yields (40%) of addition to the ketone affording an intermediate suitable for use in elaborating the "isopentenyl" side chain of nootkatin. This reaction involved treating the ketone, II, with allyl bromide and zinc in a mixture of benzene and ether as solvent, to afford a mixture of the lactones III and IV.

This procedure and result is unique and we are reporting it because of its striking success in contrast to the more usual procedures tried for effecting addition to this particularly hindered ketone.

Experimental[3]

Reformatsky Addition to Isopropyl 2-Furyl ketone.—To 50 g. of zinc (previously washed with dilute hydrochloric acid, water, acetone, and dried) and a few crystals of iodine in 200 ml. of dry benzene and 200 ml. of dry ether were added 13.8 g. of isopropyl 2-furyl ketone[4] and 13.5 ml. of ethyl bromoacetate. The mixture was heated to reflux and five additions of 50 g. of zinc with a crystal of iodine were made at 4–5-min. intervals. The reaction was stirred throughout the additions.

The reaction was cooled, made homogeneous by adding glacial acetic acid and then decanted from the zinc into water. This mixture was acidified with acetic acid, the benzene layer separated, and the aqueous layer back extracted with ether. The combined organic layers were washed with dilute ammonia, water, dried over sodium sulfate, and distilled. This gave 21.2 g. (95%) of the Reformatsky product, V, b.p. 75–80°/.15 mm.

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 64.07; H, 8.20.

Diethyl β-Isopropyl-γ-keto Pimelate, II.—Ten grams of ethyl 3-furyl-3-isopropyl-3-hydroxypropionate, V, was dissolved in 50 ml. of 95% ethanol. Anhydrous hydrogen chloride from a compressed gas cylinder was passed into the reaction mixture until the reaction mixture heated to boiling. It was allowed to boil 15 min. with continued introduction of hydrogen chloride. This was repeated and the reaction mixture then allowed to stand overnight.

The reaction mixture was concentrated *in vacuo*, the residue taken up in chloroform, washed with dilute sodium carbonate solution, water, dried over sodium sulfate, and distilled. This gave 9.9 g. (82%) of II, b.p. 120°/0.40 mm.

Anal. Calcd. for $C_{14}H_{24}O_5$: C, 61.74; H, 8.88. Found: C, 62.05; H, 8.91.

Preparation of III and IV. Diethyl β-isopropyl-p-ketopimelate 11, (5.0 g.) was mixed with 4 ml. of allyl bromide, 30 ml. of dry ether, and 20 ml. of dry benzene. The reaction mixture was refluxed 18 hr. and catalyzed by periodic additions of iodine. In one run, a small magnesium shaving was found to aid initiating the reaction. At the end of this time, all the zinc had reacted and the solution was yellow in color.

The reaction mixture was hydrolyzed using ice and dilute sulfuric acid. The organic layer was separated and the aqueous layer extracted successively with three 25-ml. portions of ether. The combined extracts were dried over sodium sulfate and distillled giving 2.0 g. (40%) of a mixture of the lactones III and IV, b.p. 92–100°/1 mm. The infrared spectrum of this material showed among other absorptions bands at 5.60 μ (1785 cm.$^{-1}$) for the lactone carbonyl and 5.75 μ (1740 cm.$^{-1}$) for the ester carbonyl. The n.m.r. spectrum of this material showed a typical vinyl group multiplet and the relative area of the vinyl protons to the —CH_2- protons of the ethoxy grouping was 3:2.

Anal. Calcd. for $C_{15}H_{24}O_4$: C, 67.25; H, 8.95. Found: C, 67.40; H, 9.01.

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Lactam Complexes of Bromine–Hydrogen Bromide

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Tafel and Wassmuth discovered that a chloroform solution of pyrrolidone-2 yielded a brick red solid on treatment with bromine.[2] This solid had the over-all elemental composition $C_4H_7NO{\cdot}Br$, corresponding to an addition complex of one atom of bromine to one molecule of pyrrolidone-2. Evidence was presented that the material was actually a mixture of the addition compound A, $(C_4H_7NO)_2{\cdot}Br_2$, and the hydrobromide B, $C_4H_7NO{\cdot}HBr$, the hydrogen bromide arising by substitution to form N-bromopyrrolidone-2 and hydrogen bromide.

Products A and B were proposed to co-crystallize from solution as the red solid, while N-bromopyrrolidone-2 remained in solution.

Their complex was unstable, decreasing in available bromine content on recrystallization from 35 to 38% until, after many recrystallizations from chloroform, a stable product was obtained with an available bromine content of between 31 and 32.5%.

Repetition of the above work yielded a product which was in full agreement with the published data. The complex had poor shelf stability, however, constantly decreasing in available bromine content until a level of 30–32% was reached, at which point no further decrease was noticed. This behavior prompted further work on our part to see whether the stable complex could be directly obtained.

It was thought that stability might be due to the formation of Br_3^- complexes, as is likely in many other complexes of halogens and hydrohalides with organic compounds.[3–7]

In accordance with this, the preparation was carried out at higher temperatures in order to promote the substitution to the point where products A and B would be formed in equal molar quantities. At 60–65° the reaction of bromine and pyrrolidone-2 in chloroform yielded beautiful orange crystals containing 30.9% free bromine. This material showed no decrease in free bromine titer over a five-month storage test at ambient temperatures. A carefully purified sample on analysis contained 31.60% available bromine, 14.18% bromine, and corresponded to the empirical formula $(C_4H_7NO)_3{\cdot}HBr{\cdot}Br_2$ (C). The purified sample melted at 88.5–90.5°.

We then attempted to form C from the compounds pyrrolidone-2, hydrogen bromide, and bromine in the respective molar ratios 3:1:1. This succeeded in

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(1) To whom inquiries should be addressed.

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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.

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Diels–Alder Addition to Pyrroles

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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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