aluminum, 69027-69-6; bis(isopropoxy)(citronellyloxy)aluminum, 69027-70-9; aluminum triisopropoxide, 555-31-7.

References and Notes

(1) E. Müller, *Methoden Org. Chem. (Houben-Weyl)*, **5**, 45–83 (1972).
(2) G. Brieger, *J. Org. Chem.*, **32**, 3720 (1967); G. Brieger, T. J. Nestrick, and C. McKenna, *ibid.*, **34**, 3789 (1969).
(3) D. C. Bradley, *Prog. Inorg. Chem.*, **2**, 303 (1960).
(4) D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, 259 (1972).
(5) W. Tishchenko, *Chem. Zentr.*, **1**, 585 (1900).
(6) K. Narayanan, C. N. Pillai, and E. Haug, *Curr. Sci.*, **35**, 566 (1966).
(7) A. C. Cope, N. A. LeBel, H. H. Lee, and W. R. Moore, *J. Am. Chem. Soc.*, **79**, 4720 (1957).
(8) W. G. Young and H. J. Lucas, *J. Am. Chem. Soc.*, **52**, 1964 (1930).
(9) F. C. Whitmore and C. T. Simpson, *J. Am. Chem. Soc.*, **55**, 3809 (1933).
(10) C. N. Pillai and H. Pines, *J. Am. Chem. Soc.*, **83**, 3270 (1961).
(11) G. L. O'Connor and H. R. Nace, *J. Am. Chem. Soc.*, **77**, 1578 (1955).
(12) H. R. Nace, D. G. Mardy, and S. Fusco, *J. Org. Chem.*, **23**, 687 (1958).
(13) W. Hückel and D. Rucker, *Justus Liebigs Ann. Chem.*, **666**, 30 (1963).
(14) A. C. Cope and E. M. Acton, *J. Am. Chem. Soc.*, **80**, 355 (1958).
(15) H. Pines and C. N. Pillai, *J. Am. Chem. Soc.*, **83**, 3271 (1961).
(16) M. A. Baldwin, D. V. Banthorpe, and A. G. Loudon, *J. Chem. Soc. B*, 509 (1967).

Ring-Size Effects in the Reaction of Benzocycloalkadiene Epoxides with Lithium Diisopropylamide

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As part of a study of ring enlargement reactions, we wished to know the behavior of benzocycloalkadiene oxides with strong base. Only indene oxide, which gives largely polymer, has been reported.[1] Studies of other epoxide systems[1-5] show that a variety of products are possible, e.g., allylic alcohols, alcohols resulting from transannular insertion, carbonyl compounds with or without rearranged carbon skeletons, and amino alcohols. The seven- and eight-membered benzo epoxides were known[6,7] but had not been reacted with strong base. The nine-membered case had not been reported previously.

Results and Discussion

The desired epoxides were prepared by the sequence shown in Scheme I. The seven-membered ketone **1a** is available

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