methanol medium to yield a complex in high yield, identical with purified C by melting point, mixed melting point, elemental analysis, and X-ray diffraction comparison. Attempts to form complexes of the type $C_4H_7NO \cdot HBr \cdot Br_2$ and $(C_4H_7NO)_2 \cdot HBr \cdot Br_2$ led only to the formation of unstable oils and small amounts of C.

The fact that *stability* occurs only when the ratio of available bromine to bromide equals 2, and that there are *three* molecules of pyrrolidone-2, points to the possibilities that (1) Br_3^- species are formed and (2) they interact with the pyrrolidone molecules to form a unified complex, rather than a physical mixture of A and B as supposed by Tafel and Wassmuth.

A change in the structure of the lactam confers a different requirement for stability upon the complexes. For example, N-methylpyrrolidone-2[8] and 3-morpholinone gave stable complexes with hydrogen bromide and bromine *only* when the reacting ratios were lactam:-HBr:Br_2 (2:1:1).

Experimental

All melting points are uncorrected. Available bromine was determined iodimetrically. Total bromine was determined by sodium fusion and subsequent Volhard analyses for bromide ion. Bromide was determined by difference.

A. Direct Preparation of Stable Complex.—A solution of 1200 g. (14.1 moles) of pyrrolidone-2 and 700 ml. of chloroform was heated to 60° and addition of 1105 g. (6.9 moles) of bromine was begun. The addition required 2 hr., maintaining the reaction temperature between 60 and 70° by intermittent cooling with ice–water. The reaction mixture was then cooled to 20° and the bright orange crystals which formed were collected on a sintered glass funnel and then dried to constant weight *in vacuo* over solid potassium hydroxide. There was obtained 1498 g. of product with a melting range of 74–78° and an available bromine content of 30.9%. Five months later a sample of this complex still contained 29.8% available bromine.

Careful recrystallization of this product from chloroform yielded product of melting point 88.5–90.5°. Elemental analysis yielded the empirical formula $(C_4H_7NO)_3 \cdot HBr \cdot Br_2$.

Anal. Calcd. for $C_{12}H_{22}N_3O_3Br_3$: C, 28.93; H, 4.85; N, 8.45; Br total, 48.20; Br^-, 16.10; Br°, 32.20. Found: C, 29.29; H, 4.61; N, 8.65; Br total, 48.51; Br^-, 14.18; Br°, 31.61.

B. Preparation of Stable Complex from the Elements of Pyrrolidone-2. Hydrogen Bromide and Bromine.—In a 1-l. flask equipped with stirrer, thermometer, and a gas inlet tube was placed 500 ml. of methanol. This was cooled to 0° with stirring, and anhydrous hydrogen bromide introduced until 117 g. (1.44 moles) had been absorbed, keeping the temperature between −1 and +5°. To this solution was added dropwise over 0.5 hr. 74.0 ml. (1.44 moles) of bromine, keeping the temperature between −1 and 7°, followed by 337 ml. (4.32 moles) of pyrrolidone-2 at 1–11°.

A heavy red crystalline mass formed as the pyrrolidone was added. This was filtered off in a sintered-glass funnel and dried over solid potassium hydroxide at about 70 mm. vacuum. This crop weighed 611.9 g. of constant weight. Two more crops totalling 63.5 g. were obtained by chilling the filtrate to first −10°, and then −40°. All product fractions had a melting point of 87–89° and contained 31.2% available bromine. A sample was purified by recrystallization from methanol. It melted at 88.5–90.5°.

Anal. Calcd. for $C_{12}H_{22}N_3O_3Br_2[(C_4H_7NO)_3 \cdot HBr \cdot Br_2]$: C, 28.93; H, 4.85; N, 8.45; Br total, 48.20; Br^-, 16.10; Br°, 32.2. Found: C, 29.35; H, 4.55; N, 8.47; Br total, 48.71; Br^-, 15.95; Br°, 32.3.

This compound showed no decrease in free bromine content over a 5-month storage period at ambient temperatures.

A mixed melting point with a sample of purified complex prepared in section A was undepressed. An X-ray diffraction comparison of the two products showed them to be identical.

C. N-Methylpyrrolidone-2 Complex with Hydrogen Bromide and Bromine.—Anhydrous hydrogen bromide was passed into a Dreschel bottle containing 75 ml. of methanol cooled to 0° until 40.5 g. (0.5 mole) was absorbed. To this was added 26.0 ml. (0.5 mole) of bromine. This was then transferred to a 600 ml. beaker and cooled in an ice bath. Addition of 99 ml. (1.0 mole) of N-methylpyrrolidone was begun. The resulting mixture rapidly deposited orange crystals. It was necessary to add 225 ml. of methanol to complete the addition. The final product was recrystallized from methanol to yield 191.6 g. of orange translucent crystals m.p. 122–124°. This represents a yield of 87.0% based on the formula $(C_5H_{10}NO)_2 \cdot HBr \cdot Br_2$.

Anal. Calcd. for $(C_5H_{10}NO)_2 \cdot HBr \cdot Br_2$: C, 27.3; H, 4.1; Br total, 54.9; Br°, 36.4. Found: C, 27.4; H, 4.5; Br total, 54.6; Br°, 36.3.

D. 3-Morpholinone Complex of Hydrogen Bromide and Bromine.—A solution of 40.5 g. anhydrous hydrogen bromide (0.5 mole) and 26.0 ml. bromine (0.5 mole) in 75 ml. of methanol at 0° was added to a solution of 101 g. (1.0 mole) of 3-morpholinone in 1.0 l. of methanol at 0°.

Long red-orange crystals formed immediately. These were filtered in a sintered glass funnel and dried to constant weight over a solid potassium hydroxide *in vacuo*. There were 121.5 g. of product obtained, m.p. 112–118°; available bromine content, 35.3%. Theoretical available bromine for $(C_4H_7NO_2)_2 \cdot HBR \cdot$-$Br_2$, 36.1%

Anal. Calcd. for $C_8H_{15}N_2O_4Br_3$: C, 21.7; H, 3.2; total bromine, 54.4. Found: C, 22.0; H, 3.7; total bromine, 53.7.

Acknowledgment.—The authors wish to thank the following persons of this laboratory: Mr. Louis Frauenfelder for elemental analyses, Mr. Robert Fredericks for X-ray comparisons, Mr. John Carberry for lactam distillations, and Mr. Walter Haney for experimental assistance in the preparation of the lactam complexes.

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[8] A bromine complex of this lactam was prepared by reacting the neat lactam with bromine by L. Smith and I. Merits, *Kgl. Fysiograf. Sallskap. Lund. Forh.*, **23**, 88 (1953); *Chem. Abstr.*, **49**, 1585a (1955). The yield was small.

Diels–Alder Addition to Pyrroles

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Received September 14, 1962

It has been reported[1] that N-benzylpyrrole reacts with acetylenedicarboxylic acid to give a Diels–Alder adduct. Recently[2,3] it was shown that N-methylpyrrole reacts with dimethyl acetylenedicarboxylate to yield products postulated as being formed *via* Diels–Alder addition intermediates. In the first work[1] it was suggested that the size of the group attached to the pyrrole nitrogen could affect the aromaticity of the system and accordingly make more or less feasible the occurrence of Diels–Alder type addition. This suggestion is unlikely in view of the more recent work. To show this, other pyrroles containing nitrogen substituents more bulky than benzyl were synthesized and their reactivity toward the Diels–Alder addition was investigated.

The N-substituted pyrroles were prepared by modifying the procedure of Clauson-Kass and Elmling.[4] This involves treating 2,5-diethoxytetrahydrofuran

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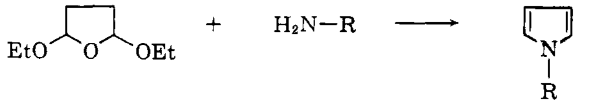
(1) L. Mandell and W. A. Blanchard, *J. Am. Chem. Soc.*, **79**, 6198 (1957).

(2) R. M. Acheson, A. R. Hands, and J. M. Vernon, *Proc. Chem. Soc.*, 164 (1961).

(3) R. M. Acheson and J. M. Vernon, *J. Chem. Soc.*, 1148 (1962).

(4) N. Clauson-Kass and N. Elmling, *Acta Chem. Scand.*, **6**, 867 (1952).

with the appropriate amine in acetic acid. By this means N-triphenylmethylpyrrole and N-(α-naphthylmethyl)pyrrole were synthesized.



It was found that N-(α-naphthylmethyl)pyrrole reacts with acetylenedicarboxylic acid to afford a 9% yield of the Diels–Alder adduct. This is about the same amount of Diels–Alder addition as in the case of N-benzylpyrrole. N-triphenylmethylpyrrole did not react with acetylenedicarboxylic acid.

From the above it is apparent that the hypothesis presented in the early work[1] is incorrect. Further, it would appear that the factor that allows isolation of the Diels–Alder adduct, in these cases, is the insolubility of the zwitter ion formed as a result of Diels–Alder addition. Thus the reaction stops when acetylenedicarboxylic acid is used, whereas with methyl acetylenedicarboxylate the reaction may proceed further as elucidated by the work of Acheson, *et al.*[2,3]

Experimental[5]

Triphenylmethylamine.—A slurry of 30 g. of chlorotriphenylmethane in 600 ml. of liquid ammonia under a Dry Ice condenser was stirred for 6 hr. The ammonia was allowed to evaporate overnight leaving a white crystalline residue. This was triturated with 500 ml. of ether and the ether supernatant washed with 10% sodium carbonate solution and thence water. After drying the ether solution over sodium sulfate, the ether was concentrated *in vacuo*. When about three quarters of the ether had been removed white crystals had formed and were filtered. The filtrate was evaporated to dryness and the residue recrystallized from ether. The total yield was 21.0 g (75.5%) of triphenylamine, m.p. 102–103.5°; reported[6] m.p. 103°.

N-Triphenylmethylpyrrole.—Five grams of triphenylmethylamine and 3.0 g. of 2,5-diethoxytetrahydrofuran were added to 40 ml. of cold glacial acetic acid. The mixture was allowed to stand in a refrigerator 2 weeks during which time crystals formed on the sides of the flask. The mixture was filtered and the solid recrystallized twice from benzene giving 2.6 g. (50%) of the pyrrole, m.p. 245–246°. The structure of the material was confirmed by comparison of its infrared and nuclear magnetic resonance spectra with those of N-benzyl- and N-methylpyrrole.

Anal. Calcd. for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 88.94; H, 6.26; N, 4.78.

Attempted Reaction of N-Triphenylmethylpyrrole with Acetylenedicarboxylic Acid.—A solution of 1.8 g. of N-triphenylmethylpyrrole and 0.67 g. of acetylenedicarboxylic acid in 20 ml. of dry ether was refluxed for 67 hr. The pyrrole was largely insoluble in the ether (0.1 g. per 20 ml. of ether). Filtration of the hot ether mixture gave 1.7 g. of solid, m.p. 242–245°, which was starting pyrrole.

α-Naphthylamine.[7]—In a 1-l. three-necked flask equipped with stirrer and reflux condenser, 28.0 g. of hexamethylenetetramine and 31.0 g. of sodium iodide were added to 320 ml. of hot 95% ethanol. To this solution 35.4 g. of 1-chloromethylnaphthalene was added. The mixture was kept warm (about 50°) and stirred for 3 hr., after which 80 ml. of conc. hydrochloric acid was added and 300 ml. of solvent distilled. The solution was concentrated further *in vacuo* until the residue solidified. This residue was slurried with 500 ml. of water, made alkaline with excess potassium hydroxide (70 g.), and extracted with five 100-ml. portions of ether. The ether was dried over sodium sulfate, concentrated under reduced pressure, and the residue distilled giving 23.5 g. (75%) of the amine, b.p. 95–100° (0.04 mm.); reported,[7] b.p. 200–205° (30 mm.).

N-(α-Naphthylmethyl)pyrrole.—In a 100-ml. flask 13.0 g. of α-naphthylmethylamine, 13.2 g. of diethoxytetrahydrofuran, and 20 ml. of glacial acetic acid were refluxed in the dark, under nitrogen, for 1 hr. The dark brown reaction mixture was diluted with 100 ml. of water and extracted with four 100-ml. portions of ether. The ether extract was washed with water, 10% sodium carbonate solution, and dried over sodium sulfate. Evaporation of the ether *in vacuo* gave a dark residue which solidified upon cooling. The residue was recrystallized several times from ethanol giving 7.8 g. (45.5%) of the pyrrole, m.p. 57–58°. It had an infrared spectrum almost identical with that of N-benzylpyrrole.

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.92; H, 6.33; N, 6.76. Found: C, 87.07; H, 6.12; N, 6.82.

Reaction of N-(α-Naphthylmethyl)pyrrole with Acetylenedicarboxylic Acid.—A solution of 10.0 g. of N-(α-naphthylmethyl)-pyrrole and 5.5 g. of acetylenedicarboxylic acid in 35 ml. of dry ether was refluxed 24 hr. during which time the solution darkened and a solid precipitated. The hot ether solution was filtered and the yellow residue (2.0 g. 12.9%) treated with charcoal and recrystallized from ethanol and water giving 1.4 g. (9%) of the Diels–Alder adduct, decomposition point, 194°. An infrared spectrum showed, among other absorptions, a band at 2.90 μ and a strong unresolved band between 6.10 and 6.90 μ, indicative of a zwitterion.

Anal. Calcd. for: $C_{19}H_{15}O_4N$: C, 71.02; H, 4.71; N, 4.36. Found: C, 70.77; H, 4.38; N, 4.32.

Facilitated Alkaline Hydrolysis of Diol Monoesters[1]

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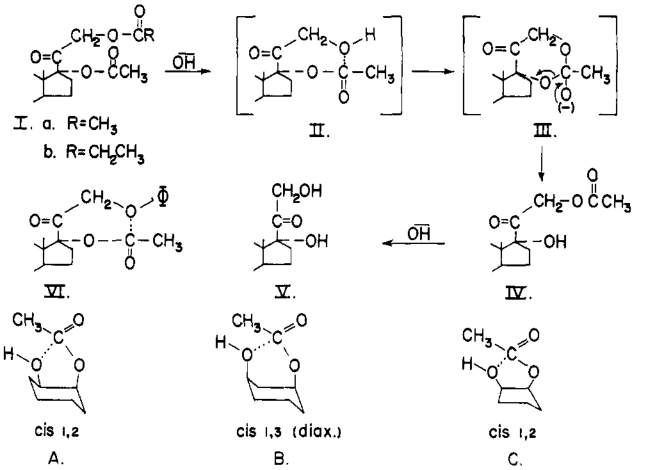
Received September 26, 1962

In 1956 H. J. R. noted[2] that 17,21-diacetate esters of steroids possessing the dihydroxyacetone side chain (Ia) undergo complete alkaline hydrolysis with remarkable ease[3] (1.15 equiv. methanolic potassium hy-



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(5) Melting points and boiling points are uncorrected. Analyses were performed by Drs. G. Weiler and F. B. Strauss, Oxford, England. Infrared spectra were determined with a Perkin-Elmer Model 21, double beam, infrared recording spectrophotometer.

(6) C. A. Kraus and R. Rosen, *J. Am. Chem. Soc.*, **47**, 2739 (1925).

(7) This is essentially a combination of the procedures of F. F. Blicke and C. E. Maxwell, *J. Am. Chem. Soc.*, **61**, 1780 (1939) and A. Galat and G. Elion, *ibid.*, **61**, 3585 (1939).

(1) This investigation was aided by grants A-4044 and CY 4550, National Institutes of Health.

(2) H. J. Ringold, G. Rosenkranz, and F. Sondheimer, *J. Am. Chem. Soc.*, **78**, 820 (1956).

(3) See also (a) Huang-Minlon, E. Wilson, N. L. Wendler, and M. Tishler, *ibid.*, **74**, 5394 (1952); (b) R. B. Turner, *ibid.*, **75**, 3489 (1953).