VI

(5) The reaction normally introduces the new alkyl group on the less alkylated side of an unsymmetrical ketone.[10] The magnesium salt of the cyclohexylimine of 2-methylcyclohexanone reacted with methyl iodide to give an 83% yield of 2,6-dimethylcyclohexanone. Alkylation on the less substituted side applies even to *methyl* alkyl ketones. Methyl isopropyl ketone gave, by the imine–magnesium salt method, with butyl iodide, 70% of 2-methyl-3-octanone (VII). Again, the major product from 2-heptanone was 6-undecanone (VIII).

VII

VIII

Alkyl groups further removed from the carbonyl than the α-carbon atoms would not be expected to exert as profound a directing influence, but an experiment is worthy of note in this respect. Alkylation of the cyclohexylimine from 3-methylcyclohexanone with isopropyl iodide, by the usual procedure, followed by acid hydrolysis of the alkylated imine, gave 61% of the equilibrium mixture of dl-menthone and isomenthone.

(10) The reason for the direction of alkylation as well as for the monoalkylation of the imine salts is of the same type as we have discussed in the case of enamines, cf. ref. 1.

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Selective Catalytic Dehydration of 2-Alcohols; a New Synthesis of 1-Olefins

Sir:

Vapor phase dehydrations of 2-butanol and 2-pentanol catalyzed by alumina yield mixtures of olefins rich in the 2-olefin.[1] Numerous other metal oxide catalyzed dehydrations have been reported to give similar product distributions.[2] Mechanisms proposed

(1) H. Pines and W. O. Haag, J. Am. Chem. Soc., 83, 2847 (1961).

(2) M. E. Winfield, "Catalytic Dehydration and Hydration," in "Catalysis," Vol. IV, P. H. Emmett, Ed., Reinhold Publ. Corp., New York, N. Y. 1960, pp. 93–182.

for dehydrations catalyzed by alumina and similar catalysts involve oxonium ion and carbonium ion intermediates or transition states.[1,2]

We have observed that thoria and other oxides of group IIIB elements catalyze the dehydration of secondary 2-alcohols to yield 1-olefins as the major products. Representative examples are listed in Table I.

TABLE I

THORIA-CATALYZED DEHYDRATION OF 2-ALCOHOLS

Alcohol	Products %[a]	
	1-Olefin	2-Olefin
2-Butanol	93	7
2-Octanol	95–97	3–5
4-Methyl-2-pentanol	96–98	2–4
1-Cyclohexyl-1-ethanol	96–98	2–4

[a] A small but erratic yield of ketone (1–6%) arising from competing dehydrogenation is not included in these calculations. Yields are based on consumed alcohol (excluding ketone). Conversions of 20–90% were obtained.

These experiments were conducted in a flow system at 350–450° with contact times of 0.1 to 0.5 sec. Products were separated by distillation and analyzed by gas chromatography,[3] infrared and n.m.r. spectroscopy.

The most active and selective thoria catalysts we have obtained were prepared by calcining thorium oxalate at 350–450° for a few hours.[4] However, thoria catalysts with equal selectivity, although with somewhat less activity, have been prepared from the acetate and carbonate. Sixteen other oxides of group IIIB elements were tested briefly as selective dehydration catalysts. In most examples studied the 1-olefin comprised 90% and often over 95% of the olefins produced. Little significance is attached to these differences at present since impurities or methods of catalyst preparation could be of major importance.[5] The oxides of W, Mo, Ti, Zr and Al were found not to be selective dehydration catalysts, in agreement with published results.[2]

While the efficiency of rare earth oxides as dehydration catalysts has long been known, the general and remarkably specific nature of this dehydration has not been recognized previously. Thoria has been used to prepare butadiene by the dehydration of 2,3-butanediol.[4] Alumina-catalyzed dehydration of 2,3-butanediol yielded chiefly methyl ethyl ketone.

We suggest that the mechanism of selective dehydration involves concerted elimination of the elements of water. This requires the alcohol to be chemisorbed on the catalyst surface in the conformations I–III. Complexes or transition states II and III are expected

(3) Silver nitrate–tetraethylene glycol, Carbowax or tricresyl phosphate on inert supports were used in g.l.c. analysis.

(4) M. E. Winfield, J. Council Sci. Ind. Res. Australia, 18, 412 (1945).

(5) Passage of a pure 1-olefin over the best catalysts under dehydration conditions resulted in 1–2% isomerization to the 2-isomer.

to be less stable than I due to eclipsing interactions[6] 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

                                  ALLAN J. LUNDEEN

CONTINENTAL OIL COMPANY   ROBERT VAN HOOZER

RECEIVED MAY 27, 1963

Acetone as a Nucleophile

Sir:

In a recent communication[1] 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.[2] By vapor phase chromatography the alcohol was determined to constitute 15 ± 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
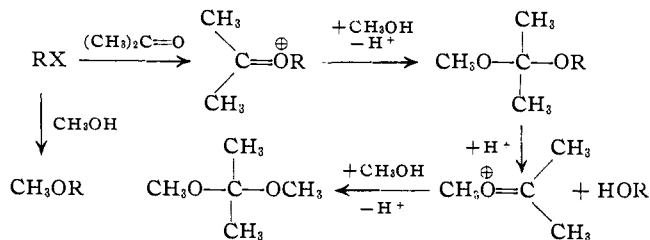
Confirmation of the suggested scheme has come from the following experiments. (1) When solvolysis was conducted in the same solvent system in the presence of a slight excess of 2,6-lutidine, no 2-octanol was detected by v.p.c. Under these buffered conditions the mixed ketal is presumably stable. However, neutral-

(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.

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 ± 2% inversion of configuration. Thus acetone, if it intervenes in this aqueous system, does so with essentially complete inversion of configuration.

Acknowledgment.—This work was supported in part by a grant from the Army Research Office (Durham) and this assistance is gratefully acknowledged.

(3) Predoctoral Fellow of the National Institutes of Health.

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RECEIVED APRIL 27, 1963

A Novel Rearrangement of Cyclic α-Nitro Ketones

Sir:

A recent communication of the rearrangement of 3-nitrocamphor[1] prompts us to report our independent findings which indicate that sterioidal α-nitro ketones undergo this novel type of rearrangement to N-hydroxy imides under acid conditions.

16-Nitro-5-androsten-3β-ol-17-one (I), m.p. 105–107°, prepared from 5-androsten-3β-ol-17-one by base-catalyzed condensation with butyl nitrate and consisting of a 1:1 mixture of 16α and 16β 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°.[2] With hydrochloric acid in acetic acid, I or its potassium salt is converted in 75% yield to 3β-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 3β-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. 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.