In the previous work[4] N-arylhydroxylamines were condensed with hydroxymethyleneacetophenone to give 3-(N-hydroxyanilino)acrylophenones, **2**. Although treatment with aqueous acid was known to lead to simple hydrolysis of compounds of type **2**,[6] it was found that dehydrative cyclization to **1** took place in concentrated sulfuric acid.

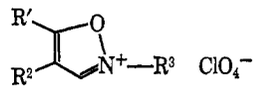
Our further examination of this approach with phenylmalonaldehyde, **3**, and N-benzylhydroxylamine, **4**, revealed that cyclization can also be achieved under mildly acidic conditions in nonaqueous media. Moreover, the condensation and cyclization steps can both be carried out simply by adding 70% perchloric acid to a solution of **3** and **4** in ether, from which the insoluble product 2-benzyl-4-phenylisoxazolium perchlorate, **5**, precipitates. The scope of the new method is demonstrated by the preparation of 2-benzyl-4-methyl-5-phenylisoxazolium perchlorate, **6**, from the more hindered dicarbonyl compound 2-benzoylpropanal, **7**, and of 2,5-diphenyl-4-methylisoxazolium perchlorate, **8**, from **7** and N-phenylhydroxylamine, **9** (Scheme I).

SCHEME I

$R'COCHR^2CHO + R^3NHOH + HClO_4 \longrightarrow$

3, $R' = H$; $R^2 = Ph$ **4**, $R^3 = PhCH_2$

7, $R' = Ph$; $R^2 = Me$ **9**, $R^3 = Ph$



5, $R' = H$; $R^2 = Ph$; $R^3 = CH_2Ph$

6, $R' = Ph$; $R^2 = Me$; $R^3 = CH_2Ph$

8, $R' = R^3 = Ph$; $R^2 = Me$

Experimental Section

Melting points were determined with a Mel-temp apparatus and are uncorrected. The nmr spectra were run on a Varian A-60 spectrometer, and the uv spectra were recorded with a Cary 14 spectrophotometer. Elemental analyses were performed by A. Bernhardt, Mikroanalytisches Laboratorium, West Germany.

2-Benzyl-4-phenylisoxazolium Perchlorate (5).—A mixture of 0.6 g (4.1 mmol) of phenylmalonaldehyde, **3**, and 0.5 g (4.1 mmol) of N-benzylhydroxylamine, **4**, in 50 ml of dry ether was stirred while 0.4 ml of 70% $HClO_4$[7] was added dropwise. After 24 hr the ether was decanted, leaving an orange oil. Several precipitations of the oil from MeCN (10-ml portions) with ether (75-ml portions) gave 0.85 g (62%) of white crystals: mp 125–125.5°; nmr (MeCN) δ 5.93 (s, 2), 7.4–7.82 (unresolved, 10), 9.37 (s, 1), 9.77 (s, 1).

Anal. Calcd for $C_{16}H_{14}ClNO_5$: C, 57.24; H, 4.20; N, 4.18. Found: C, 57.06; H, 4.24; N, 4.03.

2-Benzyl-4-methyl-5-phenylisoxazolium Perchlorate (6).—A solution of 4.0 g (24.7 mmol) of 2-benzoylpropanal, **7**, and 3.0 g (24.7 mmol) of **4** in 1 l. of ether was stirred vigorously at 0° while 2.6 ml of 70% $HClO_4$ was added dropwise. After 24 hr the crystals of **6**, 7.2 g (84%), were filtered and washed with ether. Precipitation of the product from 50 ml of MeCN with 800 ml of ether gave white crystals: mp 138–140°; uv max (CH_2Cl_2) 300 mμ (ϵ 19,000); nmr (98% H_2SO_4, positions upfield relative to H_2SO_4) δ 2.62 (s, 1), 3.7 (broad, 10), 5.5 (s, 1), 8.72 (s, 3).

Anal. Calcd for $C_{17}H_{16}ClNO_5$: C, 58.38; H, 4.61; Cl, 10.14; N, 4.00; O, 22.87. Found: C, 58.42; H, 4.65; Cl, 10.07; N, 4.18; O, 22.95.

(6) J. Thesing, A. Müller, and G. Michel, *Chem. Ber.*, **88**, 1027 (1955).

(7) In view of the explosion hazard associated with the use of perchloric acid, all reactions were carried out behind a sturdy safety shield. Although no detonations were encountered in the present work, it should be noted that some isoxazolium perchlorates have been found to be impact-sensitive explosives.[3]

2,5-Diphenyl-4-methylisoxazolium Perchlorate (8).—A solution of 4.5 g (27.8 mmol) of **7** and 3.0 g (28 mmol) of N-phenylhydroxylamine, **9**, in 1 l. of ether was stirred vigorously with protection from the light while 3 ml of 70% $HClO_4$ was added dropwise. After 3 hr a grey precipitate, 7 g (75%), was filtered, washed with ether, and dried. Precipitation of the product from MeCN with ether gave off-white, light-sensitive crystals: mp 166–167° dec; uv max (CH_2Cl_2) 332 mμ (15,900); nmr (98% H_2SO_4, positions upfield relative to H_2SO_4) δ 3.18–3.62 (m, 10), 2.05 (s, 1), 8.6 (s, 3).

Anal. Calcd for $C_{16}H_{14}NO_5Cl$: C, 57.24: H, 4.20; N, 4.18; Cl, 10.55; O, 23.82. Found: C, 57.30; H, 4.23; N, 4.28; Cl, 10.59; O, 23.79.

Registry No.—**5**, 19614-31-4; **6**, 19614-32-5; **8**, 19614-33-6.

Reaction of 2-Trichloroacetamido-5-chlorobenzhydrol with Potassium Hydroxide to Give 4-Phenyl-6-chloro-1,4-dihydro-2H-3,1-benzoxazin-2-one

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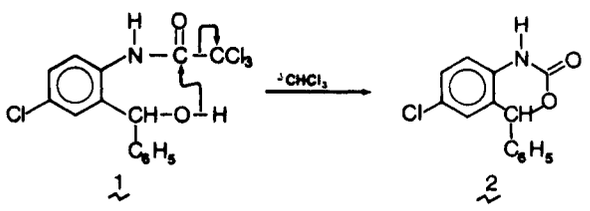
Several examples have been recently reported of cyclizations of 2-chloroacetamidobenzhydrols under basic conditions to give 1,5-dihydro-5-phenyl-4,1-benzoxazepin-2(3H)-ones.[1-4]

In the present study we investigated the reaction of 2-trichloroacetamido-5-chlorobenzhydrol (**1**) with alcoholic base. A crystalline compound $C_{14}H_{10}ClNO_2$ was the only product obtained; ir bands at 1705 and 3210 cm^{-1} suggested the presence of a RNHCOOR group,[5] and the nmr results established the oxazine structure **2**.[6] The formation of **2** might be considered as an intramolecular displacement of chloroform by the neighboring benzhydrilic function (Scheme I).

SCHEME I



An alternative mechanism, involving formation and cyclization of the intermediate isocyanate, could also be considered. To clarify this matter, we planned the synthesis of 2-(N-methyltrichloroacetamido)-5-chlorobenzhydrol, which cannot lead to an isocyanate. Unexpectedly, the reaction of 2-methylamino-5-chlorobenzhydrol with trichloroacetyl chloride in the presence

(1) E. Testa, L. Fontanella, and M. Bovara, *Farmaco, Ed. Sci.*, **18**, 815 (1963).

(2) G. I. Poos, U. S. Patent 3,122,554 (1964); *Chem. Abstr.*, **60**, 12036 (1964).

(3) Lepetit S.p.A., French Patent 1,405,271 (1965); *Chem. Abstr.*, **63**, 13298 (1965).

(4) E. Testa and L. Fontanella, *Farmaco, Ed. Sci.*, **20**, 323 (1965).

(5) L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen & Co. Ltd., London, 1962, pp 221–222.

(6) E. Testa and L. Fontanella, *Farmaco, Ed. Sci.*, **21**, 549 (1966).

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.

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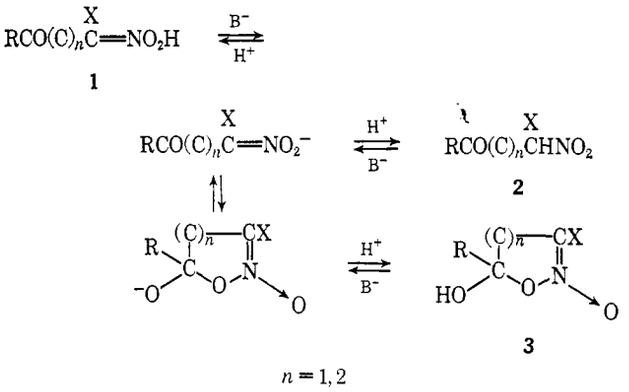
Many 3- and 4-keto-1-nitro- (and 1,1-dinitro-) alkanes are known.[2,3] Their nitronate salts on mild acidification may undergo very rapid O protonation to form the corresponding 3- and 4-ketonitronic acids (**1**) (Scheme I), which usually are consumed in solution by relatively slower C protonation of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

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(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).