Hydrogenolysis (platinum) of Ia in acetic acid–ethanol gives 5α-furostan-3β,25-diol (IIIa); m.p. 167–170°; [α] 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°, $\lambda_{\max}^{\text{CS}_2}$ 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).