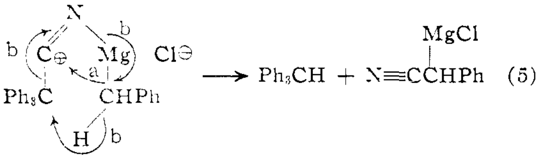
there occurs both the commonly accepted[3] 1,3-shift of the benzyl group from magnesium to nitrile-carbon (arrow a) and a concerted shift of hydrogen and electrons around a six-membered quasi-ring (arrows b). If these are the transformations which occur, phenylacetonitrile (from VI)



V II VI

should be isolable after hydrolysis. When the reaction was carried out with triphenylacetonitrile labeled in the nitrile group with carbon-14, labeled phenylacetonitrile was isolated after hydrolysis.[4,5]

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[3] C. G. Swain, THIS JOURNAL, **69**, 2306 (1947); see also pp. 767–769 in ref. 1.

[4] In this run isotopic dilution showed that the phenylacetonitrile was formed in 35% yield. All remaining carbon-14 was found in a non-volatile, amorphous, organic material formed presumably by polymerization of VI; *cf.* A. Rondou, *Bull. soc. chim. Belg.*, **31**, 231 (1922).

[5] The authors wish to acknowledge the many helpful discussions of this work with Dr. C. J. Collins.

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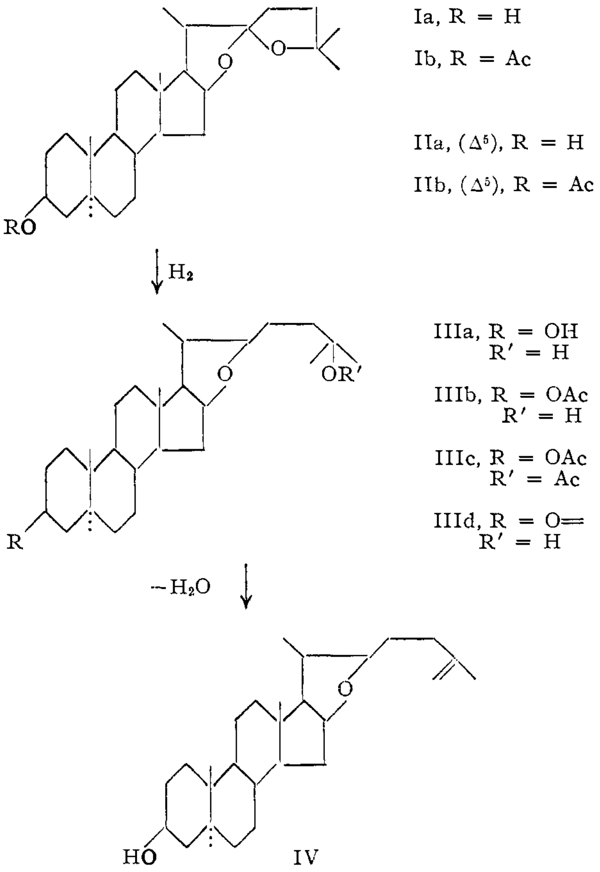
CONVERSION OF TOMATIDINE AND SOLASODINE INTO NEOTIGOGENIN AND DIOSGENIN AND INTO A COMMON CONSTITUENT, 5α-22,25-EPOXYFUROSTAN-3β-OL

Sir:

The deamination of N-nitrosotomatidine[1,2] with 30% aqueous acetic acid in ethanol leads to a mixture from which neotigogenin[3] (8–10%), m.p. 197–199°, [α]D −78.6° (chf),[4] (*Anal.* Calcd. for $C_{27}H_{44}O_3$: C, 77.83; H, 10.65. Found: C, 77.91; H, 10.53) was isolated. It was identical in all respects [derivative (acetate), m.p., mixture m.p., infrared spectrum[5]] with an authentic specimen. The major product is the isomeric 5α-22,25-epoxyfurostan-3β-ol, Ia, m.p. 178–180°, [α]D −58° (chf); (*Anal.* Calcd. for $C_{27}H_{44}O_3$: C, 77.83; H, 10.65. Found: C, 77.85; H, 11.00). Acetylation of Ia leads to the acetate, Ib, m.p. 198–201°, (*Anal.* Calcd. for $C_{29}H_{46}O_4$: C, 75.94; H, 10.11. Found: C, 75.70; H, 9.89).

In an analogous manner diosgenin (8–10%)[6] (m.p. 204–206°, [α] −125.4° (chf) *Anal.* Calcd. for $C_{27}H_{42}O_3$: C, 78.21; H, 10.21. Found: C, 78.52; H, 10.24) was obtained from N-nitrososolasodine.[7] Its properties were in agreement with an authentic sample of diosgenin. The major component in this mixture is 22,25-epoxyfurost-5-en-3β-ol[8] (IIa), m.p. 242–246°, [α]D −110.6° (chf); (*Anal.* Calcd. for $C_{27}H_{42}O_3$: C, 78.21; H, 10.21. Found: C, 78.28; H, 10.25). The acetate (IIb), m.p. 192–195°, (*Anal.* Calcd. for $C_{29}H_{44}O_4$: C, 76.27; H, 9.71. Found: C, 75.91; H, 9.54), was prepared in the usual manner.



Ia, R = H
Ib, R = Ac
IIa, (Δ^5), R = H
IIb, (Δ^5), R = Ac
IIIa, R = OH, R' = H
IIIb, R = OAc, R' = H
IIIc, R = OAc, R' = Ac
IIId, R = O=, R' = H
IV

The mild catalytic reduction (platinum–acetic acid–methanol) of IIa yields the dihydro derivative, m.p. 178–180°, whose properties as well as those of its acetate (m.p. infrared spectrum, X-ray powder diagram[8]) were identical with Ia and its acetate obtained from tomatidine. Assuming an identical mechanism for the deamination process, this conversion of IIa into Ia strongly supports the view that the same spatial arrangement exists at C-22 in tomatidine and solasodine.

The structures of Ia as well as IIa were established by the following series of reactions:

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[1] We are indebted to Dr. C. L. Ruiz of Drogaco Industria Quimica S.A. for the exceedingly generous gift of tomatine.

[2] Y. Sato, A. Katz and E. Mosettig, THIS JOURNAL, **74**, 538 (1952). The tomatidine for its preparation was purified through its hydrochloride by thoroughly washing the hydrochloride with dry ether and chromatographing the liberated aglycone. Dr. K. Schreiber of Forschungsstelle für Kartoffel Käfer-Bekämpfung, Mühlhausen, Germany, has informed us that he has isolated a small amount of neotigogenin from crude tomatidine.

[3] All melting points are uncorrected and were taken on the Kofler block.

[4] Microanalyses are from the Institutes' service analytical laboratory under the direction of Dr. W. C. Alford.

[5] Infrared spectra were determined on a Perkin-Elmer double beam spectrophotometer by Mr. H. K. Miller of this laboratory.

[6] L. H. Briggs and T. O'Shea, *J. Chem. Soc.*, 1654 (1952). In an addendum to the above article, Briggs and O'Shea announced the isolation of diosgenin from N-nitrososolasodine in small amounts. Subsequently (THIS JOURNAL, **75**, 6067 (1953)) we isolated small amounts of diosgenin from crude solasodine.

[7] Solasodine was purified in the same manner as tomatidine.

[8] We are indebted to Mr. F. A. Hildebrand, National Geological Survey, Washington, D. C., for this determination.

Hydrogenolysis (platinum) of Ia in acetic acid–ethanol gives 5α-furostan-3β,25-diol (IIIa); m.p. 167–170°; $[\alpha]$ 0° (chf); $\lambda_{\max}^{\text{chf}}$ 2.78, 2.97 μ (hydroxyl), (*Anal.* Calcd. for $C_{27}H_{46}O_3$: C, 77.46; H, 11.08; Found: C, 77.60; H, 11.05) with the consumption of 1 mole of hydrogen while the reduction of IIa leads to the same product, IIIa, with the uptake of 2 moles of hydrogen. Acetylation of IIIa at room temperature yields the monoacetate, IIIb, m.p. 60–62°, $\lambda_{\max}^{\text{chf}}$ 2.77, 2.95 μ (hydroxyl); 5.78 μ (acetate) (*Anal.* Calcd. for $C_{29}H_{48}O_4$: C, 75.60; H, 10.50. Found: C, 75.52; H, 10.69) whereas vigorous acetylation affords the diacetate, IIIc, m.p. 110–112°, $\lambda_{\max}^{CS_2}$ no hydroxyl, 5.75, 8.0 μ (acetate); (*Anal.* Calcd. for $C_{31}H_{50}O_5$: C, 74.06; H, 10.03. Found: C, 73.82; H, 10.03). Oxidation with Kiliani reagent[9] in acetone produces the 3-dehydro derivative, IIId, 5α-furostan-3-one-25-ol, m.p. 139.5–141.5° $\lambda_{\max}^{\text{chf}}$ 2.96 μ (hydroxyl); 5.84 μ (ketone); (*Anal.* Calcd. for $C_{27}H_{44}O_3$: C, 77.83; H, 10.65. Found: C, 77.82; H, 10.75). Finally the dehydration of IIIb with phosphorus oxychloride in pyridine and subsequent alkaline hydrolysis yielded some 16,22-epoxycholest-25-en-3β-ol (IV), m.p. 136–139°; (*Anal.* Calcd. for $C_{27}H_{44}O_2$: C, 80.94; H, 11.07. Found: C, 80.91; H, 11.03) identified by direct comparison with an authentic specimen.[10]

[9] H. Kiliani, *Ber.*, **46**, 676 (1913).

[10] Y. Sato, H. G. Latham, Jr., and I. Scheer, *J. Org. Chem.*, **21**, 689 (1956).

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THE DIRECT INTRODUCTION OF THE DIAZONIUM GROUP INTO AROMATIC NUCLEI. III.[1] N_2O_3–BF_3 COMPLEX AS REAGENT

Sir:

It has been shown that a variety of reagents of the type NO·X will react with aromatic nuclei to yield the corresponding diazonium salt.[2] It would be expected therefore that the recently reported N_2O_3–BF_3 complex,[3] which has been shown to be essentially NO^+–$BF_3NO_2^-$ would also yield diazonium salts from reactive aromatic compounds. This expectation has been realized.

Mesitylene (1 cc.) was treated with N_2O_3–BF_3[3] (0.58 g.) in nitrobenzene (5 cc.) for fourteen hours at room temperature. The reaction mixture was poured into cold dilute nitrous acid. The nitrobenzene was removed by solvent extraction, the aqueous residue neutralized, and the diazonium salt coupled with β-naphthol. The crude 2,4,6-trimethylphenyl-azo-β-naphthol (0.13 g., m.p. 124–126°) was isolated by filtration and recrystallization from acetone gave red needles m.p. 131° alone or in admixture with authentic material (lit. value m.p. 132°[4]). Anisole (1 cc.) was treated with N_2O_3–BF_3 (0.81 g.) in nitrobenzene (10 cc.) for two and a half hours at room temperature. Preparation of the azo-dye as above yielded crude *p*-methoxyphenyl-azo-β-naphthol (0.25 g., m.p. 132–134°), which recrystallized from acetone to give red needles m.p. 140° alone or in admixture with authentic dye (lit. value 140–141°[5]). In three experiments toluene (1 cc.) was treated with N_2O_3–BF_3 (0.63 g.) in nitrobenzene, (a) at room temperature for seven days, (b) at 55° for fourteen hours, and (c) at 55° for eighty-five hours. In (a) almost all the N_2O_3–BF_3 complex remained unreacted, rather more had dissolved in (b), while in (c) the majority had been consumed. Each of these experiments gave some dye but the crude yields were less than 10 mg.

The significance of these results lies not only in the discovery of another reagent capable of introducing a diazonium group into aromatic nuclei. Both nitration and formation of diazonium salts by this reagent almost certainly proceed through initial nitrosation by NO^+. The most abnormal proportions of *ortho* and *para*-nitrotoluenes obtained by the nitration of toluene with this reagent,[3] probably are due to differences in the rates of subsequent reactions and not to abnormal electrophilic substitution as was suggested.

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[1] Part II, J. M. Tedder and G. Theaker, *J. Chem. Soc.*, 4008 (1957).

[2] J. M. Tedder, *Tetrahedron*, I, 270 (1957); *J. Chem. Soc.*, 4003 (1957).

[3] G. B. Bachman and T. Hokama, THIS JOURNAL, **79**, 4370 (1957).

[4] E. J. Bourne, M. Stacey, J. C. Tatlow and J. M. Tedder, *J. Chem. Soc.*, 1695 (1952).

[5] L. Koch, R. F. Milligan and S. Zuckerman, *Ind. Eng. Chem., Anal. Ed.*, **16**, 755 (1944).