We have also observed segregation of deuterated species in a number of amides, but not, for example, in hydrocarbons. Thus, it appears that the segregation depends on the presence of hydrogen-bonded hydrogens.

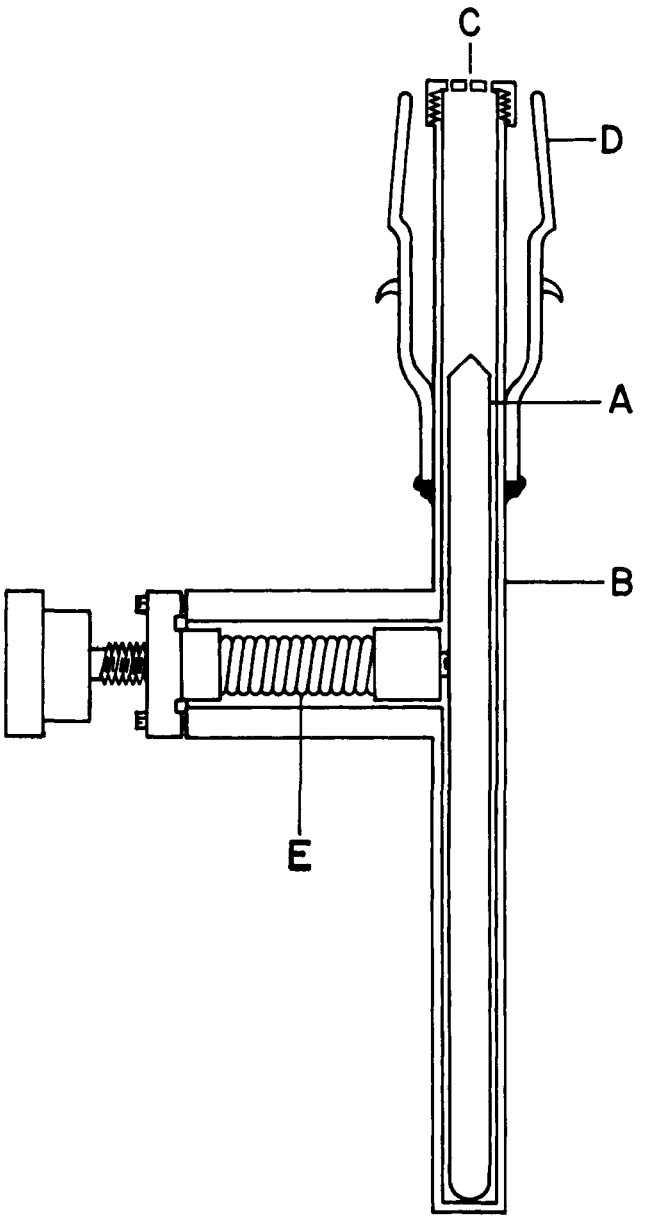


Fig. 1.—Modified tube breaker.

The analytical method of Jones and MacKenzie involves the combustion of an organic compound with copper oxide in a sealed quartz tube which must be broken in an evacuated system to recover the water formed. The tube breaker described by these workers was found to be inconvenient, since it often leaked when the vacuum distillation system was baked. The tube breaker shown in Fig. 1 is easily made, inexpensive, and very reliable. Quartz tube A, containing combustion products of a deuterated sample, is slipped into brass sleeve B, and the latter is closed by means of perforated cap C. The assembly is attached to a distillation manifold by standard-taper joint D which is permanently connected to B by epoxy resin cement. Tube A is broken by advancing the bellows mechanism E of an all-metal vacuum valve (Vacuum-Electronics Corporation, Cat. No. R12P) which is sealed with an O-ring made of Teflon polytetrafluoroethylene resin. Quartz fragments are retained by C.

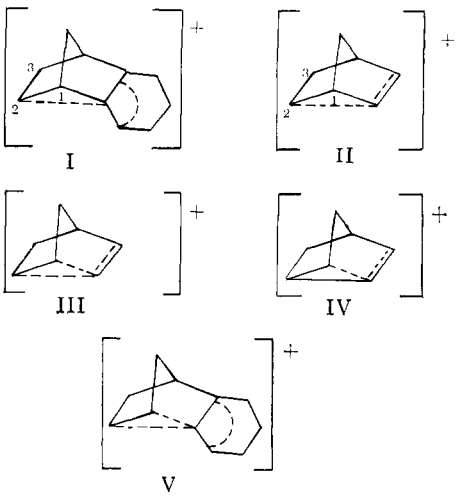
CENTRAL RESEARCH DEPT. G. J. SLOAN
EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS AND CO., INC.
WILMINGTON, DELAWARE

RECEIVED SEPTEMBER 5, 1963

Racemization in the Solvolysis of *exo*-2-Benznorbornenyl Brosylate

Sir:

Interest in the nature of intermediate ions in reactions of norbornyl derivatives has remained at a high level.[1] We wish to report racemization accompanying the solvolysis of *exo*-2-benznorbornenyl brosylate, a finding incompatible with the previously postulated nonclassical intermediate I.[2]



Optically active *exo*-2-benznorbornenol was prepared from benznorbornadiene[3] and diisopinocampheylborane,[4] which was obtained from hydroboration of α-pinene of $[\alpha]^{27}D$ $+46.8 \pm 0.05°$[5,6] by the procedure of Sondheimer and co-workers.[7] *exo*-2-Benznorbornenyl acetate of $[\alpha]^{25}D$ $-2.00 \pm 0.05°$[6] was prepared using acetic acid in pyridine to avoid possible acid-catalyzed rearrangements. The alcohol was regenerated by lithium aluminum hydride reduction of the acetate, and the brosylate was prepared as previously.[2] Solvolysis of the brosylate at 50° was carried out in glacial acetic acid containing 0.1 *M* sodium acetate for 18 hr. (well over ten half-lives[2]), yielding acetate of $[\alpha]D$ $0.000 \pm 0.001°$[8] indicating more than 99.9% racemization. Thus it is clear that the reaction proceeds through a symmetric intermediate.

The homobenzyllic ion I predicts complete retention of configuration and of optical activity. Racemization could occur through an intermediate in which carbon atoms 2 and 3 or 2 and 1 become equivalent. These results are reminiscent of the rearrangement in the

(1) For recent examples, see: H. C. Brown and F. J. Chloupek, *J. Am. Chem. Soc.*, **85**, 2322 (1963); H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963); S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963); P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, *ibid.*, **85**, 479 (1963); H. Tanida, *ibid.*, **85**, 1703 (1963).

(2) P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960).

(3) G. Wittig and E. Knauss, *Ber.*, **91**, 895 (1958).

(4) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 486 (1961).

(5) We gratefully acknowledge the gift of the optically active α-pinene from H. I. Enos, Jr., Hercules Powder Co., Wilmington, Del.

(6) Readings were taken with a Kern polarimeter using pure liquid in a 2-dm. tube. Uncertainties are average deviations from the mean of ten readings.

(7) S. Wolfe, M. Nussim, Y. Mazur, and F. Sondheimer, *J. Org. Chem.*, **24**, 1034 (1959).

(8) We are grateful to Mr. Kenneth D. Stevens, University of Washington, for this reading taken with a Bendix automatic polarimeter using a 25% chloroform solution.

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.

Acknowledgment.—This work was supported by National Science Foundation Undergraduate Science Education Grants G-21641 and GE-1216. Mr. Jon E. Malmin performed valuable preliminary experiments.

(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).

RAMSTAD RESEARCH LABORATORIES
DEPARTMENT OF CHEMISTRY
PACIFIC LUTHERAN UNIVERSITY
TACOMA, WASHINGTON 98447
WILLIAM P. GIDDINGS
JOHN DIRLAM

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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-keto-ketals 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*).

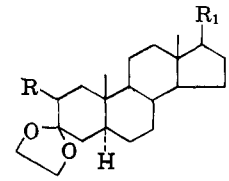
Treatment of cholestan-3-one ethylene ketal (I) with acetic anhydride and boron trifluoride etherate for 5 min. at room temperature yielded 78% of 2-acetyl-3-(β-acetoxy)ethoxy-Δ^2-cholestene (II) [m.p. 132–133°; $[\alpha]_D$ +142°; λ_{max}^{EtOH} 268 mμ (ϵ 12,500); ν_{max}^{KBr} 5.74, 6.14 (m), 6.20 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].

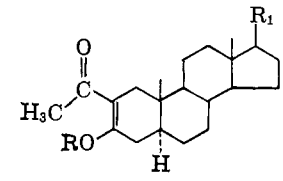
In a similar manner, androstan-17β-ol-3-one ethylene ketal (IV) yielded 28% of Δ^2-androstene-3,17β-diol diacetate[3] (V) [m.p. 172–173°, $[\alpha]_D$ +50°, ν_{max}^{KBr} 5.69, 5.75, 5.9 (w) μ. *Anal.* Found: C, 73.82; H, 9.20], 42% of 2-acetyl-3(β-acetoxy)ethoxy-Δ^2-androstene-17β-ol acetate (VI) [m.p. 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.

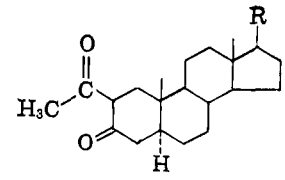
Similarly, hydrolysis of II and VI with methanolic sodium bicarbonate solution yielded 2-acetylcholestan-3-one ethylene ketal (X) [m.p. 167–168°; ν_{max}^{KBr} 5.84, 8.5–9.5 μ; λ_{max}^{EtOH} none. *Anal.* Found: C, 78.70; H, 11.08] and 2-acetylandrostan-17β-ol-3-one acetate ethylene ketal (XI) [m.p.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

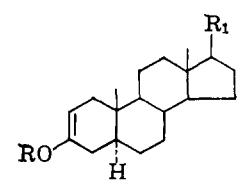


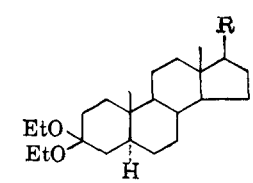


I R = H, R_1 = C_8H_{17} II R = CH_2—CH_2OAc, R_1 = C_8H_{17}
IV R = H, R_1 = OH VI R = CH_2—CH_2OAc, R_1 = OAc
X R = Ac, R_1 = C_8H_{17} XIV R = Et, R_1 = C_8H_{17}
XI R = Ac, R_1 = OAc XV R = Et, R_1 = OAc



VIII R = C_8H_{17}
IX R = OAc
III BF_2 complex of VIII
VII BF_2 complex of IX





V R = Ac, R_1 = OAc
XVI R = Et, R_1 = C_8H_{17}
XVII R = Et, R_1 = OAc

XII R = C_8H_{17}
XIII R = OAc

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