143–145° (lit.,[3] m. p. 146–147°) and was readily converted by copper chromite reduction to quinolizidine which was identified as before.

Details of the synthesis of quinolizidine and various derivatives will be reported in a subsequent publication.

[3] Ochiai, Tsuda and Yokoyama, *Ber.*, **68**, 2291 (1935).

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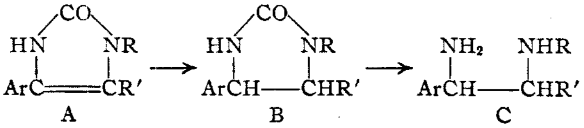
DIAMINES. I. THE SYNTHESIS OF AMINO ANALOGS OF ADRENALINE, ARTERENOL AND EPHEDRINE

Sir:

Diamines C (R and R′ = H or CH_3) wherein the alcoholic hydroxy group of arylalkanolamines, such as adrenaline, arterenol and ephedrine, is replaced by an amino group (III, IV and V) have attracted interest,[1] but only I[2] and II[3] have been described adequately. Recently Funke and Bovet reported that a group of diamines including I and IV are sympathomimetics.[4] Methods of preparation, physical and chemical properties of the new diamines were not reported.

Prior to that, we had investigated numerous α,β-diamines. Thus, α-aminoketones ArCOCH(NHR)R′ were cyclized to imidazolones (A) which, due to labilization of the double bond by aryl,[5] could be selectively hydrogenated to imidazolidones (B). Hydrolysis (for the adrenaline analog after protective benzylation) afforded C.



I, Ar = Ph; R = R′ = H.—II, Ar = Ph; R = H; R′ = CH_3.—III, Ar = 3,4-$(HO)_2C_6H_3$; R = CH_3; R′ = H.—IV, Ar = 3,4-$(HO)_2C_6H_3$; R = R′ = H.—V, Ar = Ph; R = R′ = CH_3.

Refluxing adrenalone hydrochloride with 2 moles of potassium cyanate in water and neutralizing with hydrochloric acid gave almost 100% of A (III), m. p. 276–277° (*Anal.* Calcd. for $C_{10}H_{10}O_3N_2$: C, 58.25; H, 4.89. Found: C, 58.14; H, 5.02). Hydrogenation in acetic acid with palladium charcoal at 3 atm. pressure yielded almost 100% of B (III), m. p. 167–169° (*Anal.* Calcd. for $C_{10}H_{12}O_3N_2$: C, 57.68; H, 5.81. Found: C, 57.85; H, 5.93). Benzylation[6] of B (III) gave 90% of 1-methyl-4-(3,4-dibenzyloxyphenyl)-2-imidazolidone, m. p. 128–130° (*Anal.* Calcd. for $C_{24}H_{24}O_3N_2$: C, 74.20; H, 6.23. Found: C, 74.54; H, 6.39). This compound was heated for forty-eight hours at 120° with *ca.* 4 *N* aqueous ethanolic sodium hydroxide. After extraction with ether, 72% of 3,4-dibenzyloxyphenyl-N^2-methyl-ethylenediamine was isolated as dihydrochloride, m. p. 184–185° (*Anal.* Calcd. for $C_{23}H_{26}O_2N_2 \cdot 2HCl$: C, 63.44; H, 6.48. Found: C, 63.68; H, 6.46). The latter, by palladium catalyzed hydrogenation, gave 91% of 3,4-dihydroxyphenyl-N^2-methyl-ethylenediamine dihydrochloride (C III), m. p. 202–203° (*Anal.* Calcd. for $C_9H_{14}O_2N_2 \cdot 2HCl$: C, 42.36; H, 6.32. Found: C, 42.55; H, 6.49).

The dihydrochlorides of C (IV), m. p. *ca.* 245° (dec.) (*Anal.* Calcd. for $C_8H_{12}O_2N_2 \cdot 2HCl$: C, 39.85; H, 5.85. Found: C, 40.09; H, 5.71), and of C (V), m. p. *ca.* 249° (dec.) (*Anal.* Calcd. for $C_{10}H_{16}N_2 \cdot 2HCl$: C, 50.64; H, 7.65. Found: C, 50.69; H, 7.82) were obtained from B (IV) and B (V) by acid hydrolysis.

Diamines of type C are sympathomimetics of relatively low toxicity. When administered intravenously in dogs and cats III and IV showed one-tenth of the pressor activity of adrenaline, I only 1/900. IV is therefore more potent than it appears from published data.[4] As a bronchodilator III was ten times stronger than IV.

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[1] Review by Hartung, *Ind. Eng. Chem.*, **37**, 128 (1945).

[2] Feist and Arnstein, *Ber.*, **28**, 425, 3172 (1895).

[3] Jaeger and van Dijk, *Proc. Acad. Sci. Amsterdam*, **44**, 26 (1941).

[4] Funke and Bovet, *Compt. rend. soc. biol.*, **141**, 327 (1947). I and IV appear to have equal pressor activity.

[5] *Cf.* Duschinsky and Dolan, THIS JOURNAL, **67**, 2079 (1945); "E. C. Barell-Jubilee Volume," Basle, 1946, p. 164.

[6] *Cf.* Suter and Ruddy, THIS JOURNAL, **66**, 747 (1944).

RAMAN SPECTRUM AND NORMAL MODES OF VIBRATION OF BUTADIENE-1,2[1]

Sir:

We have recently redetermined the Raman spectrum of butadiene-1,2 in an effort to improve the assignment of the normal modes of vibration. A very pure sample of butadiene-1,2 was obtained from the Cryogenic Laboratory of this College. This sample is identical with the one used in obtaining the thermodynamic properties of this molecule.[2] The Raman spectrum was obtained in two different spectrographs,[3,4] up to 2000 $cm.^{-1}$ shifts. The spectrum obtained generally agrees with the previous one of Bourguel and Piaux[5]; there were, however, a few important differences, which warrant a reassignment. The polarizations of the strong lines were also obtained and were useful guides in making the new assignment.

The following assignment has been made for the normal modes of vibration of butadiene-1,2.

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[1] The work described in this communication was carried out under Contract N60nr-269 Task Order V between the office of Naval Research and the Pennsylvania State College.

[2] Aston and Szasz, THIS JOURNAL, **69**, 3108 (1947).

[3] Rank and Wiegand, *J. Opt. Soc. Am.*, **36**, 325 (1946).

[4] Rank, Scott and Fenske, *Ind. Eng. Chem.*, *Anal. Ed.*, **14**, 816 (1942).

[5] Bourguel and Piaux, *Bull. soc. chim.*, **51**, 1041 (1932).