

to be less stable than I due to eclipsing interactions<sup>6</sup> and the necessity for a larger part of the molecule to be close to the catalyst surface. The latter factor will decrease the probability of chemisorption to form II or III and will cause these configurations to be more rigid than I. Additional information will be necessary before the importance of these and other factors which may influence the course of this reaction can be determined. In agreement with these considerations is the observation that thoria, but not alumina, catalyzes the dehydration of 2-octanol much more rapidly than 3- or 4-octanol.

**Acknowledgment.**—We thank Dr. C. M. Starks for helpful discussions.

(6) These eclipsing interactions alone are not sufficiently large to explain the observed results. Similar interactions are present in the transition states of amine oxide and acetate pyrolysis which give nearly statistical product distributions. See C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

RESEARCH AND DEVELOPMENT DEPARTMENT

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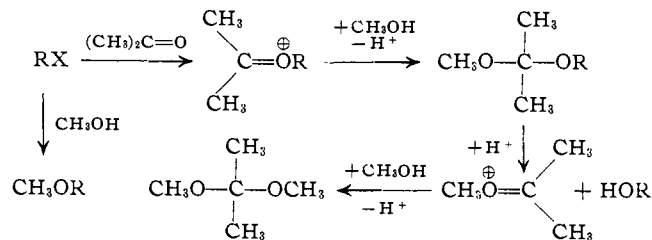
### Acetone as a Nucleophile

Sir:

In a recent communication<sup>1</sup> the intervention of dioxane as a nucleophilic agent in the hydrolysis of optically active 2-octyl brosylate in aqueous dioxane was suggested as an explanation for the observed ability of added azide ion to increase the optical purity of the inverted product alcohol from 77% in the absence of sodium azide to 100% in its presence. It was suggested that azide ion may accomplish this effect by its selective attack on the pre-formed oxonium ion intermediate, thus preventing the formation of alcohol *via* this racemizing route. These results led us to search for similar phenomena in other mixed solvents containing "inert" components. This communication reports evidence for a parallel involvement of acetone in solvolysis reactions of the 2-octyl brosylate system.

Solvolysis of 2-octyl brosylate in 80% methanolic acetone furnished, in addition to the expected 2-octyl methyl ether, 2-octanol.<sup>2</sup> By vapor phase chromatography the alcohol was determined to constitute  $15 \pm 5\%$  of the solvolysis mixture. Control experiments established that neither adventitious water nor water formed in condensation reactions of the solvent is able to account for the formation of alcohol.

The formation of alcohol under these conditions would seem to implicate acetone as an effective nucleophile, the mixed methyl 2-octyl ketal of acetone serving as an intermediate



Confirmation of the suggested scheme has come from the following experiments. (1) When solvolysis was conducted in the same solvent system in the presence of a slight excess of 2,6-lutidine, no 2-octanol was detected by v.p.c. Under these buffered conditions the mixed ketal is presumably stable. However, neutral-

ization of this reaction mixture with *p*-toluenesulfonic acid resulted in the formation of 2-octanol (by v.p.c.). (2) Although attempts to isolate the mixed ketal in a pure state have not as yet been successful, a precursor of acetone has been shown to be present among the products of a basic solvolysis (lutidine). Thus when the reaction mixture was concentrated by distillation and diluted with ether to precipitate the amine salts, a residue was obtained whose infrared spectrum was transparent in the carbonyl region. However, when this residue was treated with acidic 2,4-dinitrophenylhydrazine reagent, a solid, identified as the 2,4-dinitrophenylhydrazone of acetone, was formed.

The technique described above for detecting the nucleophilic intervention of acetone in solvolyses conducted in methanolic acetone is, of course, not applicable to solvolyses in aqueous acetone where one might also expect the phenomenon to occur. It is interesting in this connection, however, that solvolysis of 2-octyl brosylate in 80% aqueous acetone gave rise to 2-octanol, formed with  $99 \pm 2\%$  inversion of configuration. Thus acetone, if it intervenes in this aqueous system, does so with essentially complete inversion of configuration.

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### A Novel Rearrangement of Cyclic $\alpha$ -Nitro Ketones

Sir:

A recent communication of the rearrangement of 3-nitrocaphor<sup>1</sup> prompts us to report our independent findings which indicate that steroidal  $\alpha$ -nitro ketones undergo this novel type of rearrangement to N-hydroxy imides under acid conditions.

16-Nitro-5-androsten-3 $\beta$ -ol-17-one (I), m.p. 105–107°, prepared from 5-androsten-3 $\beta$ -ol-17-one by base-catalyzed condensation with butyl nitrate and consisting of a 1:1 mixture of 16 $\alpha$  and 16 $\beta$  epimers (by n.m.r.), is converted by treatment with acid in 75% yield to the N-hydroxyimide II, m.p. 260–263°, or by treatment with acetic anhydride at room temperature in 80% yield to the corresponding diacetate III, m.p. 231–232°. With hydrochloric acid in acetic acid, I or its potassium salt is converted in 75% yield to 3 $\beta$ -acetoxy-16,17-seco-5-androstene-16,17-dioic N-hydroxyimide (IV), m.p. 241–245°, which is acetylated quantitatively to III. N-Hydroxyimide IV is also obtained in 75% yield by reaction of anhydride VII with hydroxylamine. Hydrolysis of diacetate III with potassium hydroxide at room temperature leads to hydroxyimide II; with potassium *t*-butoxide III is converted to 3 $\beta$ -hydroxy-16,17-seco-5-androstene-16,17-dioic acid. N-Hydroxyimides II and IV yield corresponding N-methoxy derivatives V (95%), m.p. 214–215°, and VI (85%), m.p. 186–188°, respectively. V and VI are interconvertible by acetylation and hydrolysis.

Analogous results can be achieved in the 5,6-dihydro series: Ia, m.p. 180–182°, 95%; IIIa, m.p. 180–182°, 80%; IVa, m.p. 224–226°, 80%. Other examples of this rearrangement are provided by the formation in 75% yield of N-acetoxy-2,3-secocholestane-2,3-dioic

(1) H. Weiner and R. A. Sneen, *J. Am. Chem. Soc.*, **84**, 3599 (1962).

(2) Isolated by preparative v.p.c.; identity established by microanalysis and infrared spectrum.

(1) H. O. Larson and E. K. W. Wat, *J. Am. Chem. Soc.*, **85**, 827 (1963).

(2) Satisfactory analyses were obtained for all compounds for which melting points are given.