Full details of the work on the two species mentioned will be reported later.

Instituto de Química Agrícola
Ministério da Agricultura
Rio de Janeiro, Brazil
Otto Richard Gottlieb
Mauro Taveira Magalhães

Received October 26, 1959

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(11) M. Pailer and A. Schleppnik, *Monatsh.*, **88**, 367 (1957).

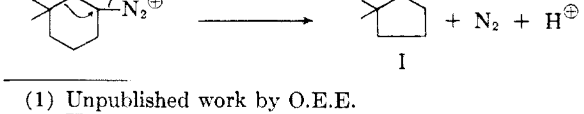
Deamination of α-Aminoketones

Sir:

Observation that nitrous acid deamination of a primary aminoketone derived from the alkaloid lycoctonine[1] gave an acid led us to consider the possibility that aliphatic α-aminoketones would give acids by Favorskii-type rearrangement on deamination.

We have now shown that 2-aminocyclohexanone hydrochloride[2] (prepared by stannous chloride reduction of 2-oximinocyclohexanone) gives up to 57% yields of carboxylic acid when treated with aqueous nitrous acid. This proved to be mainly cyclopentanecarboxylic acid (amide m.p. 179°; anilide, m.p. 165°, showing no melting point depression with authentic derivatives). Similarly, 2-amino-6,6-dimethylcyclohexanone (hydrochloride m.p. 182°, *Anal.*, Calcd. for $C_8H_{16}ONCl$: C, 54.08; H, 9.07; N, 7.82. Found: C, 53.47; H, 9.00; N, 7.92) gave a 25% yield of acid. This was mainly a saturated monocyclic acid $C_8H_{14}O_2$ (anilide, m.p. 125°, *Anal.*, Calcd. for $C_{14}H_{19}ON$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.49; H, 8.57; N, 6.44) which on mechanistic grounds and by analogy to the product from 2-aminocyclohexanone should be 2,2-dimethylcyclopentanecarboxylic acid (I). This assignment was supported by its infrared spectrum, which had the pair of peaks characteristic of a *gem*-dimethyl group (ν_{max} 1370 and 1385 cm.$^{-1}$, liquid film), and by the NMR spectrum of its methyl ester, which had two unsplit methyl signals at 186 and 199 c.p.s. (60 Mc, water reference). In addition, the spectrum contained signals due to a single hydrogen with a large chemical shift flanked by one methylene (triplet with J = 6.5 c.p.s. centered about +118 c.p.s.).

We suggest that the positive charge on the amine salt and diazonium ion aid hydration of the carbonyl, and that I is formed by the following mechanism:



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Close analogs are found in the deamination of cyclic α-aminoalcohols[3] and the silver ion initiated rearrangement of α-bromoketones.[4]

Attempts to prepare I by vigorous alkaline treatment of 2-chloro-6,6-dimethylcyclohexanone (m.p. 62°, ν_{max} 1720 cm.$^{-1}$ as Nujol mull. *Anal.*, Calcd. for $C_6H_{13}OCl$: C, 59.81; H, 8.15; Cl, 22.07. Found: C, 59.65; H, 8.09; Cl, 22.33) and by the action of silver nitrate in aqueous alcohol[4] on 2-bromo-6,6-dimethylcyclohexanone (m.p. 58°. *Anal.*, Calcd. for $C_6H_{13}OCl$: C, 46.84; H, 6.38. Found: C, 47.05; H, 6.26) failed to yield more than traces of carboxylic acid. Hence the above deamination may prove a useful alternative to the Favorskii reaction when one carbon alpha to the carbonyl is quaternary.[5] The neutral products of the reaction are under investigation.

Division of Pure Chemistry
National Research Council
Ottawa, Canada
O. E. Edwards
M. Lesage

Received November 16, 1959

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(1) Unpublished work by O.E.E.

(2) H. E. Baumgarten and F. A. Bower, *J. Am. Chem. Soc.*, **76**, 4561 (1954).

(3) G. E. McCasland, *J. Am. Chem. Soc.*, **73**, 2293 (1951); D. Y. Curtin and S. Schmukler, *J. Am. Chem. Soc.*, **77**, 1105 (1955).

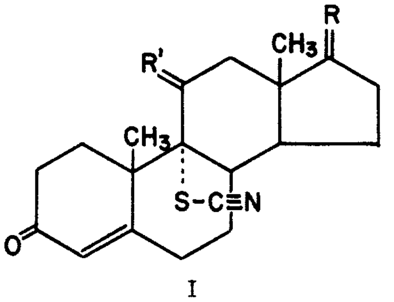
(4) A. C. Cope and E. S. Graham, *J. Am. Chem. Soc.*, **73**, 4702 (1951).

(5) R. B. Loftfield, *J. Am. Chem. Soc.*, **73**, 4707 (1951).

Synthesis of 9α- and 11β-Thiocyano Steroid Analogs

Sir:

With the intention of finding antimetabolites of steroidal hormones, some thiocyano derivatives of corticoids and androgens (Ia–f and IIIa–b) have been synthesized.



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(a) R = α-OH, -CO—CH$_2$OH
R′ = β-OH, -H
(b) R = α-OH, -CO—CH$_2$OAc
R′ = β-OH, -H
(c) R = =O
R′ = β-OH, -H
(d) R = α-OH, -CO—CH$_2$OH
R′ = =O
(e) R = α-OH, -CO—CH$_2$OAc
R′ = =O
(f) R= =O
R′ = =O