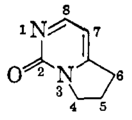
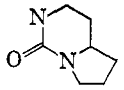
ten carbon atoms initially present in the molecule. Saxitoxin,[7] when heated with phosphorus and hydriodic acid in acetic acid, gave a 57% yield of the weakly basic compound I, $C_8H_{10}N_2O$ (m.p. 100–102°. *Anal.* Found: C, 63.6; H, 6.8; N, 18.7) which contained one C–CH_3 group but no O–CH_3 or N–CH_3 groups. On oxidation with potassium permanganate, urea and guanidinoacetic acid[8] were obtained. Hydrogenation of I in the presence of platinum oxide (200 mole % hydrogen absorption) gave II, $C_8H_{14}N_2O$ (m.p. 129–131°. *Anal.* Found: C, 62.8; H, 9.4; N, 17.9) which also contained one C–CH_3 group. Strong acid hydrolysis of II led to the strongly basic, extremely hygroscopic oily diamine III, $C_7H_{16}N_2$, and III on heating with palladium-on-carbon formed a substance which readily gave a positive Ehrlich test for pyrroles.

On the basis of these data, we assumed that III was a pyrrolidine and that II was a saturated cyclic urea, consistent also with its lack of ultraviolet absorption and its strong infrared absorption at 3410 and 1635 cm.$^{-1}$ in chloroform. That the cyclic urea was part of a six-membered ring was clear from the ultraviolet absorption of I with $\lambda_{\max}^{CH_3OH}$ 298 mμ (ε 6200), shifted to 305 mμ (ε 8900) on addition of acid. This is the same behavior observed for 1-methyl-2-pyrimidone [$\lambda_{\max}^{C_2H_5OH}$ 302 mμ (ε 5400), shifted in acid to 313 mμ (ε 7100)].[9] Therefore, I was considered to be a fused pyrrolidine-pyrimidone with one nitrogen common to both rings, and IV and V, containing the new pyrrolo[1,2-c]pyrimidine ring system, were adopted as working expressions for des-methyl I and des-methyl II, respectively.



IV



V

2-Oxo-2,4,5,6-tetrahydropyrrolo[1,2-c]pyrimidine (IV) was synthesized from 2-(2-aminoethyl)-pyrrole[10] by reduction to 2-(2-aminoethyl)-pyrrolidine (b.p. 39–41° (0.7 mm.)) *Anal.* Found: C, 63.2; H, 12.3; N, 24.7), and this was cyclized by heating with diethyl carbonate to V (m.p. 127–128°. *Anal.* Found: C, 60.0; H, 8.5; N, 19.8). Oxidation with potassium permanganate at room temperature gave IV (m.p. 126–127°. *Anal.* Found: C, 61.2; H, 5.9; N, 21.4). The ultraviolet absorption of IV [$\lambda_{\max}^{CH_3OH}$ 302 mμ (ε 6100), shifted in acid to 307 mμ (ε 7200)], was very similar to that of I, and in the infrared each compound had a broad band at 1660–1610 cm.$^{-1}$ which was split into two sharp peaks (1700, 1610 cm.$^{-1}$) in the hydrochloride. The nuclear magnetic resonance spectra[11] were practically identical except that IV had two aromatic proton peaks at τ 1.57 and 3.60 while I had only one at τ 3.73, indicating that position 8 was substituted by methyl which appeared as a singlet at τ 7.64.

To synthesize I, 2-aldehydopyrrole was condensed with nitroethane and the resulting 2-(2-methyl-2-nitrovinyl)-pyrrole (m.p. 82–83°. *Anal.* Found: C, 55.5; H, 5.4; N, 18.1) was reduced with lithium aluminum hydride to 2-(2-amino-1-propyl)-pyrrole (b.p. 68° (0.5 mm.), m.p. 30°. *Anal.* Found: C, 67.5; H, 10.0; N, 22.1). Catalytic hydrogenation gave 2-(2-amino-1-propyl)-pyrrolidine which, by heating with diethyl carbonate, was cyclized to 8-methyl-2-oxo-1,2,4,5,6,6a,7,8-octahydropyrrolo[1,2-c]pyrimidine (II), identical in infrared absorption with II derived from saxitoxin. Oxidation of synthetic II with permanganate at room temperature gave 8-methyl-2-oxo-2,4,5,6-tetrahydropyrrolo[1,2-c]pyrimidine (I), identical with I derived from saxitoxin in all respects (m.p., mixed m.p., ultraviolet, infrared, and nuclear magnetic resonance spectra; and R_f on paper).

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[7] Isolated from the siphons of toxic Alaska butter clams and supplied by Dr. T. C. Simmons of the Army Chemical Corps.

[8] C. J. West, *J. Biol. Chem.*, **34**, 187 (1918).

[9] D. J. Brown, E. Hoerger and S. F. Mason, *J. Chem. Soc.*, 211 (1955).

[10] W. Herz, *J. Am. Chem. Soc.*, **75**, 483 (1953).

[11] Taken in deuteriochloroform with tetramethylsilane as internal standard. We are grateful to Richard Moore for his assistance.

ADSORPTION ON INORGANIC MATERIALS. IV. CATION EXCHANGE PROPERTIES OF ZIRCONIUM ANTIMONATE[1,2]

Sir:

As first shown in previous papers[2,3] and since confirmed at a number of laboratories, dried (but hydrous) precipitates of Zr(IV) with polyvalent inorganic anions, such as phosphates, tungstates, molybdates, and arsenates have useful cation exchange properties including high uptakes of certain ions, reasonable exchange rates, and interesting selectivities. In a search for other inorganic materials which might exhibit unique cation exchange properties, the solid resulting from co-precipitation of Zr(IV) and Sb(V) was found particularly attractive. The material was obtained by mixing zirconium oxychloride solutions with excess of HCl solutions of antimony pentachloride, adding ammonia to decrease acidity and cause precipitation, filtering, washing, and drying at 25°. The material then was ground and screened for column use. Distribution coefficients, *D* (amount per kg. solid/amount per l. solution), were determined for a number of ions by batch equilibration experiments.

The material used in the experiments to be described had an Sb(V)/Zr(IV) ratio somewhat larger than 2 to 1, as established by radiometric analysis, and a water content of *ca.* 27%, as established by determination of weight loss on firing to 900°.

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[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory, operated by the Union Carbide Corporation, Oak Ridge, Tennessee.

[2] Previous paper: K. A. Kraus, H. O. Phillips, T. A. Carlson and J. S. Johnson, "Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy," United Nations, Geneva, 1958, Volume 28, p. 3.

[3] K. A. Kraus and H. O. Phillips, *J. Am. Chem. Soc.*, **78**, 694 (1956).

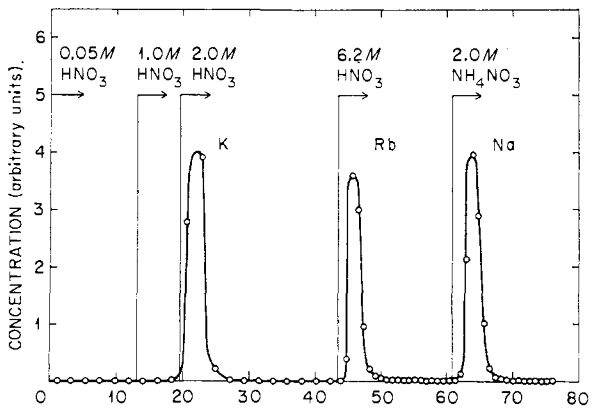

Fig. 1.—Separation of alkali metals with hydrous zirconium antimonate: (80–170 mesh, drying temp. 25°, 2.6 cm. × 0.19 cm.^{2} column.

However, it is believed that neither the Sb(V)/Zr(IV) ratio nor the water content are particularly critical. The material is reasonably stable in concentrated and dilute HNO_3 and NH_3, and it is not appreciably attacked by H_2SO_4, HCl, and NaOH up to concentrations of about 2 M. Cs^+ uptake by the solid was approximately 0.5 mole/kg. from 0.05 M $CsNO_3$ at pH 3; total Na^+ uptake by the exchanger originally in the H^+-form was about 5 moles/kg. from 0.9 M NaOH.

Some preliminary rate studies with alkali metals indicate that the material behaves comparably to other inorganic ion exchangers of this type prepared at this laboratory. The ideality of the exchange reaction was checked for the Rb^+ (tracer)–H^+ system in the range 0.2 to 2.0 M HNO_3; log D for Rb^+ was a linear function of log M HNO_3 with a slope of approximately -1 as expected.

The zirconium antimonate showed unusual selectivities for the alkali metals, alkaline earths and the rare earths compared with zirconium phosphate, zirconium tungstate, and zirconium molybdate. Distribution coefficients in 1 M HNO_3 were >100 for some alkaline earths (Ca, Sr) and rare earths. Ba(II) has a D of approximately 12 in the same medium. In contrast, the distribution coefficients for the same elements in the same medium are <1 for the zirconium phosphate. The alkali metals showed a unique order of selectivity; instead of following the order of atomic numbers, as is commonly observed, Na^+ was more strongly adsorbed than either K^+ or Rb^+, while Rb^+ is more strongly adsorbed than K^+. Differences in selectivity are large and separations can be made with small columns as indicated in Fig. 1. In this experiment, K^+ was removed by 1 M HNO_3, ahead of Rb^+ which was removed by 6.2 M HNO_3. Both ions were removed ahead of Na^+, which cannot be removed even by concentrated HNO_3, but was eluted readily by 2 M NH_4NO_3. Li^+ and Cs^+, if they had been present in the mixture, would have been eluted by <0.1 M and 6 M HNO_3, respectively.

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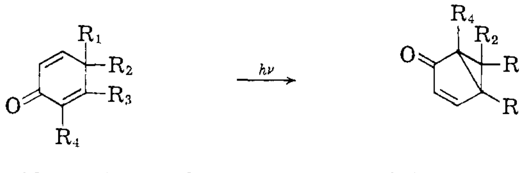
PHOTOISOMERIZATION OF Δ^4-CHOLESTEN-3-ONE[1]

Sir:

The number of dienones observed to undergo light-induced rearrangement of the santonin → lumisantonin type is sufficient to permit classification of the reaction as general.[2-4] It is stereospecific and therefore almost certainly concerted.



The obvious similarity of this reaction (excited state) to the Wagner–Meerwein rearrangement (ground state) prompted the study of unsaturated carbonyl compounds possessing less extensive pi-electron systems.

Irradiation of a 0.5% solution of Δ^4-cholesten-3-one (I) in *tert*-butyl alcohol with ultraviolet light[5] to 75% disappearance of the 240 mμ band afforded 25% of a photoisomer, *lumicholestenone* (II), m.p. 165–166°, $[\alpha]^{25}D$ $+70°$.[6] A small amount of the reported photodimer[7] also was obtained; it was removed by filtration before the isolation of II. The diminished rate of formation of this dimer is presumed to result from the use of more dilute solutions. No crystalline material other than I, II and dimer could be isolated. It is assigned formulation II on the basis of the following evidence. Its infrared spectrum possesses a sharp, weak spike at 3021 cm.$^{-1}$ (cyclopropane C–H stretching[8]) and a stronger peak at 1714 cm.$^{-1}$ (bicyclo[3.1.0]-hexan-2-one carbonyl stretching[9]). The ultraviolet spectrum has maxima at 212 mμ (ϵ 7,900), characteristic of a ketone carbonyl adjacent to a cyclopropane ring,[10] and at 285 mμ (ϵ 69). The lone proton on the cyclopropane ring gives rise to an unsplit peak at 8.5τ in the n.m.r. spectrum. This spectrum also shows the 19-Me peak at 0.16τ lower field than its position in the spectrum of cholestan-3-one. The rotatory dispersion curve[11] of II exhibits a strong positive Cotton effect with

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(1) Supported by the National Institutes of Health (Grant RG-7861).

(2) K. Weinberg, E. C. Utzinger, D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **43**, 236 (1960), and references cited therein.

(3) D. H. R. Barton, J. McGhie and M. Rosenberger, *J. Chem. Soc.*, 1215 (1961), and references cited therein.

(4) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961).

(5) All experiments were conducted with a filter of Pyrex glass at least 2 mm. in thickness. A yield of *ca.* 25% was obtained using sunlight (30 days), a 200-w. Hanovia mercury vapor lamp (170 hours) or a 1000-w. General Electric vapor lamp (24 hours). The product was isolated by chromatography on alumina.

(6) Satisfactory analytical data were obtained for all substances described. Solutions for rotation and infrared measurements were prepared in chloroform. Ultraviolet spectra were obtained using 95% ethanol.

(7) A. Butenandt, L. Poschmann, G. Failer, U. Schiedt and E. Biekert, *Ann.*, **575**, 123 (1951).

(8) H. T. Hoffman, Jr., G. E. Evans and G. Glockler, *J. Am. Chem. Soc.*, **73**, 3028 (1951).

(9) D. H. R. Barton, P. de Mayo and M. Shafiq, *J. Chem. Soc.*, 140 (1958).

(10) R. H. Eastman, *J. Am. Chem. Soc.*, **76**, 4115 (1954).

(11) We are indebted to Professor W. Klyne, The University of London, for obtaining and interpreting all of the rotatory dispersion data described. Methanol was the solvent.