continuous nature of the discharge, may account for the increased rate of production of diboron tetrachloride in a d.c. arc.

Work is in progress to increase the yield still further, and an investigation of electrode materials other than mercury is planned.

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RECEIVED JULY 14, 1958

THE ACTION OF POTASSIUM AMIDE IN AMMONIA ON *o*-CHLOROPHENYLACETONE: CORRECTION.[1]

Sir:

We recently reported a new principle of ring closure, the essence of which is the intramolecular addition of a nucleophilic center to a benzyne structure.[2]

Amongst examples of the new principle, the conversion of *o*-chlorophenylacetone to indan-2-one, through the action of potassium amide in liquid ammonia, was described. We have now discovered an error: the compound reported as indan-2-one (m.p. 60–61°)[3] is actually 2-methylindole (m.p. 62°).[4] The compound obtained, in 25% yield in recent experiments, strongly depresses the mixed melting point with authentic indan-2-one, but does not alter the mixed melting point with authentic 2-methylindole. Also, the compound gives a positive sodium fusion test for nitrogen. All our efforts to isolate authentic indan-2-one from the reaction in question have been fruitless.

It is of theoretical interest that 2-methylindole is formed in this reaction; the matter will be discussed in a future publication.

(1) Research supported in part by the Office of Ordnance Research, U. S. Army.

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RECEIVED AUGUST 4, 1958

1,2;5,6-DI-*O*-ISOPROPYLIDENE 3-DEOXY-3-AMINO-α-D-ALLOSE

Sir:

Hydrolysis of the new antibiotic kanamycin has been found[1] to yield 3-deoxy-3-amino-D-glucose (I).[2]

The crystalline amine which is formed[3] on the aminolysis of 1,2;5,6-di-*O*-isopropylidene α-D-glucofuranose tosylate (II) has been characterized[2,3] as 1,2;5,6-di-*O*-isopropylidene-3-deoxy-3-amino-α-D-glucose. These reactions therefore appear to provide a convenient route for the preparation of I.

This communication is to report that, as suspected by Cope and Shen,[4] the aminolysis actually proceeds with inversion of carbon-3 to form 1,2,5,6-di-*O*-isopropylidene-3-deoxy-3-amino-D-allose (III).

Compound III can be prepared in 83% yield by hydrogenolysis of the 1,2;5,6-di-*O*-isopropylidene-3-deoxy-3-hydrazino-D-hexose (IV) of Freudenberg and Brauns[5] in ethanol at 80° using Raney nickel catalyst and 40 p.s.i. of hydrogen. The advantage of this route is that, whereas the aminolysis of II proceeds in 16% yield,[3] the hydrazinolysis proceeds in 60% yield.[5] Acid hydrolysis of III produced an aminosugar of different paper-chromatographic properties than that obtained on the hydrolysis of methyl 4,6-benzylidene-3-deoxy-3-amino-α-D-glucoside diacetate.[2]

The N-acetyl derivative of III (V), m.p. 127–128°, $[\alpha]_D$ +71.3° (*c*, 2 in chloroform), [calcd. for $C_{14}H_{23}O_6N$: C, 55.80; H, 7.69; N, 4.65. Found: C, 55.87; H, 7.73; N, 4.85.] was hydrolyzed for two hours at 100° in 0.2 *N* hydrochloric acid. N-Acetylation was then accomplished by the addition of acetic anhydride to the neutralized hydrolyzate. Evaporation of the solvent and extraction of the residue with ethanol gave a 1,2-*O*-isopropylidene-3-deoxy-3-acetamido-α-D-hexose (VI), m.p. 154–156°. Calcd. for $C_{11}H_{19}O_6N$: C, 50.56; H, 7.33; N, 5.36. Found: C, 50.25; H, 7.44; N, 5.29.

Periodate oxidation of VI, reduction of the product with sodium borohydride and acetylation of the reduced product gave a crystalline substance which was hydrolyzed to aminosugar using *N* hydrochloric acid at 100°. On evaporation, a crystalline product was isolated whose infrared spectrum (KBr disc) and X-ray powder diagram were identical to those obtained with an authentic sample of 3-deoxy-3-amino-D-ribose hydrochloride (VII).[6] These results establish the *allo*-configuration for III-VI and provide a new synthesis of VII which is a constituent of the antibiotic puromycin.[7]

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RECEIVED JULY 21, 1958

STRUCTURE OF THE Ag^+ (CYCLOÖCTATETRAENE) COMPLEX

Sir:

Complexes between metal ions and organic π bonding systems have been of interest for some time[1,2] and are germane to general discussions[3] of weak complexes and their reactivities.[1,2,4] Aside from the Ag^+ (Benzene) complex,[5,6] few such com-

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plexes have been subjected to complete structure determination, and hence we have carried out a study of Ag^+(Cycloöctatetraene)NO_3^- by the X-ray diffraction method. We anticipate a close relation between Ag^+(Olefin) complexes[1] and the ethylene-like Ag^+(COT) complex.[7]

The strongest bonding in the complex (Fig. 1) is between one Ag^+ and one COT; these Ag^+(COT) units are then joined more weakly into infinite

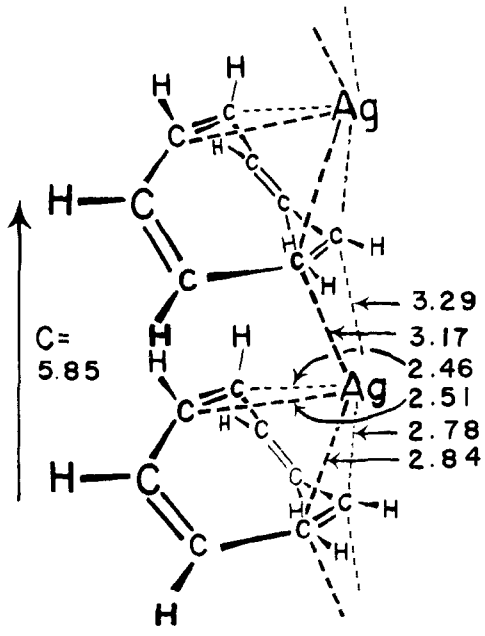

Fig. 1.—The Ag^+(COT) complex joined in infinite chains along the c axis; distances are in Å.

chains along the c axis of the crystal. The closest Ag. . .O distance to a NO_3^- is 2.43 Å., a value between the ionic and covalent sums of radii. The closest Ag. . .C distances of 2.5 Å., distinctly greater than the sum (2.3 Å.) of covalent radii, are sufficiently short that the bonding in COT may be perturbed. The COT molecule has the D_{2d} tub form, as expected from earlier studies,[8,9] and has average C=C = 1.37 and C—C = 1.46 distances, both ±0.04 Å. Corresponding distances are 1.31 and 1.46 (±0.01 Å.) in a refinement[10] of the COT crystal data, and 1.334 and 1.462 (optimistically ±0.001 Å.) in a recent electron diffraction study. Thus we claim plausibility, but not significance, for the increased C=C distance. In the infinite Ag^+(Benzene) complex[6] the average C—C distance is, however, 1.40 Å., essentially the same as in benzene itself. Ag. . .C distances[6] of 2.50 and 2.63 Å. in the Ag^+(Benzene) complex are comparable with those in Fig. 1 but indicate more distortion in the Ag^+(Benzene) complex.

The unit cell is monoclinic, the space group is $P2_1/a$ and there are four Ag^+(COT)NO_3^- in the cell. Parameters are a = 16.84, b = 8.94, c = 5.85 Å. and β = 91°7′. Values[11] of R = 0.113 and r = 0.056 for the 1136 observed reflections indicate that refinement is nearly complete.

We wish to thank Professor S. W. Fenton for suggesting this investigation, the Office of Naval Research for support, and the Minneapolis Honeywell Company for a fellowship to F.S.M.

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RECEIVED JULY 21, 1958

A NEW ADENOSINE DINUCLEOTIDE ISOLATED FROM MUSCLE EXTRACTS[1]

Sir:

A dinucleotide of adenosine (XAD) which has no color at *p*H 6 but which turns to green at *p*H 9 has been found in muscle. The adenine base was determined by its ultraviolet spectrum (values ϵ 280/ϵ260: *p*H 2, 0.368; *p*H 7, 0.122; reference values[2]: *p*H 2, 0.375; *p*H 7, 0.125) and by chromatography (Table I). The inference that the other base is a pteridine is supported by its blue fluorescence, ultraviolet spectrum and the indication that it contains 4 nitrogen per mole (calculated from the Am value worked out from the determination of phosphate and ribose). The spectral characteristics, composition and chromatographic behavior of XAD and its products of acid hydrolysis (mononucleotide (XRP), nucleoside (XR) and free pteridine (X)) are given in Fig. 1 and Table I.

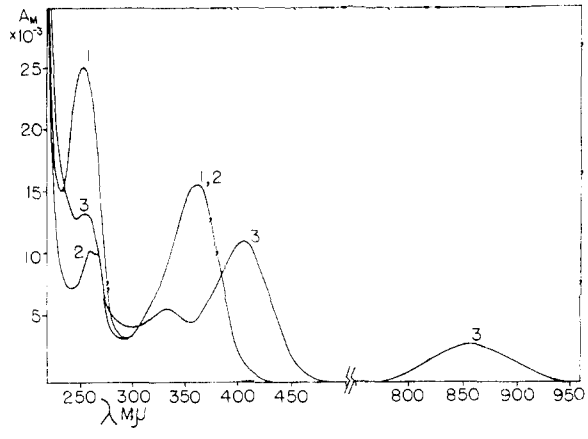

Fig. 1.—Absorption spectra of XAD and XRP: 1, spectrum of XAD at *p*H 2; 2, spectrum of XRP at *p*H 2; 3, spectrum of XRP at *p*H 12.

Adenine and the pteridine derivatives were isolated from the products of hydrolysis of XAD by electrophoresis (by this method adenine remains in the origin) and purified by chromatography with the solvents Iso and Eth. The spectrum of XRP at *p*H 2 shows a peak at 256 mμ (Am = 10.0 × 10^3) and another at 366 mμ (Am = 15.5 × 10^3). When

(1) Supported by research grants from the National Institute of Health, U. S. Public Health Service (Nos. A-1174 and H-1889).

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