of triethylamine directly yielded benzoxazinone **3**, also obtained by methylation of **2**.[6,7] The isolation of **3** in the reaction of 2-methylamino-5-chlorobenzhydrol with trichloroacetyl chloride could be explained only by the intermediate formation of 2-(N-methyltrichloroacetamido)-5-chlorobenzhydrol, in which only intramolecular nucleophilic displacement of chloroform by the neighboring benzhydrylic function could lead to **3**. These results suggest a similar mechanism for the formation of benzoxazinone **2**.

Experimental Section

Melting points were determined in open capillary tubes. Ir spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer. Nmr spectra were determined with a Varian HA-100 spectrophotometer in the indicated solvent using TMS as internal standard. Thin layer chromatograms were run on silica gel G. Spots were detected with sulfuric acid. The solvent systems used were solvent A, benzene–methanol (95:5); solvent B, carbon tetrachloride–methanol (95:5); solvent C, chloroform–ethyl acetate–diethylamine (70:10:10).

2-Trichloroacetamido-5-chlorobenzhydrol (1).—A solution of 18.2 g (0.1 mol) of trichloroacetyl chloride in 60 ml of anhydrous ether was added dropwise over 30 min to an ice-cooled stirred solution of 23.35 g (0.1 mol) of 2-amino-5-chlorobenzhydrol[1] and 10.1 g (0.1 mol) of triethylamine in anhydrous ether. After stirring at 5° for 2 hr, the resultant suspension was filtered from triethylamine hydrochloride (13.6 g); the filtrate was concentrated to dryness; and the residue was recrystallized from benzene–cyclohexane to give 30.5 g (80%) of white crystals, mp 130–131°. Tlc using solvents A and C showed single spots with R_f 0.79 and 0.70, respectively.

Anal. Calcd for $C_{15}H_{11}Cl_4NO_2$: C, 47.52; H, 2.93; Cl, 37.47; N, 3.69. Found: C, 47.68; H, 2.96; Cl, 37.17; N, 3.59.

4-Phenyl-6-chloro-1,4-dihydro-2H-3,1-benzoxazin-2-one (2).—A solution of 18.95 g (0.05 mol) of **1** and 8.4 g (0.15 mol) of potassium hydroxide in 350 ml of absolute ethanol was heated at reflux for 4 hr. The resultant suspension[8] was concentrated to *ca.* 100 ml, and 50 ml of 1 *N* HCl and 500 ml of water were added with stirring. The precipitate was filtered, washed with water, and recrystallized from ethanol to give 8.4 g (65%) of white crystals: mp 191–193° dec; ir (KBr) 3395 and 3210 (NH), 1705 cm^{-1} (C=O); nmr ($CDCl_3$–DMSO-d_6 9:1) δ 10.08 (1, s, NH), 7.36 (5, s, C_6H_5), 6.75–7.25 (3, m, the aromatic protons of the benzoxazine ring), 6.28 (1, s, CH–O); tlc, single spots with R_f 0.47, 0.62, and 0.59 in solvents A, B, and C, respectively.

Anal. Calcd for $C_{14}H_{10}ClNO_2$: C, 64.74; H, 3.88; Cl, 13.65; N, 5.39. Found: C, 64.83; H, 3.87; Cl, 13.72; N, 5.52.

4-Phenyl-6-chloro-1-methyl-1,4-dihydro-2H-3,1-benzoxazin-2-one (3). **A. From 2-Methylamino-5-chlorobenzhydrol.**—A solution of 17.7 g (0.097 mol) of trichloroacetyl chloride in 60 ml of anhydrous ether was added dropwise at −5° over 30 min to a stirred solution of 24.0 g (0.097 mol) of 2-methylamino-5-chlorobenzhydrol[1] and 9.8 g (0.097 mol) of triethylamine in 200 ml of anhydrous ether. After stirring at −5° for 2 hr, the resultant suspension was filtered, and the precipitate was washed twice with 50 ml of a hot mixture of tetrahydrofuran–ether (3:1); the insoluble triethylamine hydrochloride (13.2 g) was discarded. The filtrates were combined and the solvents evaporated. Recrystallization of the residue from ethanol gave 14.6 g (55%) of white crystals: mp 185–187° dec; ir (KBr) 1705 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.38 (5, s, C_6H_5), 6.80–7.30 (3, m, the aromatic protons of the benzoxazine ring), 6.18 (1, s, CH–O), 3.34 (3, s, N–CH_3); tlc, a single spot with R_f 0.84 in the solvent A.

Anal. Calcd for $C_{15}H_{12}ClNO_2$: C, 65.82; H, 4.42; Cl, 12.95; N, 5.12. Found: C, 65.78; H, 4.44; Cl, 13.01; N, 5.23.

B. From 2.—A mixture of 52.0 g (0.20 mol) of **2** and 10.6 g (0.22 mol) of sodium hydride (50% oily suspension) was treated with a solution of 56.5 g (0.33 mol) of methyl iodide in 100 ml of anhydrous dimethylformamide. As the exothermic reaction that initially took place had subsided, the mixture was refluxed for 2.5 hr to give a clear solution. Upon standing overnight at 5°, a crystalline product separated, which was washed and recrystallized from ethanol to give 34.0 g (60%) of **3**, mp 185–187°. This product was identical in all respects (ir spectra, tlc, and mixture melting point) with the substance obtained from procedure A.

(7) R. L. Dannley and M. Lukin, *J. Org. Chem.*, **22**, 268 (1957).

(8) Filtration after cooling at room temperature gave 9.3 g (0.125 mol) of potassium chloride.

Registry No.—**1**, 19639-69-1; potassium hydroxide, 1310-58-3; **2**, 13213-86-0; **3**, 13213-94-0.

Acknowledgments.—We wish to thank Professor V. Rosnati of the University of Milan for helpful discussion through the experiment and Professor C. J. Cavallito of the University of North Carolina for his valuable comments to the manuscript.

The 6-Hydroxy-5,6-dihydro-4H-1,2-oxazine 2-Oxide System. Absence of Ring–Chain Tautomerism in 5,5-Dinitro-2-pentanone

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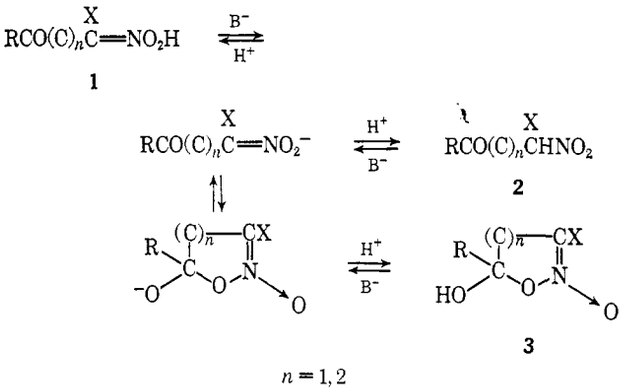
Many 3- and 4-keto-1-nitro- (and 1,1-dinitro-) alkanes are known.[2,3] Their nitronate salts on mild acidification may undergo very rapid O protonation to form the corresponding 3- and 4-ketonitronic acids (**1**) (Scheme I), which usually are consumed in solution by relatively slower C protonation of their nitronate

SCHEME I



anions leading ultimately to ketonitroalkanes (**2**). Spectra and other properties which have been determined for 3- and 4-keto-1-nitroalkanes and 3-keto-1,1-dinitroalkanes indicate that they exist in the chain form.[3–5] Reported ring–chain tautomerism with these substances is limited to two examples; the rings are

(1) National Research Council Postdoctoral Research Associate, 1967–1968.

(2) E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. Reactions*, **10**, 179 (1959).

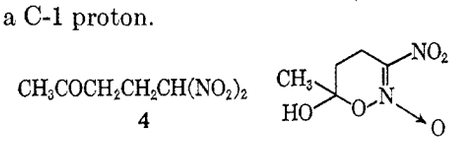
(3) (a) D. J. Glover and M. J. Kamlet, *J. Org. Chem.*, **26**, 4734 (1961); (b) M. J. Kamlet and D. J. Glover, *ibid.*, **27**, 537 (1962).

(4) M. E. Kuehne and L. Foley, *ibid.*, **30**, 4280 (1965).

(5) (a) A. Risaliti, M. Forchiassin, and E. Valentin, *Tetrahedron*, **24**, 1889 (1968); (b) G. F. Tereshchenko, B. I. Lonin, L. I. Bagal, and G. I. Koldobskii, *Zh. Org. Khim.*, **4**, 1125 (1968); (c) K. V. Altukhov, V. A. Tartakovskii, V. V. Perekalin, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 197 (1967); (d) K. V. Altukhov and V. V. Perekalin, *Zh. Org. Khim.*, **3**, 2003 (1967).

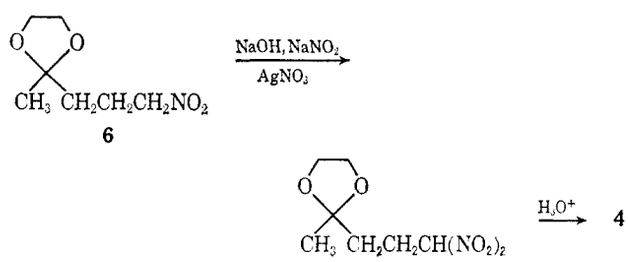
6-hydroxy-5,6-dihydro-4H-1,2-oxazine 2-oxides (**3**, n = 2).[6-8] We have reexamined these reports and have corroborated one of them. No other examples of ring–chain tautomerism of this type have been found.

5,5-Dinitro-2-pentanone (**4**) has been reported to exist in methanol solution to a large extent as 6-hydroxy-6-methyl-3-nitro-5,6-dihydro-4H-1,2-oxazine 2-oxide (**5**).[6] This conclusion rests principally on the observation that the rate of sodium borohydride reduction of **4** to the corresponding nitro alcohol in 1:1 methanol–water at pH 3–4 is slow, relative to rates of reduction of other 4-keto-1,1-dinitroalkanes lacking a C-1 proton.



4 **5**

The preparation of **4** itself has not been described in the literature, although the potassium salt has been made from 5,5,5-trinitro-2-pentanone.[3] We found direct oxidative nitration of 5-nitro-2-pentanone to yield **4** in only 5% yield, but ethylene ketal **6** could be converted into ketal **7** in 43% yield; acid hydrolysis of **7** led to an 83% yield of **4**.

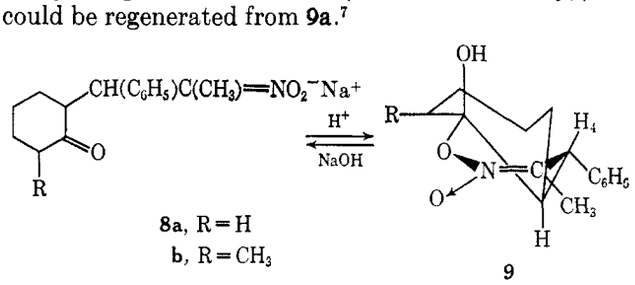


6 **7**

Properties of **4** reveal no evidence of its existence as ring form **5**. Infrared spectra determined neat and in carbon tetrachloride or dimethyl sulfoxide-d_6 reveal no absorption in the region 3100–4000 cm^{-1} (no hydroxyl stretching bands); characteristic strong asymmetric and symmetric nitro bands appear at *ca.* 1560 and 1350 cm^{-1}, respectively, and a normal carbonyl stretching band is found at 1720 cm^{-1}. No C=N stretching bands are evident (no bands near 1630–1690 cm^{-1}).[9] The nmr spectra of **4** determined in 1:1 methanol–water at pH 5 and 3.5, in deuteriochloroform and dimethyl sulfoxide-d_6 agree with chain structure **4**. The ultraviolet spectra of **4** determined in water, ethanol, or 1:1 methanol–water show the same absorption maximum as the corresponding nitronate anion determined in aqueous or ethanolic potassium hydroxide solution (*ca.* 380 mμ). Ketal **7** and other 1,1-dinitroalkanes have very similar absorption maxima (*ca.* 380 mμ).[3] Cyclic α-nitronitronic esters such as **5** would be expected to absorb at wavelengths 40–60 mμ lower than the corresponding 1,1-dinitronate anions.[9] In 1:1 methanol–water at pH 3.5 the ionization of **4** is almost completely repressed as evidenced by the absence of significant electronic absorption above 250 mμ.

The ionization constant of **4** was determined by rapid potentiometric titration in water at 25° and revealed only one equivalence point (pK_a = 4.84);[10] 1,1-dinitro-n-alkanes have pK_a values of 5.2–5.6.[11] There appears to be no acid weakening of **4** which would be associated with a stable ring form **5**. Rather, an expected acid strengthening owing to an inductive effect of the β-acetyl group is apparent (calculated for **4**, $pK_a \cong$ 4.85[3,11b]). The observation that reduction of **4** in methanol at pH 3–4 is slow and requires a large excess of sodium borohydride may possibly be explained by the fact that this reducing agent is destroyed exceedingly rapidly in this medium.[12]

Many 2-(2-nitroalkyl)cyclohexanones are known.[2-5,13] One of these has been reported to exist as a ring tautomer.[7] Condensation of cyclohexanone with 2-nitro-1-phenylpropene in aqueous sodium hydroxide led to a Michael adduct (**8a**), which on acidification with methanolic acetic acid gave a crystalline solid, tentatively assigned structure **9a** (no stereochemistry); **8a** could be regenerated from **9a**.[7]



8a, R = H
b, R = CH_3

9

Structure **9a** is in agreement with its infrared spectrum and chemical behavior, previously reported,[7] and its ultraviolet spectrum which we have determined, λ_{max}^{EtOH} 228 mμ (ε 17,000).[14] We find that the nmr spectrum of **9a** establishes its structure and stereochemistry, assuming a *trans*-fused chair form of cyclohexane ring as shown. A ten-cycle coupling of the C-4 proton with the adjacent bridgehead proton supports a structure having a pseudoequatorial C-4 phenyl. Cyclic structure **9a** must be considered unique. Low solubility coupled with high crystallinity and melting point facilitates its isolation. Its ease of formation and stability may be associated, in part, with the slow rate of C protonation of **8a**, and slow proton removal from the axial hydroxyl in **9a**. Slow C protonation is observed with α,β,β-substituted nitronic acids.[14,15]

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(7) (a) E. B. Hodge and R. Abbott, *J. Org. Chem.*, **27**, 2254 (1962); (b) E. B. Hodge, U. S. Patent 3,024,232 (1962); *Chem. Abstr.*, **57**, 8501 (1962).

(8) P. R. Jones, *Chem. Rev.*, **63**, 461 (1963).

(9) 3-Nitro-2-isoxazoline 2-oxide has $\lambda_{max}^{H_2O}$ 320 mμ (ε 8366); ν 1640–1650 cm^{-1} (C=N). (a) V. I. Slovetskii, A. I. Ivanov, A. A. Fainzilberg, S. A. Shevelev, and S. S. Novikov, *Zh. Org. Khim.*, **2**, 937 (1966); *Chem. Abstr.*, **65**, 16827 (1966); (b) A. I. Ivanov, I. E. Chlenov, V. A. Tartakovskii, V. I. Slovetskii, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1491 (1965); *Chem. Abstr.*, **63**, 16152 (1965); (c) V. A. Tartakovskii, B. G. Gribov, I. A. Arostyanova, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1644 (1965); *Chem. Abstr.*, **64**, 2080 (1966).

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(11) (a) V. I. Slovetskii, A. A. Fainzilberg, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 989 (1962); *Chem. Abstr.*, **58**, 5487 (1963); (b) V. I. Slovetskii, S. A. Shevelev, V. I. Erashko, L. I. Biryukova, A. A. Fainzilberg, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 655 (1966); *Chem. Abstr.*, **65**, 3714 (1966).

(12) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, pp 242–247.

(13) V. V. Perekalin and K. S. Parfenova, *Zh. Obshch. Khim.*, **30**, 388 (1960); *Chem. Abstr.*, **54**, 24582 (1960).

(14) Ultraviolet spectra of acyclic or cyclic aliphatic nitronic esters lacking an α-nitro or aryl substituent have not been reported; *cf.* N. Kornblum and R. A. Brown, *J. Amer. Chem. Soc.*, **86**, 2681 (1964). The spectra of these substances should resemble those of the corresponding nitronic acids. For octane-2-nitronic acid λ_{max}^{EtOH} 226 mμ (ε 12,800); for the corresponding nitronate anion λ_{max}^{EtOH} 232 mμ (ε 12,800); A. T. Nielsen and H. F. Cordes, *Tetrahedron Suppl.*, **20** (1), 235 (1964).

(15) E. B. Hodge, *J. Amer. Chem. Soc.*, **73**, 2341 (1951).

2-Methylcyclohexanone and 2-nitro-1-phenylpropene gave a solid (**9b**) which was too unstable to characterize. Attempts to prepare other 5,6-dihydro-4H-1,2-oxazine 2-oxides were unsuccessful. Normal Michael adducts or recovered reactants are usually obtained in the condensation of 2-nitro-1-phenylpropene and other nitro olefins with various ketones under conditions whereby **9a** is formed.[7,16]

Ring–chain tautomerism of 3- and 4-ketonitronic acids in which both ring and chain forms coexist in solution in stable equilibrium is unknown. It is unlikely to be observed. The ring form (**3**) should be only slightly less acidic (0.5–1 pK_a) than the nitronic acid (**1**).[17] With nitronic acids derived from the weakly acidic mononitroalkanes (**2**, X = H, alkyl) pK_a^{nitro}–$pK_a^{aci} \cong$ 3–7.[18] Even 1-nitro-3- and -4-ketoalkanenitronic acids derived from the more acidic 1,1-dinitroalkanes (**2**, X = NO_2; pK_a^{nitro}–$pK_a^{aci} \cong$ 1–2),[18] or certain nitronic acids stabilized by substitution of bulky groups, should be expected to behave like 3- and 4-ketoalkanoic acids and exist in the chain form.[5c,d,8,16,17] On the other hand, an intramolecular addition of nitronate anion oxygen to carbonyl can occur in certain systems if a stable product results. This process is observed in the formation of **9a** and **b**, and the reaction of 1,3-cyclohexanedione with some nitro olefins to yield 3-oxo-2,3-dihydro-4H-1,2-benzoxazines.[19,20]

Experimental Section

2-Methyl-2-(3-nitropropyl)-1,3-dioxolane (**6**) was prepared from 5-nitro-2-pentanone and ethylene glycol:[21] 44% yield; bp 87–90° (0.5 mm); $n^{25}D$ 1.4523; $\nu_{neat}^{cm^{-1}}$ 1560, 1380 (NO_2), 1060 (ether), no bands between 1600 and 1800. The nmr spectrum (neat) showed a methylene triplet signal at τ 5.94 (J = 7 Hz, two protons), methylene singlet at 6.41 (four protons), multiplet methylene signal centered at 8.5 (four protons), and a methyl singlet at 9.2 (three protons).

Anal. Calcd for $C_7H_{13}NO_4$: C, 47.99; H, 7.48; N, 8.00; mol wt, 175.18. Found: C, 48.13; H, 7.75; N, 7.85; mol wt, 175 (mass spectroscopy).

2-Methyl-2-(3,3-dinitropropyl)-1,3-dioxolane (**7**).—A solution of 15.6 g (0.089 mol) of ketal **6** in 100 ml of methanol was added to a solution of 3.6 g of sodium hydroxide and 5.0 g of sodium nitrite in 50 ml of water. This solution was allowed to stand for 30 min at 25°, cooled to 0°, and added slowly to a cold solution of 30 g of silver nitrate in 75 ml of water covered with 60 ml of ether. When addition was complete, the reaction mixture was kept at 0° for 30 min, filtered, and extracted three times with 100 ml of ether. The combined ether extracts were evaporated and the residue distilled to yield 8.5 g (43%) of ketal **7**: bp 110–114° (0.3 mm); $n^{25}D$ 1.4604; $\nu_{neat}^{cm^{-1}}$ 1580, 1340 (NO_2); λ_{max}^{EtOH} 381 mμ (ε 4590); λ_{max} in ethanolic potassium hydroxide (1 × 10^{-4} M hydroxide, 5 × 10^{-5} M compound **7**) 238 mμ (ε 7000), 381 (17,200). The nmr spectrum ($CDCl_3$) showed a triplet methine signal at τ 3.60 (J = 7 Hz, one proton), methylene signals at 6.08 (s, four protons), 7.40 (m, two protons), and 8.05 (m, two protons), and a methyl singlet at 8.70 (three protons).

Anal. Calcd for $C_7H_{12}N_2O_6$: C, 38.18; H, 5.49; N, 12.72; mol wt, 220. Found: C, 37.92; H, 5.75; N, 12.97; mol wt, 213 (in acetone by osmometry).

5,5-Dinitro-2-pentanone (**4**).—A solution of 5.4 g (0.025 mol) of ketal **7** in 50 ml of ethanol and 50 ml of 2.9 M hydrochloric acid, after standing at 25° for 76 hr, was concentrated to a small volume and extracted three times with 75-ml portions of ether. The combined ether extracts were evaporated and the residue was distilled to yield 3.6 g (83%) of 5,5-dinitro-2-pentanone: bp 123–125° (0.5 mm); $n^{25}D$ 1.4594; $\nu_{neat}^{cm^{-1}}$ 1560, 1350 (NO_2), and 1720 (C=O); $\nu_{CCl_4}^{cm^{-1}}$ 1550, 1720; $\nu^{cm^{-1}}$ (DMSO-d_6) 1570, 1340, 1720; λ_{max}^{EtOH} 379 mμ (ε 9000); λ_{max} in ethanolic potassium hydroxide (1.0 × 10^{-3} M hydroxide, 5 × 10^{-5} M compound **4**) 379 mμ (ε 17,200); $\lambda_{max}^{H_2O}$ 382 mμ (ε 8200); λ_{max} in aqueous potassium hydroxide (1.0 × 10^{-3} M hydroxide, 5 × 10^{-5} M compound **4**) 382 mμ (ε 16,500) [lit.[3] 379 mμ (ε 16,600)]; in 1:1 methanol–water, λ_{max} 377 mμ (ε 5700); in methanol–water containing sulfuric acid (pH 3.5), λ_{max} 377 mμ (ε 26). No change in these spectra occurred during 1 hr. The nmr spectrum ($CDCl_3$) showed a complex methine signal at τ 3.49, methylene singlets at 7.21 and 7.26 (four protons), and a methyl singlet at 7.79 (three protons). The same proton signals were observed neat, in acetone-d_6, and in DMSO-d_6. However, in $CDCl_3$–benzene (1:1) there appeared a normal methine triplet at τ 3.93 (J = 7 Hz, one proton), a complex methylene signal centered at τ 7.6 (four protons), and a methyl singlet at 8.12 (three protons). The proximity of the methylene chemical shifts in $CDCl_3$ solution explains the virtual coupling effect observed for the methine proton signal in this solvent. A 10% solution of **4** in 1:1 methanol–water (pH *ca.* 5) showed the C-1 proton multiplet centered at τ 3.25 (one proton), a complex methylene signal centered at 7.22 (four protons), and a methyl singlet at 7.82 (three protons). In the same solvent adjusted to pH 3.5 with sulfuric acid the spectrum was essentially the same with a slight increase in the intensity of the C-1 proton signal. These solutions are similar to those employed in the reported sodium borohydride reductions.[6] In a 1:1 methanol-d_4–D_2O solution of **4** the C-1 methine signal was absent owing to very rapid exchange of the C-1 proton in this solvent; the remainder of the spectrum was similar to that observed for **4** in methanol–water. The observed spectra remained unchanged during 24 hr.

Anal. Calcd for $C_5H_8N_2O_5$: C, 34.09; H, 4.58; N, 15.91; mol wt, 176.13. Found: C, 34.32; H, 4.93; N, 15.62; mol wt, 176 (mass spectroscopy).

A 2,4-dinitrophenylhydrazone derivative of **4** was prepared and crystallized from ethanol, mp 114–115°.

Anal. Calcd for $C_{11}H_{12}N_6O_8$: N, 23.59. Found: N, 23.46.

8a-Hydroxy-3-methyl-4-phenyl-4a,5,6,7,8,8a-hexahydro-4H-1,2-benzoxazine 2-Oxide (**9a**).—2-Nitro-1-phenylpropene (6.0 g, 0.037 mol) in 20 ml of cyclohexanone was treated with a solution of 2.0 g of sodium hydroxide in 3 ml of water and the mixture stirred for 2 hr (after *ca.* 10 min an exothermic reaction occurred and a homogeneous solution resulted). The mixture was poured into 100 ml of acetone containing 20 ml of acetic acid. The solid which precipitated was removed by filtration and recrystallized from ethanol to yield 3.9 g (40%) of **9a**, colorless prisms, mp 137–139° dec (lit.[7] mp 137–139° dec). The nmr spectrum ($CDCl_3$) revealed an aryl multiplet centered at τ 2.74 (five protons), a broad singlet at 3.11 (OH, one proton), a doublet centered at 6.53 (J = 10 Hz, one proton), a complex multiplet at 7.4–8.9 (nine protons), and a methyl doublet at 8.15 (J = 1 Hz, three protons). Owing to the very slight solubility of **9a** in water and ethanol we were unable to determine its pK_a in these solvents.

Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.96; H, 7.21; N, 5.19.

The above procedure employed with 2-methylcyclohexanone gave an unstable solid product upon acidification with acid. However, it decomposed very rapidly and could not be characterized. It is believed to be an impure sample of **8a-hydroxy-3,8-dimethyl-4-phenyl-4a,5,6,7,8,8a-hexahydro-4H-1,2-benzoxazine 2-oxide** (**9b**). Unsuccessful attempts were made to extend the reaction, employing the above procedure and various modifications of it, to the reaction of 2-nitro-1-phenylpropene with cyclopentanone, acetone, 3-pentanone, 2,4-pentanedione, 1-indanone, 1,3-indandione, dimedone, 1,3-cyclohexanedione, and 2,6-dimethylcyclohexanone. β-Nitrostyrene, 1-nitropropene, and 2-nitro-1-butene were also allowed to react with some of these ketones. Products obtained were usually the normal 1:1 adducts,[2,7,12] recovered reactants, or intractable tars. Some of these reactions gave previously unreported compounds which will be described in a forthcoming publication.[20] Michael

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(20) A. T. Nielsen and T. G. Archibald, *Tetrahedron*, **25** (1969), in press.

(21) Procedure of W. D. S. Bowering, V. M. Clark, R. S. Thakur, and Lord Todd, *Ann.*, **669**, 106 (1963).

addition of nitromethane and nitroethane to benzalacetone and chalcone gave the normal 1:1 adducts.[2] No evidence of 6-hydroxy-5,6-dihydro-4H-1,2-oxazine 2-oxides was found upon examination of the infrared and nmr spectra of product mixtures or selected fractions thereof from each of these reactions.

Registry No.—**4**, 19639-72-6; **4** (2,4-dinitrophenylhydrazone), 19639-73-7; **6**, 19639-74-8; **7**, 19639-75-9; **9a**, 19640-00-7.

Acknowledgment.—The authors are indebted to Donald W. Moore for helpful discussions.

Some Reactions of 2,4,4-Trimethyl-1-pyrroline 1-Oxide

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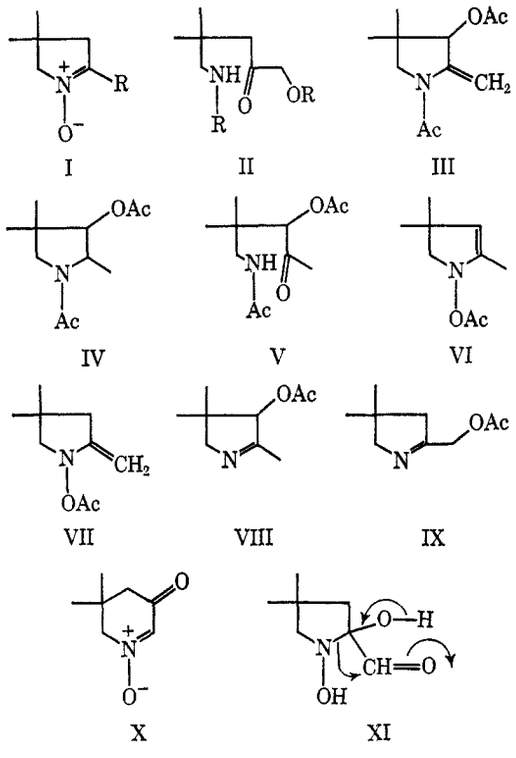
In connection with other work we had need to investigate some reactions of the title compound. Many of the interesting properties of cyclic nitrones have already been delineated.[1,2] For example, treatment of 2,4,4-trimethyl-1-pyrroline 1-oxide (I, R = Me) with benzoyl chloride under Schotten–Baumann conditions gave smoothly a ketobenzoate to which the structure II (R = PhCo) was assigned.[1] We were interested in carrying out the corresponding process of acetylation to give II (R = Ac).[3]

Treatment of the nitrone (I, R = Me) with acetic anhydride in carbon tetrachloride at −20° gave in reasonable yield a crystalline derivative of the composition $C_{11}H_{17}O_3N$ and therefore not the diacetyl compound (II, R = Ac) (Chart I). The new derivative showed in the ^1H nmr spectrum two acetyl groups, two vinyl hydrogens, and one hydrogen on a carbon to which an acetoxyl (or equivalent) function was attached. This, and other spectroscopic evidence, suggested structure III. The following experiments confirmed the correctness of this suggestion. Hydrogenation of derivative III over palladized charcoal (1-mol uptake) gave a compound (IV) which showed an additional secondary methyl group in its nmr spectrum. Treatment of derivative III with aqueous acetic acid containing a little hydrochloric acid at 0° gave smoothly ketoamide V in which the methyl ketone function could be readily recognized in the nmr spectrum. Ketoamide V was characterized as its crystalline 2,4-dinitrophenylhydrazone derivative, a compound which could be prepared directly by treating III with acidic 2,4-dinitrophenylhydrazine solution. The acid-catalyzed hydration of III to give V is a conventional enamide reaction, but the acetylation process itself deserves brief comment. Acetylation of nitrone I should give either enamine VI or its analog VII. The rearrangement of this type of compound to the corresponding imines (VIII and IX,

CHART I



respectively) has much precedent.[4] The N acetylation of VIII and concommitant loss of methyl proton would furnish III directly. A route from IX would require a further allylic rearrangement which would be improbable in the presence of only a small amount of acetic acid at −20 to 0°. The driving force for such an additional rearrangement would also appear to be lacking. We favor, therefore, the direct route I (R = Me) → VI → VIII → III.

Since the methyl group of nitrone I (R = Me) was not functionalized by the acetylation process, we considered also a direct oxidation procedure to give aldehyde I (R = CHO), or other equivalent derivative. It had been shown earlier[5] that oxidation of I (R = Me) with selenium dioxide in methanol[6] under reflux gave a dark oil which with dilute hydrochloric acid afforded crystalline nitrone X. We have found that the selenium dioxide oxidation of I (R = Me) will proceed smoothly at room temperature in ether to give I (R = CHO) in satisfactory (65%) yield. This aldehyde readily afforded a crystalline dimedone derivative and showed the expected aldehyde proton in the nmr spectrum. Oxidation of the aldehyde with silver oxide afforded the corresponding crystalline acid (I, R = CO_2H). A by-product from the selenium dioxide oxidation was the rearranged nitrone X. Indeed if the initial selenium dioxide oxidation solution was left to stand at room temperature substantial amounts of nitrone X were formed. An attempted formation of the 2,4-dinitrophenylhydrazone of aldehyde I (R = CHO) afforded only the known derivative of X. The facile rearrangement of I (R = CHO) to X

(1) R. Bonnett, R. F. C. Brown, V. M. Clark, I. O. Sutherland, and A. Todd, *J. Chem. Soc.*, 2094 (1959), and sequential papers.

(2) J. Hamer and A. Macaluso, *Chem. Rev.*, **64**, 473 (1964); G. R. Delpierre and M. Lamchen, *Quart. Rev.* (London), **19**, 329 (1965).

(3) Compare F. Agolini, R. Bonnett, D. E. McGreer and G. F. Stephenson, *J. Chem. Soc., C*, 1491 (1966).

(4) *Inter alia* T. Cohen and J. H. Fager, *J. Amer. Chem. Soc.*, **87**, 5701 (1965); T. Cohen and G. L. Deets, *ibid.*, **89**, 3939 (1967); R. F. C. Brown, W. D. Crow, L. Subrahmanyan, and C. S. Barnes, *Aust. J. Chem.*, **20**, 2485 (1967); R. Bodalski and A. R. Katritzky, *Tetrahedron Lett.*, 257 (1968).

(5) R. F. C. Brown, V. M. Clark, and A. Todd, *J. Chem. Soc.*, 2105 (1959).

(6) Compare M. Lamchen, *J. Chem. Soc.*, 2300 (1966).