ease of formation of compounds of the Martius Yellow type.

The 2,4,6-trinitro-1-naphthol is an acidic compound and generally resembles its isomers in most properties. A pyridine salt was prepared and analyzed. This reacted with phosphorus oxychloride (8) to form 2,4,6-trinitro-1-chloronaphthalene.

EXPERIMENTAL

Melting points are uncorrected and were taken on a melting point block.

6-Nitro-1,4-naphthaquinone 4-oxime. While cooling to 5–10°, 5 g. (0.023 mole) of 1,7-dinitronaphthalene was added slowly, with stirring, to 100 ml. of 30% oleum and the solution left 19 hr. on ice. It was then poured slowly onto 1 kg. of ice and the precipitate filtered and washed. The product was extracted a number of times with dilute sodium carbonate solution and filtered from some insoluble material. On acidifying the combined filtrates, the nitroquinone oxime was precipitated and filtered, washed, and dried; yield 4.4 g., 88%. The compound was treated with charcoal in aqueous isopropyl alcohol and recrystallized from this solvent mixture. On heating, it sintered at 165–170° and darkened above 195°, with partial fusion and decomposition at 204–207°, forming a black mass.

Anal. Calcd. for $C_{10}H_6N_2O_4$; N, 12.84. Found: N, 12.8.

This conversion of 1,7-dinitronaphthalene into an alkali-soluble nitroquinone oxime allows a separation to be made from 1,3,5-trinitronaphthalene (the product of further nitration of 1,7-dinitronaphthalene), as the trinitro compound is unaffected by oleum under the conditions used.

2,4,6-Trinitro-1-naphthol. (a). *From 6-nitro-1,4-naphthaquinone 4-oxime.* A mixture of 1.2 g. (0.0055 mole) of the nitroquinone oxime and 40 ml. of acetic acid was warmed for solution and cooled to about 30°. To this solution, was added dropwise 3 ml. of 70% nitric acid. The first half of the acid caused considerable heating, and the temperature was kept below 45°. After mixing, the solution was kept at room temperature for 6 hr. and then diluted with 6–8 volumes of water. Next day, the yellow crystalline deposit was filtered, washed, and dried; yield 1.2 g., 78.2%. The product was recrystallized from aqueous methanol and then from water. It sintered 151–152° with m.p. 155.5–157°.

Anal. Calcd. for $C_{10}H_5N_3O_7$: C, 43.01; H, 1.79; N, 15.05. Found: C, 43.01; H, 2.12; N, 15.11.

(b). *From 6-nitro-1-naphthol.* A solution of 0.2 g. (1.06 mmoles) of this nitronaphthol in 2 ml. of acetic acid was treated dropwise (spontaneous warming) with 0.5 ml. of 70% nitric acid while keeping the temperature below 30°. The color soon lightened and the mixture was left to stand. After 1.5 hr., a considerable amount of crystalline material had deposited, and water (8 ml.) was added during 0.5 hr. to precipitate the remainder in crystalline form. The mixture was left to stand 8 hr. and the product filtered, washed with water, and dried. The yield was 0.22 g., 74.5%. A little is lost in washes.

(c). *From 4,6-dinitro-1-naphthol.* The nitration of this compound was similar to the preceding and gave a comparable yield.

The infrared spectra of the three nitration products were the same. Like the 2,4,7-trinitro-1-naphthol, this isomer gives a sparingly soluble sodium salt which may be used in its purification or recovery.

2,4,6-Trinitro-1-naphthol, pyridine salt. A solution of 1.05 g. (0.00376 mole) of the trinitronaphthol in 100 ml. of benzene was mixed with a solution of 2 ml. of anhydrous pyridine in 50 ml. of benzene, giving an immediate bright yellow precipitate. This was washed thoroughly with benzene and dried under vacuum; yield 1.20 g., 91.7%. It was not recrystallized but was analyzed directly. On heating, it melted at 160–185° dec.

Anal. Calcd. for $C_{16}H_{10}N_4O_7$: C, 50.28; H, 2.79; N, 15.64. Found: C, 50.41; H, 2.91; N, 15.61.

2,4,6-Trinitro-1-chloronaphthalene. This was prepared from the pyridine salt by the method of Gray, Schmidt, and Smith.[8]

Phosphorus oxychloride (15 ml.) was treated slowly with 6.3 g. (0.00176 mole) of the pyridine salt and the mixture stirred 10 min. at 45–50°. It was then cooled and poured onto an excess of ice, and stirred until the product was solid. After filtering and washing, it was dissolved in acetone, filtered, and re-precipitated by water. When washed and dried, this material weighed 5.0 g., 95.5%. The compound was recrystallized four times from methanol and then had m.p. 132–133°.

Anal. Calcd. for $C_{10}H_4N_3O_6Cl$: Cl, 11.9. Found: Cl, 11.5.

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Studies on Lactams. II.[1] A Simplified Synthesis

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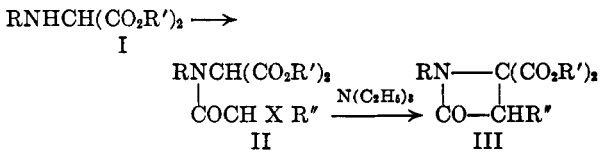
A general method for the synthesis of β-lactams of type III has been described by Sheehan and Bose[2] which involves the acylation of a substituted aminomalonate I to the amidomalonate II followed by its cyclization to III in the presence of a weak base such as triethylamine.



The acylation step has usually been carried out under nonbasic conditions[3] using a halo acid and phosphorus trichloride in benzene solution at the reflux temperature.

Further work has now shown that the conversion of a substituted aminomalonate I to the corresponding β-lactam III can be carried out in one operation. When to a benzene solution of I there are added the appropriate α-haloacyl halides and then an excess of triethylamine, heat is evolved and a solid starts to separate. This reaction mixture may either be allowed to stand at room temperature for about three days or heated under reflux for

(1)(a) Abstract of the 140th Meeting of the American Chemical Society, Chicago, Ill., September 1961, p. 1102. (b) Part I, ref. 4. (c) Part III, A. K. Bose and M. S. Manhas, *J. Org. Chem.*, **27**, 1244 (1962).

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TABLE I

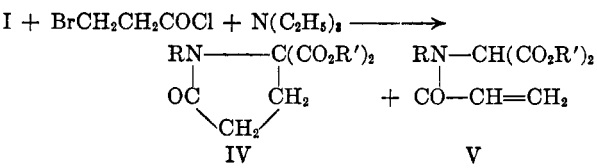
α-Halo Acid Halide	R	R′	R″	M.P.	Yield, %
$ClCH_2COCl$	C_6H_5	C_2H_5	H	38–39[a]	72
$BrCH_2COBr$	C_6H_5	C_2H_5	H	"	75
$ClCH_2COCl$	p-$CH_3C_6H_4$	C_2H_5	H	89–91[a]	83
$ClCH_2COCl$	$C_{10}H_7$	C_2H_5	H	75–76[a]	79
$C_6H_5CHClCOCl$	C_6H_5	C_2H_5	C_6H_5	87–88	74

[a] See ref. 2.

about three hours. The product from this reaction is the β-lactam III in about 70–80% yield (based on I).

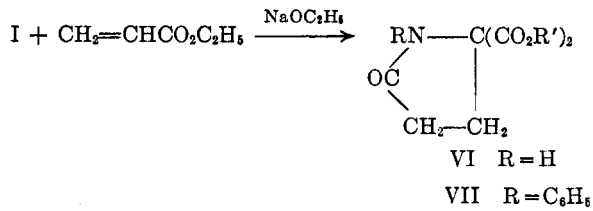
The preparation of several β-lactams (III) obtained by this one-step method is summarized in Table I.

Bose, Ghosh-Mazumdar, and Chatterji[4] have shown that γ-lactams of type IV can also be prepared by a two-step sequence similar to that used for the synthesis of the β-lactam III. When the conversion of I to IV in one operation was attempted using a β-halo acid halide and triethylamine, the yield of the γ-lactam IV was very poor. On the basis of infrared and proton magnetic resonance spectra, it was found that the major by-product was the substituted acrylamide V.



Cocolas and Hartung[5] have observed that the prolonged reaction of diethyl acetamidomalonate with ethyl acrylate in presence of sodium ethoxide leads to the γ-lactam VI.

When we allowed I (R = phenyl) to react with ethyl acrylate in presence of sodium ethoxide, the γ-lactam VII[4] was obtained in one operation in high yield.



EXPERIMENTAL

A typical procedure for the one-step synthesis of β-lactams of type III is illustrated by the following preparation.

1,3-Diphenyl-4,4′-dicarbethoxyazetidin-2-one. To a solution of 2.5 g. of diethyl anilinomalonate in 25 ml. of benzene were added 2.0 g. of α-chlorophenylacetyl chloride and 3 g. of triethylamine. A white solid separated out and the reaction mixture became warm. The mixture was allowed to stand at room temperature for 3 days and then filtered. The filtrate was washed with dilute hydrochloric acid and with water. After drying the washed filtrate over anhydrous magnesium sulfate, the solvent was removed under reduced pressure when 7.6 g. of a brown, semisolid mass was obtained. Recrystallization from a mixture of petroleum ether and ethyl acetate afforded 6 g. (74% yield) of colorless needles, m.p. 87–88°, λ_{max}^{Nujol} 5.62 μ (1783 cm.$^{-1}$, β-lactam carbonyl), 5.68 μ and 5.72 μ (1761 cm.$^{-1}$ and 1748 cm.$^{-1}$, ester groups).

Anal. Calcd. for $C_{21}H_{21}NO_5$: C, 68.65; H, 5.76; N, 3.81. Found: C, 69.14; H, 6.54; N, 3.85.

1-Phenyl-5,5-dicarbethoxypyrrolidin-2-one.[4] A solution of 5 g. of diethyl anilinomalonate in 50 ml. of absolute ethanol was added to a solution of 78 mg. of sodium in 5 ml. of absolute ethanol taking the usual precautions for precluding moisture. Three grams of ethyl acrylate was then added with stirring over a period of 30 min., and the mixture was heated under reflux for 10 hr. After cooling the reaction mixture was neutralized with glacial acetic acid and then stripped of solvent by distillation under reduced pressure. The residue was taken up in ether and washed successively with sodium bicarbonate solution, dilute hydrochloric acid, and water. The ethereal layer was dried over anhydrous magnesium sulfate and the solvent removed from it under reduced pressure; 4.7 g. (81% yield) of a viscous liquid was obtained. After purification by evaporative distillation the product, n_D^{20} 1.5183, λ_{max} 5.72 μ (1749 cm.$^{-1}$, ester), 5.83 μ (1715 cm.$^{-1}$, γ-lactam) was found to be identical with the sample of the γ-lactam prepared by the two-step sequence.[4]

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(6) National Science Foundation undergraduate research participant.

A Study of the Chlorination of 2-Thenylamines with Sulfuryl Chloride[1]

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The purpose of this paper is to describe a novel general method for introducing chlorine into the

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