[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

Action of Nitrosyl Chloride on Oximino Esters[1]

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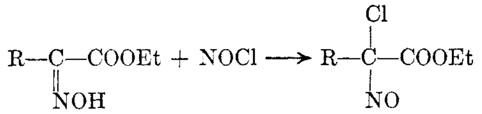
Nitrosyl chloride reacts with α-oximino esters to give good yields of α-chloro-α-nitroso esters. The new esters have been characterized by infrared and ultraviolet absorption spectra and oxidized to α-chloro-α-nitro esters. The limitations of the reaction have been investigated.

Nitrosyl chloride reacts with aldoximes[2] and ketoximes[3] to give chloro nitroso compounds which also can be prepared from oximes by reaction with dry chlorine in ether.[4] Their structures are based on oxidation[3] and reduction[4] reactions and conversion of the bromine analogs to pseudo nitroles with silver nitrite.[5]

The reaction of nitrosyl chloride with α-oximino esters (I, R = alkyl) proceeds smoothly at 0° in methylene chloride or ether *in the absence of light* to give α-chloro-α-nitroso esters (II, R = alkyl). Under the same conditions the first member of the series (I, R = H) is converted in good yield to the hydroxamic acid chloride I (R = Cl), the isomer of II (R = H). Oximino esters with strong electrophilic groups (I, R = Cl, C≡N, NO_2) are unchanged by nitrosyl chloride except for ethyl α-oximinoacetoacetate (I, R = CH_3CO), which reacts with nitrosyl chloride in methylene chloride to give a mixture of chloro and chloronitro esters. Ethyl aminooximinoacetate (I, R = NH_2) reacts with nitrosyl chloride in methylene chloride with formation of ethyl chloroöximinoacetate and an ester $C_4H_6ClNO_2$, which is tentatively assigned the structure of ethyl chloroiminoacetate.



$$\underset{\text{I}}{R{-}\underset{\underset{\text{NOH}}{\|}}{C}{-}COOEt} + NOCl \longrightarrow \underset{\text{II}}{R{-}\overset{\text{Cl}}{\underset{\text{NO}}{C}}{-}COOEt}$$

The results of the addition reactions are consistent with an ionic mechanism involving the addition of NO^+Cl^- to the carbon nitrogen double bond of oximino esters (I) to give nitrosohydroxylamine intermediates (III) which can decompose spontaneously to the nitroso esters II.[6] *N*-Nitrosohydroxylamines have been isolated previously as low melting and rather unstable solids which tend to decompose to nitroso compounds.[7]

$$\underset{\text{I}}{R{-}\underset{\underset{\text{NOH}}{\|}}{C}{-}COOEt} + NOCl \longrightarrow \underset{\text{III}}{\left[R{-}\underset{\underset{\text{N(NO)OH}}{|}}{C}ClCOOEt\right]}$$

The new nitroso esters are blue liquids, sensitive to light and heat. Their structures have been established by oxidation to the corresponding α-chloro-α-nitroesters with peroxytrifluoroacetic acid.

Absorption spectral data indicate that the esters are essentially monomeric nitroso compounds. Thus they exhibit a weak absorption maximum near 640 mμ[4,8] and characteristic infrared absorption bands at 6.39μ (N=O),[4,9] while dimer bands are absent.

The infrared band at 6.39μ ± 0.01μ is given by the α-chloro-α-nitroso esters, 2-chloro-2-nitrosopropane, 1-chloro-1-nitrosocyclohexane and propylpseudonitrole (Table I).

TABLE I

INFRARED ABSORPTION SPECTRA OF NITRO AND NITROSO COMPOUNDS[a]

	C=O	N=O	As NO_2	*sym*-NO_2
$CH_3CCl(NO)CH_3$	—	6.39	—	—
$CH_3C(NO)NO_2CH_3$[b]	—	6.40[c]	6.31[c]	7.42
$CH_3CCl(NO)COOEt$	5.71	6.39	—	—
$CH_3CCl(NO_2)COOEt$	5.67	—	6.33	7.46
$C_2H_5CCl(NO)COOEt$	5.72	6.39	—	—
$C_2H_5CCl(NO_2)COOEt$	5.68	—	6.34	7.42

[a] Determined as capillary films except as noted. [b] Dissolved in chloroform, 10% solution. [c] The band assignments in this case are apparently opposite to those of Lüttke, who gives the nitroso band as 6.31μ.[9] The present assignment is favored because the nitro band occurs at the lower wave lengths (6.33–6.34μ) in α-chloronitro esters.

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] H. Rheinboldt and M. Dewald, *Ann.*, **451**, 161, 273 (1927).

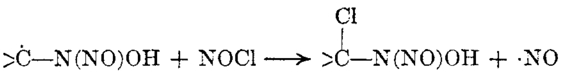
[3] H. Rheinboldt and M. Dewald, *Ann.*, **455**, 300 (1927).

[4] E. Müller, H. Metzger, and D. Fries, *Chem. Ber.*, **87**, 1450 (1954).

[5] O. Piloty and A. Stock, *Ber.*, **35**, 3093 (1902).

[6] An alternate path to the same nitrosohydroxylamine intermediates III involving free radicals could, however, be written as follows:

$$>C{=}NOH + \cdot NO \longrightarrow >\dot{C}{-}N(NO)OH$$



$$>\dot{C}{-}N(NO)OH + NOCl \longrightarrow >\overset{\overset{\text{Cl}}{|}}{C}{-}N(NO)OH + \cdot NO$$

[7] E. Müller and H. Metzger, *Chem. Ber.*, **89**, 396 (1956).

[8] S. Mitchell and co-workers, *J. Chem. Soc.*, 1964 (1938); 602 (1941); D. L. Hammick and M. W. Lister, *J. Chem. Soc.*, 489 (1937); G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **67**, 994 (1945); G. Kortüm, *Z. Elektrochem.*, **47**, 55 (1941); J. R. Schwartz, *J. Am. Chem. Soc.*, **79**, 4353 (1957).

[9] W. Lüttke, *Z. Elektrochem.*, **61**, 302 (1957).

The N=O stretching band is observed occasionally in pure liquid nitroso esters (II) as a doublet (6.32–6.33μ and 6.38–6.39μ), as is found for 1-chloro-1-nitrosocyclohexane (6.34 and 6.39μ). Splitting into two bands of nearly equal intensity is believed to be due to rotational isomerism.[9] Weaker bands, which occur in the region of 7.3μ, 9.0μ, and 12μ, could not be observed in all nitroso compounds and were not assigned for this reason.

The reactions of nitrosyl chloride with ethyl oximinoacetoacetate and ethyl aminoöximinoacetate involve steps other than simple addition, such as cleavage of carbon-carbon bonds, chlorination, oxidation, and elimination reactions which require further investigation for their complete elucidation.

While ketoximes can be chlorinated in dry ether to give chloro nitroso compounds,[4] the corresponding reaction of α-oximino esters (I, R = alkyl) gives products devoid of nitro or nitroso groups.

EXPERIMENTAL

All temperatures uncorrected. Analyses by M. Naranjo.

Ethyl α-chloro-α-nitrosopropionate. A solution of ethyl α-oximinopropionate (5.0 g., 0.038 mole) in methylene chloride (80 ml.) was immersed in an ice bath and treated with a slow stream of nitrosyl chloride until the weight increase was 4.0 g. (A large excess of nitrosyl chloride must be avoided.) The mixture was allowed to stand at 0° for 45 hr., concentrated on a steam bath to half its volume, and evaporated at 50 mm. and then at 1 mm. The residual blue oil weighed 5.5 g. (89%) and had n_D^{25} 1.4334, λ_{max} (cyclohexane) 635 mμ, ϵ 5.0.

Anal. Calcd. for $C_5H_8ClNO_3$: C, 36.28; H, 4.86; N, 8.46. Found: C, 35.54; H, 4.59; N, 8.58.

The nitroso esters were sensitive to light, heat, and air and proved difficult to burn in the standard micro combustion procedure.

Oxidation of α-chloro-α-nitrosopropionate (5.0 g., 0.030 mole) with 90% hydrogen peroxide (1.05 ml., 0.035 mole) and trifluoroacetic anhydride (7.35 g., 0.035 mole) in chloroform (40 ml.) at 0° gave 4.0 g. (63%) of crude nitro ester, b.p. 45° (0.05 mm.), n_D^{25} 1.4358.

Anal. Calcd. for $C_5H_8ClNO_4$: C, 33.09; H, 4.44; N, 7.72. Found: C, 32.67; H, 4.58; N, 8.31.

Ethyl α-chloro-α-nitrosobutyrate. The reaction of ethyl α-oximinobutyrate with nitrosyl chloride was carried out essentially as for the lower homolog. The product, obtained in 80% yield, had n_D^{25} 1.4348, λ_{max} (cyclohexane) 640 mμ, ϵ 5.4.

Anal. Calcd. for $C_6H_{10}ClNO_3$: C, 40.12; H, 5.61; N, 7.80. Found: C, 40.83; H, 5.73; N, 7.80.

Oxidation with peroxytrifluoroacetic acid gave an 84% yield of ethyl α-chloro-α-nitrobutyrate, b.p. 45° (0.05 mm.), n_D^{25} 1.4371.

Anal. Calcd. for $C_6H_{10}ClNO_4$: C, 36.85; H, 5.15; N, 7.16. Found: C, 37.35; H, 5.26; N, 7.48.

The reaction of ethyl oximinoacetate with nitrosyl chloride. Ethyl oximinoacetate (2.39 g., 0.0204 mole), dissolved in methylene chloride (50 ml.), was treated with nitrosyl chloride at 0° until the weight increase was in excess of the theoretical amount (1.33 g., 0.0204 mole) and the red solution was allowed to stand at 0° for 16 hr. Evaporation of the solution under reduced pressure gave 2.90 g. of crystalline residue which was recrystallized from benzene-petroleum ether (b.p. 30–60°). The melting point and mixed m.p. with authentic ethyl chloroöximinoacetate was 78–79° (lit. m.p. 80°),[10] yield 1.86 g. (65%), λ(OH) 3.02, λ(C=O) 5.71, 5.80, λ(C=N) 6.16μ (liquid film).

Ethyl oximinoacetate. A mixture of ethyl glyoxylate hemiacetal (7.40 g., 0.05 mole) and hydroxylamine hydrochloride (3.47 g., 0.05 mole) was heated on a steam bath with 5 ml. of 95% ethanol for 3 hr. The hydrochloride went gradually into solution and hydrogen chloride was evolved. The solution was evaporated under reduced pressure and the residual oil was distilled from a Hickman still. The oximino ester boiled at 70° (0.03 mm.), yield 2.39 g. (41%), λ(OH) 3.03, λ(C=O) 5.80, λ(C=N) 6.15μ (liquid film). The distillate solidified on cooling to colorless prisms, m.p. 31° (lit. m.p. 35°).[11]

The reaction of ethyl α-oximinoacetoacetate with nitrosyl chloride. Ethyl α-oximinoacetoacetate (5.0 g., 0.031 mole), dissolved in 100 ml. of methylene chloride, was treated with nitrosyl chloride at 0° until the weight of the mixture had increased by 7.5 g. The brown solution was allowed to stand at 0° for 16 hr. Excess nitrosyl chloride and solvent were removed on a steam bath and the remaining liquid was evaporated under reduced pressure. The crude residue, n_D^{25} 1.4495, was separated by chromatographic adsorption on silica gel. The benzene eluate contained 8% of nearly colorless chloronitro ester, n_D^{25} 1.4493, λ(C=O) 5.69μ, $\lambda(NO_2)$ 6.29, 7.36 μ.

Anal. Found: C, 39.40; H, 4.38; N, 2.55.

The ether eluate of the chromatogram furnished 62% of yellow oil yielding 32% of alkali-insoluble oil which contained chlorine and carbethoxyl but was devoid of nitro group, and a small quantity of alkali-soluble chloronitro ester, λ(C=O) 5.73μ, $\lambda(NO_2)$ 6.38, 7.32μ.

The reaction of ethyl aminoöximinoacetate with nitrosyl chloride. The product from ethyl aminoöximinoacetate (0.50 g.), methylene chloride (50 ml.) and a slight excess of nitrosyl chloride (18 hr. at 0°) was purified by distillation from a Hickman still. A small amount of distillate (50 mg.) boiled at 60° (0.05 mm.), contained chlorine, and partially solidified on standing, λ(NH) 3.10μ, λ(C=O) 5.75μ, λ(C=N) 6.14μ.

Anal. Calcd. for $C_4H_6ClNO_2$: C, 35.45; H, 4.46; N, 10.35. Found: C, 35.51, 36.10; H, 4.31, 5.14; N, 10.05.

Some residue which remained in the flask decomposed into volatile products on further heating, a behavior ascribed to imino chlorides.[12]

The product from a duplicate run was purified by crystallization from hexane (30 ml.) and yielded colorless needles, m.p. 77–78°, yield 0.28 g., identified as ethyl chloroöximinoacetate.

Anal. Calcd. for $C_4H_6ClNO_3$: C, 31.69; H, 3.99; N, 9.24. Found: C, 31.88; H, 3.12; N, 9.19.

Ethyl oximinocyanoacetate, ethyl chloroöximinoacetate, and ethyl nitroöximinoacetate were recovered unchanged when their solutions in methylene chloride or other solvents were allowed to stand with nitrosyl chloride for 14–24 hr. at 0°.

Absorption Spectra. Ultraviolet absorption spectra were determined in 1-cm. cells with a model DR Beckman spectrophotometer. Since the nitroso esters were photosensitive, their solutions were protected from light. Fading of the blue color, however, could not be entirely prevented. Infrared absorption spectra were obtained as capillary films or in chloroform solution with a Model 21 Perkin-Elmer spectrophotometer.

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[10] G. S. Skinner, *J. Am. Chem. Soc.*, **46**, 738 (1924).

[11] L. J. Simon and G. Chavanne, *Compt. rend.*, **143**, 906 (1906).

[12] E. Ott, *Ber.*, **52**, 660 (1919).