yield) of yellow solid, m.p. 248–251°. (Additional product was obtainable by further dilution.) Crystallization from acetic acid or xylene raised the m.p. to 257–258°.

Anal. Calcd. for $C_{21}H_{14}O_4S$: C, 69.6; H, 3.9; S, 8.8. Found: C, 69.4; H, 3.6; S, 8.8.

5-Benzamido-1-(p-toluenesulfonyl)anthraquinone (II). 5-Benzamido-1-chloroanthraquinone crystallized from acetic acid as orange-yellow needles, m.p. 221.5–222.5°.

Anal. Calcd. for $C_{21}H_{12}ClNO_3$: C, 69.7; H, 3.3; Cl, 9.8; N, 3.9. Found: C, 69.8; H, 3.4; Cl, 9.8; N, 3.7.

A mixture of 1.8 g. (5.0 mmol.) 5-benzamido-1-chloroanthraquinone and 1.0 g. (5.6 mmol.) sodium *p*-toluenesulfinate in 25 ml. of diethylene glycol monoethyl ether was stirred under reflux for 7 hr. in an oil bath at 195–200°, cooled partially, diluted with about 3 ml. of water, cooled to room temperature, and filtered. The orange-yellow product was crystallized from 40 ml. xylene, giving a yield of 1.40 g. (58%) with m.p. 257–260°. Crystallization from acetic acid or xylene raised the m.p. to 259–260°.

Anal. Calcd. for $C_{28}H_{19}NO_5S$: C, 69.8; H, 4.0; N, 2.9; S, 6.6. Found: C, 69.7; H, 3.7; N, 3.2; S, 6.8.

4-Amino-1-(p-toluenesulfonyl)anthraquinone (III). 4-Benzamido-1-chloroanthraquinone crystallized from acetic acid as yellow needles of m.p. 234.5–236°.

Anal. Calcd. for $C_{21}H_{12}ClNO_3$: C, 69.7; H, 3.3; Cl, 9.8; N, 3.9. Found: C, 69.5; H, 3.5; Cl, 9.9; N, 3.9.

A mixture of 5.0 g. (0.014 mole) 4-benzamido-1-chloroanthraquinone, 3.0 g. (0.017 mole) sodium *p*-toluenesulfinate, and 50 ml. of diethylene glycol monoethyl ether was stirred and refluxed for 16 hr., cooled slightly, diluted with 5 ml. of water, cooled to room temperature, and filtered. The product was washed with a little methanol and crystallized from 500 ml. of xylene, giving 2.6 g. (50%) of orange solid, m.p. 254–259°. Crystallization from acetic acid raised the m.p. to 260–261°.

Anal. Calcd. for $C_{21}H_{15}NO_4S$: C, 66.9; H, 4.0; S, 8.5. Found: C, 67.2; H, 3.8; S, 8.6.

As with others of these sulfones, yields were lower on larger runs. On 5 hr. refluxing in sirupy phosphoric acid, this product is converted to 1-aminoanthraquinone, identified by m.p., analysis, and formation of the benzoyl derivative.

The *N*-benzoyl derivative (IV) of the sulfone was prepared by 3 hr. refluxing with benzoyl chloride in *o*-dichlorobenzene. It crystallized from acetic acid in fine yellow needles, m.p. 273–275°.

Anal. Calcd. for $C_{28}H_{19}NO_5S$: C, 69.8; H, 4.0; N, 2.9; O, 16.6; S, 6.6. Found: C, 70.0; H, 4.0; N, 2.8; O, 16.5; S, 6.7.

2-(p-Toluenesulfonyl)anthraquinone (V). A mixture of 2.9 g. (0.010 mole) 2-chloro-3-anthraquinonecarboxylic acid and 6.0 g. (0.034 mole) sodium *p*-toluenesulfinate in 75 ml. of diethylene glycol monoethyl ether was stirred under reflux for 24 hr. in an oil bath at 190–195°. After cooling, dilution with water, and filtration, the product was crystallized from 30 ml. of acetic acid containing 4 ml. of water, giving 0.95 g. (26% yield) yellow solid, m.p. 194–205°. Further crystallization from acetic acid alternating with mixed amyl alcohols gave 0.60 g. (17% yield) of white product, m.p. 211.5–212.5°. It was insoluble in ammonium or sodium hydroxide.

Anal. Calcd. for $C_{21}H_{14}O_4S$: C, 69.6; H, 3.9; S, 8.8. Found: C, 69.5; H, 3.8; S, 8.8.

A mixture of 2.4 g. (0.010 mole) 2-chloroanthraquinone and 2.0 g. (0.011 mole) sodium *p*-toluenesulfinate in 75 ml. of diethylene glycol monoethyl ether, stirred and refluxed at 185–195° for 5 hr., gave 2.1 g. yellow solid, m.p. approximately 175–190°, unchanged upon crystallization first from acetic acid and then from ethylene glycol monomethyl ether. The presence of the sulfone in the mixture was indicated by a prominent infrared absorption band at 1143 cm.$^{-1}$, which is in the region characteristic of sulfone absorption,[3] and is also shown by the pure sulfone but not by 2-chloroanthraquinone.

Elementary analysis for chlorine and sulfur was in agreement with a mixture containing 47% sulfone and 53% 2-chloroanthraquinone.

Anal. Calcd. for 47% $C_{21}H_{14}O_4S$ and 53% $C_{14}H_7ClO_2$: Cl, 7.7; S, 4.1. Found: Cl, 7.9; S, 4.1.

When the reaction was run for 24 hr. with a 3:1 mole ratio of sodium *p*-toluenesulfinate to 2-chloroanthraquinone, a chlorine-free mixture was obtained, again too low in sulfur content for the sulfone.

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(3) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2d. ed., J. Wiley & Sons, Inc., New York, 1958, p. 361.

Nitrosation of α-Aceto-γ-butyrolactone. Isolation of an *O*-Acetyloximino Intermediate

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In the course of some synthetic work in the amino acid field we had occasion to prepare α-oximino-γ-butyrolactone (IV). When this preparation was carried out by the method of Feofilaktov and Onishchenko,[1] a procedure which involves the reaction of nitrous acid with α-aceto-γ-butyrolactone (I), an intermediate compound, not previously described by the Russian workers, was isolated. This white, crystalline product (m.p. 89–90°) is sensitive to solvolytic action and thus is slowly hydrolyzed in the presence of moisture to form the desired α-oximino-γ-butyrolactone (IV) with the liberation of acetic acid. Hydrolysis with dilute hydrochloric acid readily converts this intermediate compound to IV in 68% yield.[2]

From similar experiments, Sudo and co-workers[3] and also Reppe and co-workers[4] reported the isolation of an intermediate compound (m.p. 88°) which appears to be identical to the one described above. These investigators assumed that this compound was α-aceto-α-nitroso-γ-butyrolactone (II). The compound isolated in our laboratory showed infrared absorption bands at 5.98μ and 8.50μ. The presence of these bands, which were interpreted as corresponding to a C=N grouping and to

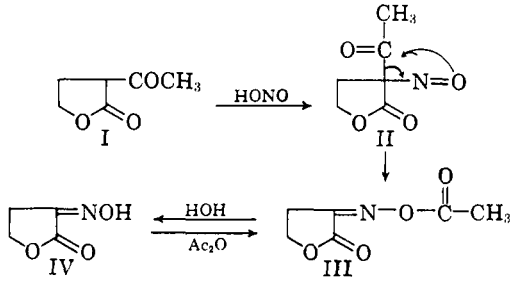
(1) V. Feofilaktov and A. Onishchenko, *J. Gen. Chem. (U.S.S.R.)*, **9**, 304 (1939); *Chem. Abstr.*, **34**, 378 (1940).

(2) Gas evolution was observed during the course of this hydrolysis. It is possible that some of the lactone is opened and the resulting α-oximino (or α-keto) acid undergoes decarboxylation to produce β-hydroxypropionaldehyde or the corresponding oxime.

(3) R. Sudo, Y. Akiyama, T. Kato, and M. Ohta, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **74**, 1009 (1953); *Chem. Abstr.*, **49**, 6829 (1955).

(4) W. Reppe and co-workers, *Ann.*, **596**, 164 (1955).

an acetoxy group of the enol acetate type, respectively, and the apparent absence of a nitroso band in the spectrum indicated that this compound was probably not the nitroso derivative II, as claimed by the previous workers,[3,4] but was rather *O*-acetyl-α-oximino-γ-butyrolactone (III). Furthermore, this product showed an ultraviolet absorption maximum in acetonitrile solution at 210 mμ (ϵ = 13,400) indicating the presence of a conjugated chromophoric grouping. The presence of such a group is consistent with structure III but not with structure II. Isolation of unchanged III from acetonitrile solution indicated that the ultraviolet absorption was due to the oximino acetate III and not to its hydrolytic product IV (λ_{max}^{MeCN} 218 mμ, ϵ = 11,200). Confirming evidence for structure III was obtained by comparison with a sample of III, prepared by acetylation of α-oximino-γ-butyrolactone (IV).



The formation of the *O*-acetyloximino derivative may be interpreted as proceeding *via* an intramolecular 1,3-rearrangement of the initially formed α-aceto-α-nitroso-γ-butyrolactone (II). This rearrangement may be considered analogous to the prototropic isomerization of a nitroso compound to its tautomeric oxime.[5]

It is interesting to note that Feofilaktov and Onishchenko[6] similarly observed the formation of *O*-acetyl-α-oximino-γ-chloromethyl-γ-butyrolactone on nitrous acid treatment of α-aceto-γ-chloromethyl-γ-butyrolactone. These workers considered the formation of the *O*-acetate as indicative of an anomalous course of reaction. However, in view of our results it is probable that the *O*-acetate is the usual intermediate for this type of reaction. Indeed, we would point out that these results are suggestive of a possible mechanism for the general reaction[7] whereby nitrous acid treatment of an α-substituted β-keto ester, malonic acid or ester, or cyanoacetic ester results in the replacement of an acyl group by an oximino group. It is possible that these reactions all involve an initial nitrosation followed by a rearrangement to a readily-solvolyzable *O*-acyloximino intermediate.

EXPERIMENTAL[8]

O-Acetyl-α-oximino-γ-butyrolactone (III). (A) *Nitrosation of α-aceto-γ-butyrolactone.* To a cooled (+5°) solution of α-aceto-γ-butyrolactone (I, 250 g., 1.95 mole) and sodium nitrite (160 g., 2.32 mole) in 400 ml. of water was added 400 ml. of 6*N* aqueous hydrochloric acid over a period of 1 hr. The reaction mixture was allowed to stand at +5° for an additional 3 hrs. and the precipitate which had formed was collected by filtration, washed with cold (+5°) water and dried *in vacuo* over phosphorus pentoxide to give 235 g. (77%) of crude III as tacky yellow crystals. Several recrystallizations from isopropanol gave 90 g. (29%) of III as colorless crystals, m.p. 89–90° ($\lambda_{max}^{CHCl_3}$, 5.56μ, 5.60μ, 5.98μ, 8.50μ; λ_{max}^{MeCN} 210 mμ; ϵ = 13,400).

Anal. Calcd. for $C_6H_7NO_4$: C, 45.9; H, 4.49; N, 8.92. Found: C, 46.0; H, 4.58; N, 8.97.

(B) *Acetylation of α-oximino-γ-butyrolactone* (IV). A suspension of α-oximino-γ-butyrolactone (IV, 3.45 g., 0.03 mole) in 25 ml. of acetic anhydride was heated for 15 min. at 90°. The resulting solution was allowed to cool slowly to room temperature over a period of 1 hr. and concentrated *in vacuo* on a water bath (50°). The residual oil was poured into 50 ml. of ethyl ether and the resulting solid was collected by filtration and dried *in vacuo* over phosphorus pentoxide to give 4.50 g. (95%) of colorless crystals, m.p. 86–89°. Recrystallization from isopropanol gave 4.15 g. of III, m.p. 89–90°. The infrared spectrum for this material was identical with that of the product obtained *via* the nitrosation of α-aceto-γ-butyrolactone (III) and admixture melting point gave no depression.

α-Oximino-γ-butyrolactone (IV). A suspension of *O*-acetyl-α-oximino-γ-butyrolactone (III, 70 g., 0.45 mole) in 250 ml. of 2*N* hydrochloric acid was heated to 50° for 30 min. and cooled to 10°. The precipitate which formed was collected by filtration, washed with water, and dried *in vacuo* at 50° to give 35.0 g. (68%) of IV as colorless crystals, m.p. 180–183°; λ_{max}^{MeCN} 218 mμ, ϵ = 11,200. Feofilaktov and Onishchenko[1] report m.p. 192–193°; Sudo *et al.*,[3] report m.p. 183°; Snyder *et al*,[9] report m.p. 183–185°.

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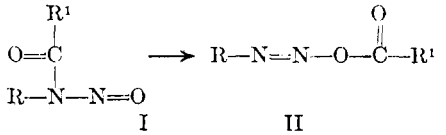
(5) A. Streitweiser and W. D. Schaeffer [*J. Am. Chem. Soc.*, **79**, 2893 (1957)] have postulated that rearrangement to a diazoester (II) represents the first step in the decomposition of acylnitroso amines (I).



We wish to thank one of the referees of this manuscript for calling this analogous rearrangement to our attention.

(6) V. Feofilaktov and A. Onishchenko, *Compt. rend. acad. sci., U.R.S.S.*, **20**, 133 (1938); *Chem. Abstr.*, **33**, 1725 (1939).

(7) For a review of this reaction see O. Touster, *Org. Reactions*, **VII**, 336 (1953).

(8) Melting points are uncorrected.

(9) H. R. Snyder, J. H. Andreen, G. W. Cannón, and C. P. Peters, *J. Am. Chem. Soc.*, **64**, 2082 (1942).