solvolysis of C^{14}-labeled *exo*-2-norbornenyl brosylate found by Roberts and co-workers,[9] where the previously postulated homoallylic intermediate II[10] predicted no rearrangement in the unsaturated product. On the basis of only 38% observed rearrangement in the norbornenyl case, Roberts proposed partial conversion of the initial ion II to either III or IV. From our complete racemization in the benznorbornenyl case, intermediate V is the most attractive to us. This ion may be formed either directly in the rate-determining step with anchimeric assistance from both σ and π electrons, or subsequently from ion I. Further experiments to distinguish between these possibilities are planned.

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(9) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **77**, 3034 (1955).

(10) J. D. Roberts, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3329 (1950); M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954).

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Acylations of Ketals and Enol Ethers

Sir:

Acid-catalyzed acylations of ketones and enol acetates have been reported in recent years.[1] We wish to report a novel method of acylation of ketals and enol ethers which results in a one-step synthesis of β-ketoketals and β-ketoenol ethers.

The procedure involves treatment of ketals or enol ethers with an excess of acetic anhydride and boron trifluoride etherate at room temperature for 5 min.

The acylation of ketals with acetic anhydride probably involves interaction of the ketal with an oxonium ion of the acetic anhydride and boron trifluoride, to form the corresponding enol ether. This may undergo a Friedel Crafts type condensation with a second oxonium ion to give the observed product.

Marquet, *et al.*,[2] have suggested a similar type of mechanism for the bromination of ketals, but have not been able to isolate any of the suggested intermediates. In contrast, we have been able to trap, isolate, and identify these intermediates by our method (*vide infra*).

Treatment of cholestan-3-one ethylene ketal (I) with acetic anhydride and boron trifluoride etherate for 5 min. at room temperature yielded 78% of 2-acetyl-3-(β-acetoxy)ethoxy-Δ^2-cholestene (II) [m.p. 132–133°; $[\alpha]_D$ +142°; λ_{max}^{EtOH} 268 mμ (ϵ 12,500); ν_{max}^{KBr} 5.74, 6.14 (m), 6.20 μ. *Anal.* Found: C, 76.97; H, 10.86] and 4% of the boron difluoride complex of the 2-acetylcholestan-3-one (III) [m.p. 167–170°; $[\alpha]_D$ +12°; λ_{max}^{EtOH} 303 mμ (ϵ 12,200); $\lambda_{max}^{EtOH-NaOH}$ 310 mμ (ϵ 21,300); ν_{max}^{KBr} 6.25, 6.65 μ. *Anal.* Found: C, 73.30; H, 9.84].

In a similar manner, androstan-17β-ol-3-one ethylene ketal (IV) yielded 28% of Δ^2-androstene-3,17β-diol diacetate[3] (V) [m.p. 172–173°, $[\alpha]_D$ +50°, ν_{max}^{KBr} 5.69, 5.75, 5.9 (w) μ. *Anal.* Found: C, 73.82; H, 9.20],

(1) C. R. Hauser, P. W. Swamer, and J. T. Adams, *Org. Reactions*, **3**, 98 (1954), and references cited; R. M. Manyik, F. C. Frostick, J. J. Sanderson, and C. R. Hauser, *J. Am. Chem. Soc.*, **75**, 5030 (1953); G. N. Walker, *ibid.*, **78**, 2370 (1956); G. N. Walker, *ibid.*, **79**, 3508 (1957); P. J. Hamrick, Jr., C. F. Hauser, and C. R. Hauser, *J. Org. Chem.*, **24**, 583 (1959); D. P. N. Satchell, *Quart. Rev.* (London), **17**, 194 (1963).

(2) A. Marquet, M. Dvolaitzky, H. B. Kagan, L. Mamlok, C. Ouannes, and J. Jacques, *Bull. Soc. Chim. France*, 1822 (1961).
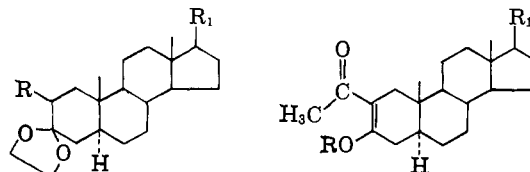
(3) R. Villotti, H. J. Ringold, and C. Djerassi, *J. Am. Chem. Soc.*, **82**, 5693 (1960).

42% of 2-acetyl-3(β-acetoxy)ethoxy-Δ^2-androstene-17β-ol acetate (VI) [m.p. 195–196°, $[\alpha]_D$ +115°, λ_{max}^{EtOH} 269 mμ (ϵ 12,200); ν_{max}^{KBr} 5.74, 6.15 (m), 6.24 μ. *Anal.* Found: C, 70.47; H, 8.82], and 8% of the boron difluoride complex of 2-acetylandrostan-17β-ol-3-one acetate (VII) [m.p. 262–265°; $[\alpha]_D$ +48°; λ_{max}^{EtOH} 304 mμ (ϵ 12,000); $\lambda_{max}^{EtOH-NaOH}$ 310 mμ (ϵ 20,100); ν_{max}^{KBr} 5.74, 6.24, 6.64 μ. *Anal.* Found: C, 65.67; H, 7.70].

Hydrolysis of III and VII with sodium bicarbonate gave 2-acetylcholestan-3-one (VIII) [m.p. 98–102°; λ_{max}^{EtOH} 289 mμ (ϵ 9,900), $\lambda_{max}^{EtOH-NaOH}$ 310 mμ (ϵ 19,600); ν_{max}^{KBr} 6.2 (w) μ] and 2-acetylandrostan-17β-ol-3-one acetate (IX)[4] [m.p. 180–183°; $[\alpha]_D$ +52°; λ_{max}^{EtOH} 290 mμ (ϵ 8,850), $\lambda_{max}^{EtOH-NaOH}$ 310 mμ (ϵ 21,000); ν_{max}^{KBr} 6.2 (w), 5.74 μ. *Anal.* Found: C, 73.86; H, 9.10], respectively, which were reconverted to III and VII by the addition of acetic anhydride and boron trifluoride etherate.

Similarly, hydrolysis of II and VI with methanolic sodium bicarbonate solution yielded 2-acetylcholestan-3-one ethylene ketal (X) [m.p. 167–168°; ν_{max}^{KBr} 5.84, 8.5–9.5 μ; λ_{max}^{EtOH} none. *Anal.* Found: C, 78.70; H, 11.08] and 2-acetylandrostan-17β-ol-3-one acetate ethylene ketal (XI) [m.p. 223–225°; ν_{max}^{KBr} 5.74, 5.84, 8.5–9.5 μ; λ_{max}^{EtOH} none. *Anal.* Found: C, 71.74; H, 9.20].

Analogous treatment of cholestan-3-one diethyl ketal (XII) and androstan-17β-ol-3-one acetate diethyl ketal (XIII) with acetic anhydride and boron trifluoride etherate yielded 8% of III and 62% of 2-acetyl-3-ethoxy-Δ^2-cholestene (XIV) [m.p. 140–144°; $[\alpha]_D$ +109°, λ_{max}^{EtOH} 272 mμ (ϵ 12,700); ν_{max}^{KBr} 6.12 (m), 6.24 μ. *Anal.* Found: C, 81.52; H, 11.26], 11% of VII, and 47% of 2-acetyl-3-ethoxy-Δ^2-androsten-17β-ol acetate (XV) [m.p. 229–232°; $[\alpha]_D$ +110°; λ_{max}^{EtOH} 272 mμ (ϵ 12,800); ν_{max}^{KBr} 5.75, 6.12 (m), 6.24 μ. *Anal.* Found: C, 74.59; H, 9.50], respectively.

I R = H, R₁ = C₈H₁₇   II R = CH₂—CH₂OAc, R₁ = C₈H₁₇
IV R = H, R₁ = OH   VI R = CH₂—CH₂OAc, R₁ = OAc
X R = Ac, R₁ = C₈H₁₇;   XIV R = Et, R₁ = C₈H₁₇
XI R = Ac, R₁ = OAc   XV R = Et, R₁ = OAc
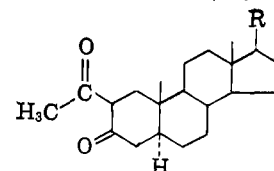
VIII R = C₈H₁₇
IX R = OAc
III BF₂ complex of VIII
VII BF₂ complex of IX
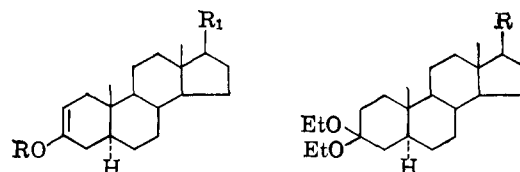
V R = Ac, R₁ = OAc   XII R = C₈H₁₇
XVI R = Et, R₁ = C₈H₁₇   XIII R = OAc
XVII R = Et, R₁ = OAc

(4) A. J. Manson, F. W. Stonner, H. C. Neumann, R. G. Christiansen, R. L. Clarke, J. H. Ackerman, D. F. Page, J. W. Dean, D. K. Phillips, G. O. Potts, A. Arnold, A. L. Beyler, and R. O. Clinton *J. Med. Chem.*, **6**, 1 (1963); Y. Mazur, private communication.

Reaction of 3-ethoxy-Δ^2-cholestene (XVI) and 3-ethoxy-Δ^2-androstene-17β-ol acetate (XVII) with acetic anhydride and boron trifluoride etherate under the same reaction conditions yielded 58% of XIV and 53% of XV, respectively.

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A Solvent-Sensitive Rearrangement of 7-Substituted Norbornadienes to Cycloheptatriene Using Complex Hydrides

Sir:

Recently 7-substituted norbornadienes (I) have been found to react with hydrides to afford norbornadiene (II) and the tricyclic hydrocarbon III.[1,2] These reductions have been postulated to proceed *via* a hydride

Ia, X=Cl   d, X=OH
b, X=OTs
c, X=OAc   e, X=O—C—Ph

II   III
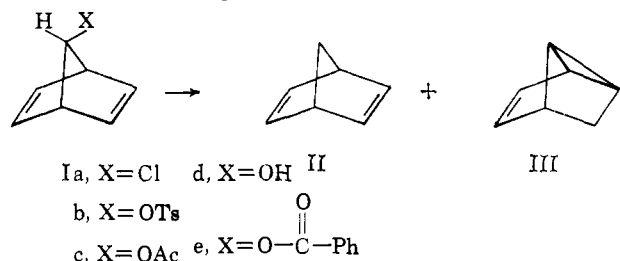
displacement at the bridge carbon and/or *via* hydride abstraction by an intermediate with carbonium ion character.[1,3] We here describe observations which

for 6–16 hr. affords high (80–90%) yields of cycloheptatriene (IV). In a small-scale preparative experiment cycloheptatriene was isolated from Ie in 63.4% yield. Positive identification of a sample isolated by v.p.c. was made by comparison of its infrared and n.m.r. spectra and its retention time on v.p.c. with those of an authentic sample. The concordance of yield data from quantitative ultraviolet measurements on the crude reaction mixture and those from quantitative v.p.c. measurements provides assurance that IV is a primary product of reaction rather than an artifact of work-up procedures. The stability of III under the reaction conditions demonstrates it is not a precursor of IV. This same rearrangement occurs with other hydrides (*e.g.*, NaBH$_4$, LiBH$_4$) in THF and/or diglyme at 60° using Ic or Id, although IV is formed in much lower yields (25–50% by quantitative ultraviolet and v.p.c.).[4] When the reduction was performed with lithium aluminum deuteride 1.00 atoms of deuterium was incorporated into cycloheptatriene, all of which was in the methylene group.

The course of reaction described above stands in sharp contrast to results of reduction in diethyl ether as solvent. With Ic or Id a stereospecific carbon–carbon double bond reduction occurs to afford anti-7-norbornenol (V) in high yield[5] with approximately 5.5% IV formed.

All observations described above are consistent with the reaction proceeding according to 1 in diethyl ether and 2 in THF. Path 1 is fully consistent with deuterium labeling experiments[6] as is path 2. The difference between the two paths we ascribe solely to the coordinating ability of the solvent. If the latter interpretation is correct we would predict that the course of reduction should be a function of the Lewis base properties of the solvent or

Path 1

Path 2
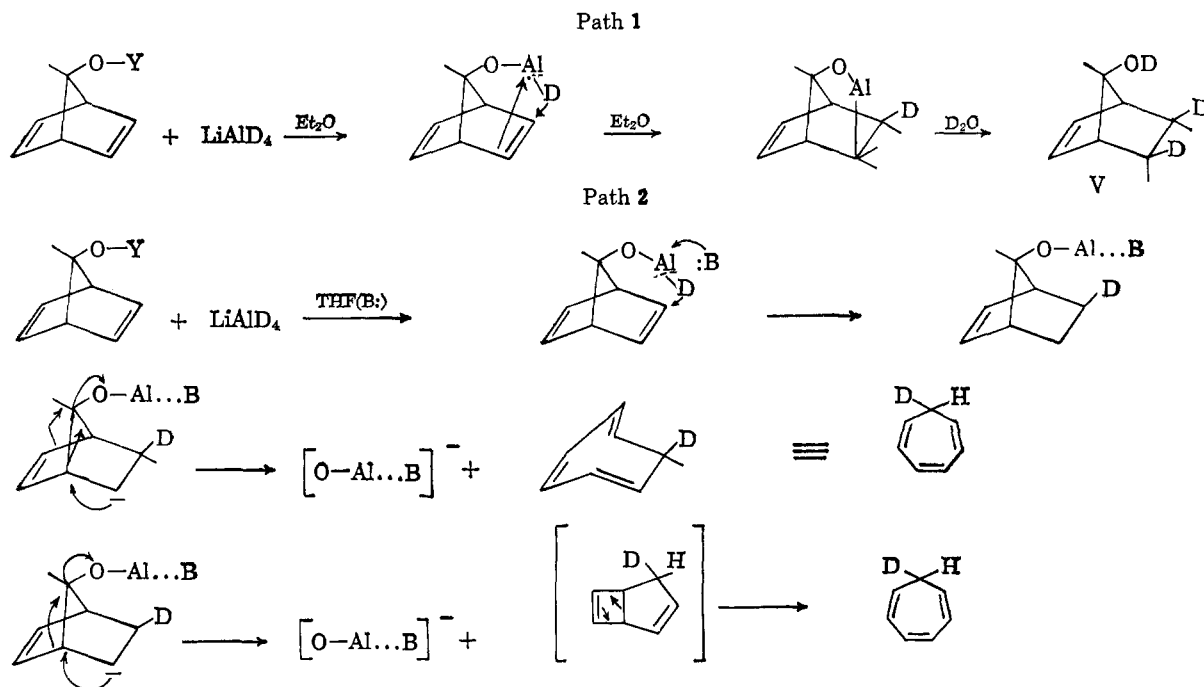
demonstrate the incursion of still another process in hydride reactions with 7-substituted norbornadienes which can, perhaps, be best described as a solvent-sensitive anionic carbon skeletal rearrangement.

Treatment of the 7-acetate, alcohol, or benzoate (Ic–e) with excess lithium aluminum hydride (LAH) in tetrahydrofuran (THF) solution at or below 40°

of any other constituents present in the reduction system. We also hope to distinguish between the two modes of decomposition indicated in path 2.

(1) P. R. Story, *J. Am. Chem. Soc.*, **83**, 3347 (1961).
(2) H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963).
(3) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

(4) Cycloheptatriene also accompanies norbornadiene and the tricyclic hydrocarbon III in reductions of 7-chloronorbornadiene (Ia) with various complex hydrides. These latter results will be elaborated upon in the full paper describing results of reductions of 7-substituted norbornadienes.
(5) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).
(6) B. Franzus and E. I. Snyder, unpublished results; see also footnote 8 of reference 1.