DEGRADATION OF TOMATIDINE

Sir:

In view of the recent interest in tomatidine[1,2,3] we wish to report our results on the degradation of tomatidine.[4]

Our analytical data of tomatidine and derivatives agree with the empirical formula $C_{27}H_{45}NO_2$ proposed by Fontaine, *et al.*,[5] rather than $C_{27}H_{43}NO_2$, suggested tentatively by Kuhn, *et al.*[3] Tomatidine. *Anal.* Calcd. for $C_{27}H_{45}NO_2$: C, 78.02; H, 10.91; N, 3.37; for $C_{27}H_{43}NO_2$: C, 78.40; H, 10.48; N, 3.39. Found: C, 78.02; H, 10.96; N, 3.43.

Tomatidine hydrochloride. *Anal.* Calcd. for $C_{27}H_{46}ClNO_2$: C, 71.73; H, 10.26; for $C_{27}H_{44}ClNO_2$: C, 72.05; H, 9.85. Found: C, 71.83; H, 10.35.

N,O-Diacetyltomatidine.[6]—*Anal.* Calcd. for $C_{31}H_{49}NO_4$: C, 74.50; H, 9.88; for $C_{31}H_{47}NO_4$: C, 74.81; H, 9.52. Found: C, 74.66; H, 9.92.

Tomatidine forms a sparingly soluble digitonide. On treatment with sodium nitrite in acetic acid a N-nitroso derivative is obtained, m.p. 234–237°[7]; λ_{max} 233 mμ, log ε 3.87: λ_{max} 360, log ε 1.83 (ethanol). *Anal.* Calcd. for $C_{27}H_{44}N_2O_3$: N, 6.30. Found: N, 6.36.

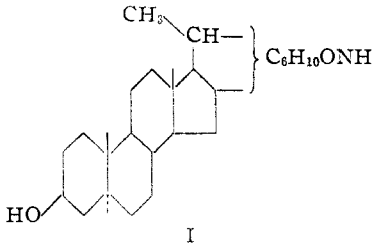
Treatment of tomatidine with acetic anhydride yielded an unsaturated triacetyl derivative (A), m.p. 105–107°. *Anal.* Calcd. for $C_{33}H_{51}NO_5$: C, 73.16; H, 9.49. Found: C, 73.12; H, 9.78.

A gave with dilute alkali a monoacetyl derivative, m.p. 210–215°. *Anal.* Calcd. for $C_{29}H_{47}NO_3$: C, 76.10; H, 10.35; N, 3.06. Found: C, 76.11; H, 10.42; N, 3.08.

Oxidation of A with chromic acid anhydride in acetic acid, and subsequent hydrolysis resulted in the formation of Δ^{16}-allopregnen-3(β)-ol-20-one, m.p. 205–206°, no depression when admixed with an authentic sample. *Anal.* Calcd. for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19. Found: C, 79.55; H, 10.30.

The acetate of the compound likewise agrees well (m.p. 167–168°, mixed m.p., ultraviolet and infrared spectra) with authentic samples.[8] *Anal.* Calcd. for $C_{23}H_{34}O_3$: C, 77.05: H, 9.56. Found: C, 77.58; H, 9.80.

The isolation of the allopregnenolone establishes



I

the structure of the steroidal moiety of tomatidine (I) and the attachment of the portion containing the secondary nitrogen, at C-20. The second point of attachment is most likely at position 16.

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RECEIVED DECEMBER 8, 1950

(1) Fontaine, Irving, Ma, Poole and Doolittle, *Arch. Biochem.*, **18**, 467 (1948).

(2) Kuhn and Löw, *Chem. Ber.*, **81**, 552 (1948).

(3) Kuhn, Löw and Gauhe, *ibid.*, **83**, 448 (1950).

(4) Kindly supplied to us by Dr. Thomas D. Fontaine, Bureau of Agricultural and Industrial Chemistry.

(5) Fontaine, Ard and Ma, THIS JOURNAL, **73**, 000 (1951).

(6) Purified by chromatography.

(7) All melting points were taken on the Kofler block and are uncorrected.

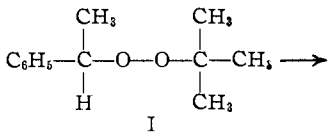
(8) A sample was kindly supplied to us by Dr. R. B. Wagner of Pennsylvania State College. Another generous sample was given to us by Dr. George Rosenkranz of Syntex, S. A.

(9) Organisch-chemische Anstalt, University of Basel.

THE BASE CATALYZED DECOMPOSITION OF A DIALKYL PEROXIDE

Sir:

We have found that bases, such as potassium hydroxide, sodium ethoxide, or piperidine, catalyze the decomposition of 1-phenylethyl-*t*-butyl peroxide (I)



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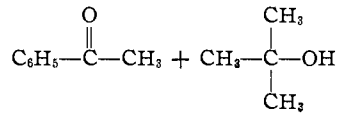
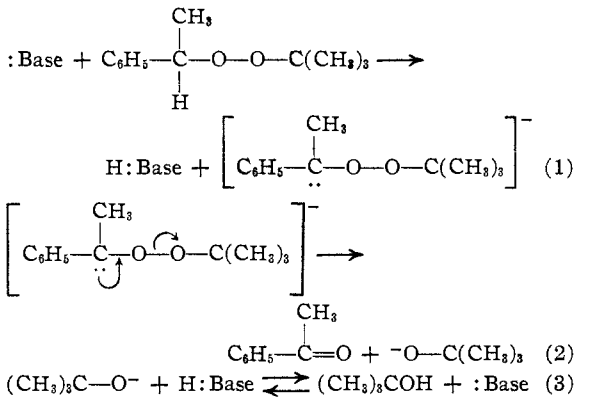


This reaction takes place smoothly at room temperature and apparently is the first demonstration of the instability of a dialkyl peroxide toward base. The facile decomposition of I contrasts sharply with the inertness of di-*t*-butyl peroxide to potassium hydroxide[1] or piperidine.

The following mechanism, which is in accord with all the known facts, emphasizes the relationship of this reaction to the well-known elimination reaction[2]; steps (1) and (2) presumably are synchronous.



(1)

(2)

(3)

This mechanism also affords a reasonable explanation for the conversion of α-tetralin hydroperoxide (II) to α-tetralone under the influence of sodium hydroxide.

It is a consequence of this mechanism that only those dialkyl peroxides and alkyl hydroperoxides having a hydrogen on the carbon attached to the peroxide linkage will undergo base catalyzed decomposition. That the aromatic nucleus in I and II is not a necessary structural feature is indicated

(1) N. A. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 205 (1946).

(2) E. D. Hughes, C. K. Ingold, *et al.*, *J. Chem. Soc.*, 2093 (1948).