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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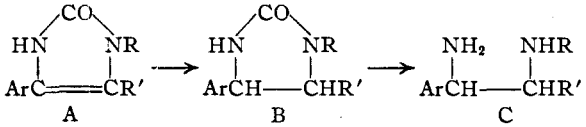
RECEIVED NOVEMBER 14, 1947

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.



A B 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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RECEIVED NOVEMBER 18, 1947

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.

(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).

(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).

	Symmetry class[7]	Frequency	Intensity	Polarization
C—C stretching	A′	876	10	0.11
C=C stretching	A′	1072	7	0.37
	A′	1961	0.2	
Skeleton angle change in plane	A′	210	10 (broad)	
	A′	555	5	0.24
Skeleton angle change out of plane	A″	322	0.9	
$=CH_2$ torsion	A″	523	0.5	
CH_3 internal angle change	A′	1374	5	
	A′	1439	1	
	A″	1462	5	0.88
CH_2 internal angle change	A′	1391[6]		
CH_2 wagging (rocking)	A″	1003	0.2	
	A′	1132	10	0.40
CH_2 wagging (rocking)	A′	858[6]		
	A″	1102	5	dp
CH bending	A″	842	3	
	A′	1327	2	0.26
CH stretching		2870 2910 2931		
		2954 2993 3061		

This assignment leads to the following improved agreement between the calculated and experimental entropies:

T, °K.	230	250	273.25	290
S^0 Calculated	65.26	66.65	68.21	69.45
S^0 Experimental[2]	64.87 ± 0.30	66.58 ± 0.17	68.40 ± 0.14	69.39 ± 0.18

These calculated entropies were obtained using a value of 1900 cal./mole for the potential barrier hindering the rotation of the methyl group—in fair agreement with a value predicted from other considerations.[2]

We wish to thank Dr. N. Sheppard for helpful discussions.

(6) Lines observed in the infrared spectrum only. Infrared data obtained from American Petroleum Institute Research Project 44. Catalog of Infrared Spectrograms, Serial No. 41.

(7) Notation according to Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., New York, N. Y., 1945, p. 105.

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RECEIVED SEPTEMBER 26, 1947

PAPER CHROMATOGRAPHY APPLIED TO THE ISOTOPIC DERIVATIVE METHOD OF ANALYSIS

Sir:

We have described a method of analysis of amino acids in the form of isotopic, *p*-I^{131}-phenyl sulfonyl (pipsyl), derivatives.[1] The estimation of these derivatives using paper chromatography is reported here.

One mg. of amino acids in 0.6 ml. of 0.3 *M* sodium bicarbonate was shaken at 100° with 9 mg. of I^{131}-pipsyl chloride. After acidification, derivatives were extracted with ether, the aqueous layer evaporated, sodium bicarbonate added, and the procedure repeated twice. Residual *p*-iodophenylsulfonic acid was removed from the ether by appropriate extractions. The ether was evaporated, the residue dissolved in 0.5 ml. of ammoniacal alcohol, and an aliquot, equivalent to 1–7 micrograms of protein placed as a transverse line on Whatman No. 1 paper, 2 × 57 cm. The chromatogram was developed with *n*-pentanol saturated with 2 *N* ammonia.

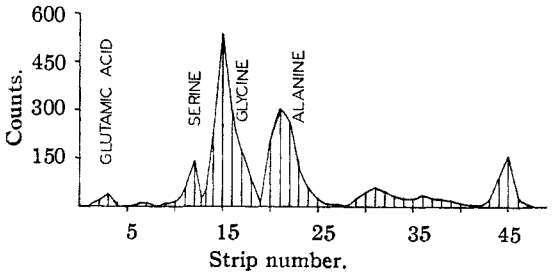

Fig. 1.

The diagram shows counts of successive 5-mm. strips of a chromatogram prepared from a mixture simulating silk hydrolysates. Total counts in a resolved band divided by C_r, counts per mole of isotopic reagent, gives equivalents of amino acid. Recoveries were: glutamic acid 104%, serine 91%, glycine 100%, alanine 100%. The ostensible pipsylglycine was eluted and identified by adding pipsylglycine carrier and demonstrating unchanged isotope concentration after purification. Analyses indicated 41% of silk nitrogen in glycine.

Estimations may be made independent of complete resolution of bands by adding indicators (either unlabelled derivative or derivative labelled with a second isotope) before chromatography.

(1) Keston, Udenfriend and Cannan, THIS JOURNAL, 68, 1390 (1946).