Anal. Calcd. for $C_{25}H_{31}O_5NBr_2$: N, 2.40. Found: N, 2.59.

This substance gives a positive color test with ferricyanide–ferric chloride reagent.[14]

3,5-Dibromo-3′,5′-di-*t*-butylthyronine (Vh). A. By Acid Hydrolysis of N-Acetyl-3,5-dibromo-3′,5′-di-*t*-butylthyronine (Ve).—A solution of 100 mg. (0.17 mmole) of Ve in a mixture of 4 ml. of acetic acid, 2 ml. of concentrated hydrochloric acid and 1 ml. of water was refluxed for 3.5 hr. The precipitate formed upon neutralization with a 5% aqueous solution of sodium bicarbonate was dissolved in 2 ml. of 2 *N* sodium hydroxide and the solution was extracted with 1-butanol. The butanol layer was evaporated *in vacuo* and the residue was dissolved in aqueous tetrahydrofuran. The solution was acidified with acetic acid and evaporated *in vacuo* to give a sirup which solidified on treatment with water. Recrystallization from methanol gave 12 mg. (13%) of Vh as colorless prisms, m.p. 233–234°. Infrared spectrum (Nujol): 3600, 3380, 3110, *ca.* 1620, 954 cm.$^{-1}$.

Anal. Calcd. for $C_{23}H_{29}O_4NBr_2$: C, 50.82; H, 5.38; N, 2.58. Found: C, 51.08. H, 5.90; N, 2.58.

This substance shows positive color tests with ninhydrin and with ferricyanide–ferric chloride reagent.[14]

B. By Alkaline Hydrolysis of 3,5-Dibromo-3′,5′-di-*t*-butylthyronine Methyl Ester (Vd).—A solution of 75 mg. (0.14 mmole) of Vd in 3 ml. of ethanol was refluxed with 2.6 ml. of 0.1 *N* sodium hydroxide for 30 min. Upon neutralization of the hydrolyzate with 2.6 ml. of 0.1 *N* sulfuric acid a precipitate formed. Crystallization from methanol gave 27 mg. (37%) of colorless prisms, m.p. 233–234°, identical with the 3,5-dibromo-3′,5′-di-*t*-butylthyronine obtained in procedure A.

Ultraviolet Spectra of 3′,5′-Di-*t*-butylthyropropionic Acid and of 3,5-Dibromo-3′,5′-di-*t*-butylthyropropionic Acid.—3′,5′-Di-*t*-butylthyropropionic acid[1]: $\lambda_{max}^{C_2H_5OH}$ 211 mμ (log ε 4.54), 275.5 mμ (3.62), 282 mμ (3.55). 3,5-Dibromo-3′,5′-di-*t*-butylthyropropionic acid[1]: $\lambda_{max}^{C_2H_5OH}$ 210 mμ (log ε 4.76), 281 mμ (3.55).

Acknowledgment.—This work was supported by the National Institutes of Health, U.S. Public Health Service (Grant A-3706). We are indebted to Dr. H. J. Cahnmann of the National Institutes of Health for helpful discussions and also to Prof. T. Kubota for his interest in this work.

Enols of 4-Bromo- and 4-Methyl-2,3-dioxopyrrolidines. Ketone α-Monomethylation under Acidic or Neutral Conditions[1]

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Received April 18, 1962

The 1-benzyl- and 1-cyclohexyl-2,3-dioxopyrrolidines (Ia and Ib) yielded enols of corresponding 4-bromo-2,3-dioxopyrrolidines (IIa and IIb) when brominated in chloroform solution. The bromo derivatives underwent condensation with two moles of formaldehyde to yield crystalline products which appear to be sesquiketals, 6-benzyl- or 6-cyclohexyl-4a-bromo-7a-hydroxy-4,4a,5,7a-tetrahydro-1,3-dioxino[4,5-*c*]pyrrol-7(6*H*)-one (IIIa or IIIb). Acetic acid hydrolysis of the condensation product IIIb yielded 1-cyclohexyl-4-bromo-4-hydroxymethyl-2,3-dioxopyrrolidine (IVb); catalytic hydrogenation of IIIa, IIIb, or IVb in acetic acid solution over a platinum catalyst yielded enols of 1-benzyl- or 1-cyclohexyl-4-methyl-2,3-dioxopyrrolidine (XIa or XIb). Chlorine derivatives (Vb and VIIb) corresponding to IIIb and IVb were also obtained. Infrared and particularly n.m.r. data showed that the 4-bromo and 4-methyl compounds were fully enolized; with respect to ferric chloride colors and acidity the compounds resembled phenols.

Those 2,3-dioxopyrrolidines which are unsubstituted in the 4-position undergo self-condensations of the aldol type very rapidly in alkaline solutions.[3,4b] It has therefore not been feasible to attempt the preparation of 4-monoalkyl-2,3-dioxopyrrolidines by direct alkylation of sodium enolates of 2,3-dioxopyrrolidines, although a few 4-monoalkyl or 4-monoaralkyl derivatives have been made by other synthetic routes.[4,5] In order to obtain 4-methyl-2,3-dioxopyrrolidines we have successfully exploited a new reaction sequence which began with 2,3-dioxopyrrolidines unsubstituted in position 4 and introduced a single methyl group at that position without recourse to any process requiring basic reaction conditions. The steps involved are summarized in Chart I. It is quite possible that other α-bromo ketones which are sufficiently reactive toward formaldehyde might be methylated in a similar way.

The sequence was tested with two initial starting materials (Ia. R = benzyl; Ib. R = cyclohexyl). These compounds were brominated in chloroform to afford the α-bromo compounds IIa or IIb in yields of 70 and 93%, respectively. Formula II depicts these compounds as enols; the infrared spectra showed no ketonic carbonyl absorption at or near 5.67μ, where ketonic absorption in such compounds is normally found,[3–6] but did exhibit hydroxyl absorption at 3.12 to 3.18 μ. Moreover, the compounds gave strong purple ferric chloride colors. The expected lactam carbonyl absorption was observed at *ca.* 6.0 μ, and carbon-carbon double

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[1] This investigation was supported by a research grant (RG-4371) from the National Institutes of Health, Public Health Service.

[2] Taken principally from a thesis submitted by Julius A. Vida in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology, December, 1960.

[3] P. L. Southwick, E. P. Previc, J. Casanova, Jr., and E. H. Carlson, *J. Org. Chem.*, **21**, 1087 (1956).

[4] (a) W. L. Meyer and W. R. Vaughan, *ibid.*, **22**, 98, 1554, 1560 (1957); (b) W. R. Vaughan and I. S. Covey, *J. Am. Chem. Soc.*, **80**, 2197 (1958).

[5] P. L. Southwick and E. F. Barnas, *J. Org. Chem.*, **27**, 98 (1962).

[6] H. H. Wasserman and R. C. Koch, *Chem. Ind.* (London), 428 (1957); *J. Org. Chem.*, **27**, 35 (1962).

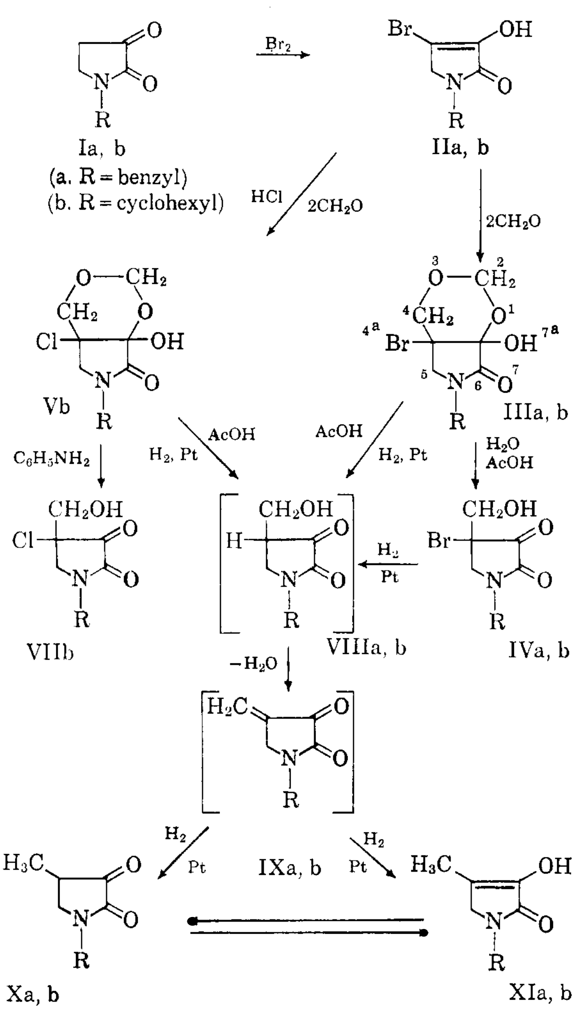

Chart I

bond absorption at 6.12 μ. The 60-Mc. high-resolution n.m.r. spectrum in deuterochloroform gave striking confirmation of the enolic structure of the compound IIa; a single line for the two methylene protons at position 5 appeared at τ = 6.19.[7] In the keto form the absorption of these protons should be split because of coupling with the proton at position 4 and an asymmetric environment contributed mainly by the two unlike substituents at position 4. No such splitting was seen; the n.m.r. spectrum did not reveal the presence of any of the keto form.

When treated with formalin solution in methanol, compounds IIa and IIb yielded crystalline products the composition of which indicated combination with two molecules of formaldehyde as, for example, in formulas IIIa and IIIb. The infrared spectra revealed the presence of hydroxyl groups, ether linkages (three or four closely spaced bands between 8.50 and 8.80 μ), and but one carbonyl group absorbing at wave lengths (5.86–5.92 μ) corresponding to a pyrrolidone lactam function. Hydrolysis, which was conducted with the cyclohexyl compound, occurred readily in aqueous acetic acid to yield formaldehyde and 1-cyclohexyl-4-bromo-4-hydroxymethyl-2,3-dioxopyrrolidine IVb; the product corresponded in composition to IVb, and showed hydroxyl absorption at 3.04 μ, as well as the very characteristic carbonyl bands of a 2,3-dioxopyrrolidine at 5.64 μ (ketonic absorption) and 5.86 μ (lactam absorption).[3–6] Structure IV represented the products we had originally expected from the condensation of formaldehyde with bromo compounds II.

The sesquiketal structures IIIa and IIIb [6-benzyl- and 6-cyclohexyl-4a-bromo-7a-hydroxy-4,4a,5,7a-tetrahydro-1,3-dioxino[4,5-*c*]pyrrol-7(6*H*)-one] for the initial formaldehyde condensation products would explain their lack of ketonic carbonyl absorption, the presence of hydroxyl absorption, and the hydrolysis to formaldehyde plus the α-bromo-α-hydroxymethyl derivative (IV). The n.m.r. spectra of structures of both types III and IV were expected to be rather complex, with quartets of the AB type[8] likely to arise from pairs of spin-coupled protons of non-equivalent environment in the methylene group of the pyrrolidine ring, in the —CH_2O— substituent at position 4 of the pyrrolidine ring and, in the case of III, in the —OCH_2O— unit of the sesquiketal ring. Complex spectra were indeed obtained, but their complete analysis presented difficulties because of the overlapping of lines; the only well separated quartets of the AB type were those centered at *ca.* τ = 5.05 in the spectra of IIIa and IIIb. Perhaps some uncertainty remains on the question of whether the sesquiketal structure III correctly represents the initial condensation products, although that type of structure appears to be in excellent accord with the spectroscopic observations and with the relationship of the initial product IIIb to the derived compound IVb. The assumed sesquiketals were formed in good yields: 85% for IIIa, nearly 100% for IIIb.

It was anticipated that the compounds of structure IV would be converted directly to 4-methyl-2,3-dioxopyrrolidines (X) or their enols (XI) by catalytic hydrogenation. Removal of bromine by catalytic hydrogenolysis was expected to yield the β-hydroxy ketones (VIII). The well known procedure for the synthesis of α-methyl ketones *via* hydrogenation of α-hydroxymethylene ketones[9] can no doubt be assumed to proceed through intermediate products of this type; once the struc-

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[7] N.m.r. spectra were determined with a Varian Model V-4302 60-Mc. dual purpose instrument. Tetramethylsilane was used as an internal reference in all determinations.

[8] See (a) H. J. Bernstein, J. A. Pople, and W. G. Schneider, *Can. J. Chem.*, **35**, 65 (1957); (b) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, 1959, pp. 119–123; (c) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, pp. 89–90.

[9] See, for example, (a) Y. Abe, T. Harukawa, H. Ishikawa, T. Miki, M. Sumi, and T. Toga, *J. Am. Chem. Soc.*, **75**, 2567 (1953); (b) H. J. Ringold, E. Batres, O. Halpern, and E. Necoechea, *ibid.*, **81**, 427 (1959); and (c) C. Djerassi, N. Finck, R. C. Cookson, and C. W. Bird, *ibid.*, **82**, 5488 (1960).

ture VIII was produced its conversion to the methyl derivatives (X or XI) seemed assured. Results of a previous investigation[5] of the hydrogenation of 4-benzylidene-2,3-dioxopyrrolidines over a platinum catalyst suggested that enols of 4-methyl-2,3-dioxopyrrolidines, the 3-hydroxy-2-oxo-3-pyrrolines (XI), would result if unsaturated intermediates (IX) were formed.[10] Catalytic hydrogenation of compound IVb (R = cyclohexyl) in acetic acid over a platinum oxide catalyst did, in fact, yield the expected methyl derivative (XIb) in 67% yield. The infrared spectrum of the product indicated that it was essentially fully enolized; the ketonic carbonyl band at 5.67 μ was missing and hydroxyl absorption was evident in the form of a rather broad band at 3.10 μ. The enolic nature of the product was confirmed by the observations that it gave a strong purple color with ferric chloride and was soluble in sodium hydroxide. Both the spectrum and the chemical behavior of the compound were completely analogous to those of the enolic 4-benzyl-2,3-dioxopyrrolidines recently described.[5]

Catalytic hydrogenation of the initial formaldehyde condensation products IIIa and IIIb under the same conditions used with IVb also produced the methyl derivatives XIa and XIb; the yields were approximately 97% in both cases.[11] Compound XIa was very similar to XIb in infrared spectrum and chemical behavior. Thus it was possible to convert the original 2,3-dioxopyrrolidines Ia and Ib to the enols of corresponding 4-methyl derivatives by a three-step procedure in over-all yields of 57 and 90%, respectively. The n.m.r. spectrum of XIa in deuterochloroform indicated complete enolization and verified other structural details. In accordance with structure XIa there was no splitting of lines by spin-spin coupling, and the spectrum consisted of single lines having the expected intensity relationships for the methyl group at $\tau = 8.16$, the methylene group of the pyrrolidine ring at $\tau = 6.48$,[12] the benzyl methylene group at $\tau = 5.40$ and the aromatic protons of benzyl at $\tau = 2.72$. There was a broad absorption for the enolic hydroxyl at $\tau =$ *ca.* 1.80 at room temperature which moved to $\tau =$ *ca.* 2.44 when the temperature was raised to 60°. There was no evidence of the presence of the keto form Xa.

When the bromo compound IIb was treated with formalin solution in the presence of hydrochloric acid, a compound nearly identical in spectrum and chemical behavior to IIIb was produced. Analytical results showed, however, that the product contained chlorine rather than bromine and therefore corresponded to formula Vb rather than IIIb. The yield was 58%. The question of whether the halogen exchange occurs with the sesquiketal itself or at some earlier stage in the course of the reaction has not been investigated as yet. The chloro sesquiketal (Vb) was converted into the 4-chloro-4-hydroxymethyl-2,3-dioxopyrrolidine (VIIb), which closely resembled the corresponding bromo compound (IVb). The removal of formaldehyde from Vb to yield VIIb was accomplished by treatment with aniline, a procedure which had been applied successfully to the apparently similar sesquiketals derived from 4-benzyl-2,3-dioxopyrrolidines and formaldehyde.[13] Catalytic hydrogenation in acetic acid over a platinum catalyst converted Vb into the 4-methyl compound XIb; the yield was 65%. The over-all yield of XIb from Ib *via* the three-step procedure Ib→IIb→Vb→XIb was 35%; reaction with formaldehyde in the presence of hydrochloric acid did not represent the method of choice for the condensation step of the methylation procedure in this instance, although it might be useful in other cases.

It had been noted previously[4,5] that apparently all 4-monosubstituted 2,3-dioxopyrrolidines are highly enolized, regardless of the nature of the 4-substituent, whereas 2,3-dioxopyrrolidines unsubstituted in the 4-position are obtained in unenolized form. The observations recorded here on the 4-bromo and 4-methyl derivatives provide an excellent illustration of this phenomenon, which is the subject of a continuing investigation.

Experimental[14]

Bromination of 1-Substituted 2,3-Dioxopyrrolidines.—Bromination of the 1-substituted 2,3-dioxopyrrolidines in chloroform was often very slow in starting and initiation of the reaction was brought about by irradiating the stirred reaction mixtures with a mercury lamp or, if necessary, by withdrawing and heating a small portion of the bromination mixture until reaction occurred, then reintroducing the resulting solution of hydrogen bromide and bromination product into the main portion of the reaction mixture. Once initiated, bromination proceeded smoothly at room temperature and the products crystallized from the reaction solutions. In some experiments the mixtures were stirred for an hour at 0° after the bromine was consumed in order to complete the separation of the product, which was collected by filtration, washed with chloroform, and freed of hydrogen bromide by washing with water, or by drying in a desiccator over sodium hydroxide.

(a) **Enol of 1-Benzyl-4-bromo-2,3-dioxopyrrolidine (IIa).**—The yield was 40 g. (70.6%) of a product melting at151–153° from 40 g. (0.21 mole) of 1-benzyl-2,3-dioxopyrrolidine[15]

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[10] Direct formation of the enol *via* a 1,4-addition of hydrogen is a possibility. *Cf.* (a) R. C. Fuson, J. W. Corse, and C. H. McKeever, *J. Am. Chem. Soc.* **62**, 3250 (1940); (b) R. C. Fuson and C. A. Sperati, *ibid.*, **62**, 2643 (1941).

[11] The higher yield of XIb from IIIb than from IVb or Vb can probably be attributed to the fact that the experiments with IVb and Vb were conducted on a much smaller scale.

[12] L. M. Jackman, ref. 8c, p. 56, reports the value $\tau = 6.63$ for the hydrogens at position 5 of 2-oxopyrrolidine. A small additional shift of the methylene line toward lower frequency (lower field) would be expected to result from the adjacent double bond in XIa.

[13] E. F. Barnas, Ph.D. thesis, Carnegie Institute of Technology, May, 1960.

[14] Melting points are uncorrected. Microanalyses are by Drs. G. Weiler and F. B. Strauss, Oxford, England.

[15] P. L. Southwick and R. T. Crouch, *J. Am. Chem. Soc.*, **75**, 3413 (1953).

in 250 ml. of chloroform treated with 33.6 g. (0.21 mole) of bromine. Recrystallization from 240 ml. of toluene gave a 94% recovery of the compound as pale yellow needles, m.p. 154–156° (dec.).

Anal. Calcd. for $C_{11}H_{10}NO_2Br$: C, 49.27; H, 3.75; N, 5.23. Found: C, 49.62; H, 3.85; N, 4.88.

Infrared spectrum (Nujol mull)[16]: 3.12i; 3.41i; 3.47i; 5.94si; 5.96i; 6.10sm; 6.66w; 6.80i; 6.85i; 6.95m; 7.02m; 7.26sm; 7.34bi; 7.56m; 7.68m; 7.84m; 8.04m; 8.32w; 8.56w; 8.64w; 8.89w; 9.24w; 9.64bw; 9.96w.

N.m.r. spectrum in deuterochloroform: τ = 2.71 (phenyl protons); τ = 5.40 (benzyl methylene protons); τ = 6.21 (pyrrolidine methylene protons). Hydroxyl proton absorption was too broad to be definitely identified.

(b) **Enol of 1-Cyclohexyl-4-bromo-2,3-dioxopyrrolidine (IIb).**—The yield was 86 g. (93%) of a product melting at 151–152° (dec.) from 64 g. (0.353 mole) of 1-cyclohexyl-2,3-dioxopyrrolidine[3] in 1140 ml. of chloroform treated with 57.5 g. (0.353 mole) of bromine. Recrystallization from a petroleum ether (b.p. 65–110°)–chloroform mixture gave white crystals, m.p. 152–153° (dec.).

Anal. Calcd. for $C_{10}H_{14}NO_2Br$: C, 46.17; H, 5.42; N, 5.38. Found: C, 46.24; H, 5.32; N, 5.27.

Infrared spectrum (Nujol mull; bands below 7.5 μ given): 3.18bm; 3.42i; 3.49i; 6.02bi; 6.12sm; 6.85i; 7.27i; 7.44m.

Condensation of Enolic 1-Substituted 4-Bromo-2,3-dioxopyrrolidines with Formaldehyde.—The 4-bromo derivatives were suspended in solutions of 37% formalin containing methanol and the mixtures were refluxed for 2 to 3 hr. The starting materials dissolved during the first hour of heating. The reaction mixtures were allowed to stand overnight at room temperature, then were extracted repeatedly with benzene. The benzene extracts were dried over sodium sulfate and concentrated under reduced pressure. The residual oils were dissolved in a small volume of absolute ethanol and the resulting solutions were diluted with approximately an equal volume of hot water. Crystallization occurred when the solutions were stored for several hours at 0°. Decolorization with Norit-A and further crystallization from aqueous ethanol (50% by volume) were employed when further purification was necessary.

(a) **Formaldehyde Condensation Product (IIIa) from the Enol of 1-Benzyl-4-bromo-2,3-dioxopyrrolidine.**—The yield was 2.8 g. (85%) of white cubes, m.p. 126–128°, from 2.7 g. (0.01) mole of IIa and 350 ml. of 37% formalin containing 70 ml. of methanol heated for 3 hr. Initial crystallization was from 15 ml. of ethanol and 15 ml. of water.

Anal. Calcd. for $C_{13}H_{14}NO_4Br$: C, 47.58; H, 4.30; N, 4.27. Found: C, 47.36; H, 3.97; N, 4.48.

Infrared spectrum (Nujol mull): 3.00bm; 3.42i; 3.49i; 5.86bi; 6.22w; 6.68m; 6.76m; 6.85i; 7.00m; 7.27m; 7.38m; 7.90m; 7.98bi; 8.26m; 8.56bm; 8.76m; 9.26bm; 9.60bm; 10.00bi.

(b) **Formaldehyde Condensation Product (IIIb) from the Enol of 1-Cyclohexyl-4-bromo-2,3-dioxopyrrolidine.**—The yield was 2.34 g. (ca. 100%) of a product melting at 128–130° from 1.9 g. of IIb and 250 ml. of 37% formalin containing 50 ml. of methanol heated for 2 hr. Initial crystallization was from 5 ml. of ethanol and 5 ml. of water.

Anal. Calcd. for $C_{12}H_{18}NO_4Br$: C, 45.01; H, 5.67; N, 4.37; Br, 24.95. Found: C, 44.85; H, 5.69; N, 4.70; Br, 25.00.

Infrared spectrum (Nujol mull): 2.90sm; 3.12bm; 3.42i; 3.49i; 5.91bi; 6.76m; 6.85bm; 7.27m; 8.02bi; 8.24m; 8.53bi; 8.76i; 9.16m; 9.58i; 9.90bi.

Molecular weight values, obtained with a Mechrolab vapor pressure osmometer, were somewhat variable, possibly because of association on the one hand, and dissociation to release formaldehyde on the other. However, the values found (Calcd. for $C_{12}H_{18}NOBr$: 320. Found: 350, 218) seem to indicate that the molecular weight corresponds to the empirical formula rather than to some multiple of it.

The compound gave a positive Benedict's test.

1-Cyclohexyl-4-bromo-4-hydroxymethyl-2,3-dioxopyrrolidine (IVb).—The formaldehyde condensation product IIIb, m.p. 128–130° (1.0 g., 0.0031 mole), was dissolved in 10 ml. of glacial acetic acid and the solution was poured into 100 ml. of distilled water. A white precipitate appeared. The reaction mixture was then allowed to stand for 24 hr. at room temperature. During this period the precipitate completely dissolved. The solution was extracted repeatedly with benzene. The benzene extract was dried over sodium sulfate, filtered, and evaporated under reduced pressure to yield 0.85 g. (94%) of a white solid of m.p. 119–127°. The infrared spectrum of the crude compound showed bands at 3.04 μ, 5.64 μ, and 5.86 μ. Recrystallization from toluene yielded white needles in 86% yield, m.p. 129–130°. The compound contained halogen and gave no ferric chloride test.

Anal. Calcd. for $C_{11}H_{16}NO_3Br$: C, 45.60; H, 5.55; N, 4.82. Found: C, 45.49; H, 5.75; N, 4.51.

Infrared spectrum (Nujol mull): 3.04i; 3.42i; 3.49i; 5.64i; 5.86i; 6.85i; 7.27i; 7.66i; 7.84w; 7.98w; 8.12w; 8.40w; 8.48m; 8.80i; 8.94m; 9.36m; 9.58i; 9.84m.

The aqueous layer from the extraction yielded yellow needles of formaldehyde 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. with an authentic sample 163–165°, when tested with methanolic 2,4-dinitrophenylhydrazine.

The Enol Form of 1-Cyclohexyl-4-methyl-2,3-dioxopyrrolidine (XIb).—The formaldehyde condensation product IIIb, m.p. 128–130° (10.0 g., 0.031 mole), was dissolved in 50 ml. of glacial acetic acid. Platinum oxide (Adams') catalyst (0.1 g.) was added to the solution and the compound was hydrogenated at an initial hydrogen pressure of 65 lb./sq. in. (gage) for 16 hr. in a Parr apparatus. By the end of the hydrogenation period a crystalline solid had precipitated. The solid was dissolved by heating the mixture to 100°, the catalyst was removed by filtration, and the solution was allowed to cool to room temperature. The white needles which precipitated were collected by filtration to yield 4.3 g. (70.5%) of a product of m.p. 176–178°. Evaporation of the mother liquor to dryness under reduced pressure yielded a residue which was dissolved in benzene and freed from traces of insoluble materials by filtration of the solution. Removal of the benzene by evaporation, and crystallization of the residue from 10 ml. of acetone gave 1.6 g. (26.2%) of additional product, m.p. 175–177°. The total yield was 5.9 g. (96.7%). Recrystallization from 50% aqueous ethanol gave white needles, m.p. 176–178°.

Anal. Calcd. for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.50; H, 8.71; N, 7.09.

Infrared spectrum (Nujol mull): 3.10bm; 3.42i; 3.49i; 5.86w; 6.04bi; 6.85bi; 7.18m; 7.26m; 7.36m; 7.70bm; 7.92w; 8.04m; 8.26w; 8.76w; 9.22w; 10.00w.

The same product was obtained by means of a similar hydrogenation procedure from compounds IVb and Vb. In the case of IVb 0.18 g. (67%) of XIb was obtained from 0.4 g. (1.38 mmoles) of starting material; in the case of Vb the yield of XIb was 0.23 g.(65%) from 0.5 g. (1.8 mmoles) of starting material.

The Enol of 1-Benzyl-4-methyl-2,3-dioxopyrrolidine (XIa).—Hydrogenation of 1.5 g. (0.0018 mole) of condensation product IIIa was carried out in 10 ml. of glacial acetic acid over 20 mg. of platinum oxide catalyst for 18 hr. at an initial pressure (gage) of 75 lb./sq. in. The catalyst was removed by filtration and the solvent evaporated under reduced pressure to yield a light colored oil, which solidified when allowed to stand for a number of hours at room temperature. The product was pressed on a filter, washed with water, and dried. The yield was 0.90 g. (97%) of

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(16) Infrared spectra were determined with a Perkin-Elmer Model 21 spectrophotometer. Figures given are wave lengths in microns. Letters following the figures describe bands as follows: i = intense, >60% absorption; m = medium, 30–60% absorption; w = weak, <30% absorption; b = broad band; s = shoulder. Unless otherwise indicated, bands are quoted from 2.5 to 10.0 μ.

white crystals, m.p. 140–142°. Recrystallization from toluene afforded 0.77 g. (83%) of white needles, m.p. 146–148°.

Anal. Calcd. for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.45; N, 6.89. Found: C, 70.84; H, 6.59; N, 7.09.

Infrared spectrum (Nujol mull): 3.10bm; 3.42i; 3.49i; 5.86sm; 5.98bi; 6.68m; 6.80m; 6.85i; 7.02w; 7.18i; 7.27m; 7.38i; 7.70bm; 8.00i; 8.30w; 8.60w; 9.16bi; 9.32w; 9.70w; 9.98w.

Formaldehyde Condensation Product Vb.—The enol of 1-cyclohexyl-4-bromo-2,3-dioxopyrrolidine, m.p. 150–151° (26.0 g., 0.1 mole), was suspended in a mixture of 2.25 kg. of 37% formalin solution, 450 ml. of methanol, and 300 ml. of concentrated hydrochloric acid. The reaction mixture was refluxed for 3 hr. During the first hour of the heating period the compound completely dissolved. The solution was allowed to cool to room temperature and stand overnight, then was extracted repeatedly with benzene. The benzene extract was dried over sodium sulfate, filtered, and evaporated under reduced pressure to yield a solid residue. The residue was dissolved in 100 ml. of hot ethanol. The hot solution was treated with Norit-A, filtered, and diluted with 100 ml. of hot distilled water. When the solution was cooled white platelets appeared. The product was collected by filtration, washed with 50% aqueous ethanol, and dried. The yield was 16 g. (58%) of a product melting at 155–156°. The melting point did not change on further recrystallization from aqueous ethanol. The product gave no ferric chloride test.

Anal. Calcd. for $C_{12}H_{18}NO_4Cl$: C, 52.27; H, 6.58; N, 5.09; Cl, 12.84. Found: C, 52.27; H, 6.62; N, 4.73; Cl, 12.41.

Infrared spectrum (Nujol mull): 3.18bi; 3.42i; 3.49i; 5.92bi; 6.76m; 6.90m; 7.27m; 8.00bi; 8.22i; 8.54i; 8.76i; 9.10i; 9.50bi; 9.88i; 9.98bi.

1-Cyclohexyl-4-chloro-4-hydroxymethyl-2,3-dioxopyrrolidine (VIIb).—The formaldehyde condensation product Vb, m.p. 155–156° (0.45 g., 0.0016 mole), was dissolved in 20 ml. of hot 95% ethanol. To the solution was added 0.2 ml., (0.002 mole) of aniline and the reaction mixture was refluxed for 3 hr. The solution was cooled to room temperature. The solvent was evaporated under reduced pressure to leave a yellow oil. The oil was dissolved in 50 ml. of hot benzene, treated with Norit-A, filtered, and concentrated to a volume of 20 ml. On cooling, white crystals separated. After the mixture had been allowed to stand for 48 hr. at room temperature, the product was collected by filtration and washed with absolute ether. The yield was 0.13 g. (32%) of material melting at 149–153°. Recrystallization from toluene gave a compound of m.p. 152–154° which contained chlorine and gave a negative ferric chloride test.

Anal. Calcd. for $C_{11}H_{16}NO_3Cl$: C, 53.80; H, 6.58. Found: C, 54.03; H, 6.78.

Infrared spectrum (Nujol mull; bands below 7.5 μ given): 3.04m; 3.42i; 3.49i; 5.62i; 5.86i; 6.85i; 7.27m.

From the mother liquor an oil was obtained after evaporation under reduced pressure. The oil solidified on treatment with absolute ether. It weighed 0.15 g. (37%) and melted at 80–130°. It had the same infrared spectrum as the first crop of the product.

Acknowledgment.—The authors are indebted to George E. Milliman and Dr. Robert J. Kurland for the n.m.r. measurements and to Dr. Nazih Latif for other assistance.

The Preparation of 2-Imidazolones. A Novel Ring Closure of Propynylureas with Phosphorus Pentachloride

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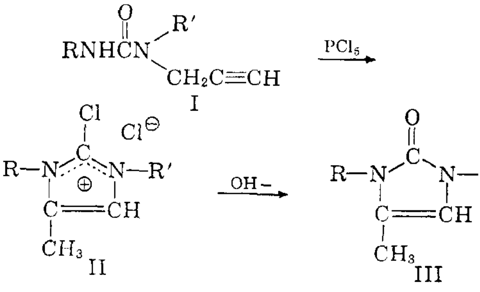
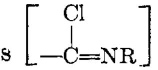
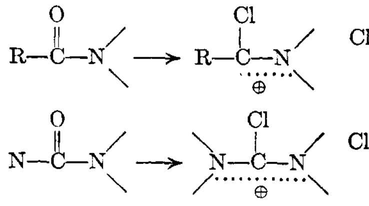
Received May 10, 1962

The facile preparation of otherwise inaccessible 1,3-disubstituted 2-imidazolones is reported. The action of phosphorus pentachloride on propynylureas I gave the imidazolium salts II. These on treatment with base were converted to the imidazolones III. A short discussion of the proposed mechanism is included.

We wish to report a novel ring closure effected by treating a suitable propynylurea I with phosphorus pentachloride. A 2-imidazolone III is obtained *via* a stable isolable imidazolium chloride II.



The formation of imidoyl chlorides  $\left[-\overset{\mathrm{Cl}}{\overset{|}{\mathrm{C}}}=\mathrm{NR}\right]$ on treatment of amides and ureas is well known. Recent reports show the formation of stable acylic amido chlorides and carbamido chlorides from the corresponding amides[1-3] and ureas.[2,4]



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