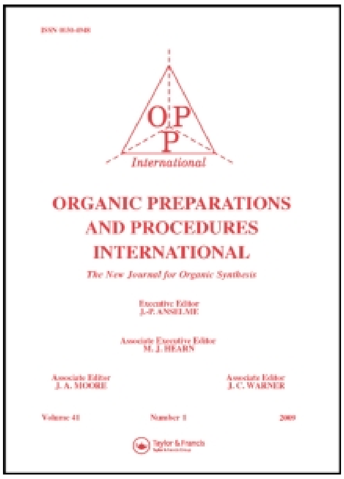

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SYNTHESIS OF 2-NITROCYCLOOCTANONE

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SYNTHESIS OF 2-NITROCYCLOOCTANONE

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(02/03/84)

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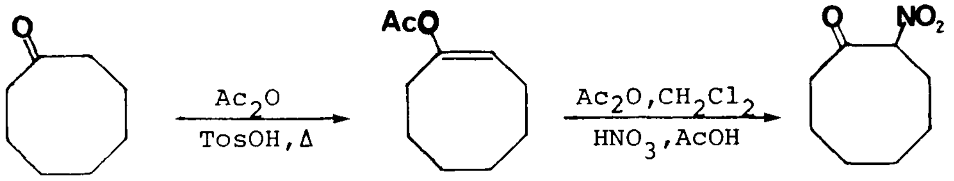
The synthetic utility of cyclic α-nitroketones as well as the preparation of these useful synthetic intermediates has recently been reviewed.[1] α-Nitrocyclooctanone can be prepared by reaction of cyclooctene with dinitrogen tetroxide,[2] but this procedure requires a tedious work-up. On the other hand, two methods are known to prepare the title compound starting from cyclooctanone. Feuer and Pivawer[3] proposed the nitration of cyclooctanone by amyl nitrate at -50° but unfortunately the reaction gave amyl 8-nitrooctanoate as an undesired product while the title compound was obtained in a very low yield. Feuer et al.[4] reported the synthesis of 2-nitrocyclooctanone by nitration of cyclooctanone with potassium amide and amyl nitrate in liquid ammonia at -45° and the title compound was obtained in 60% yield; however, at the same time, amyl 8-nitrooctanoate (21%) was obtained.

For projected synthesis of natural substances, we required large amounts of 2-nitrocyclooctanone and found the published routes unsatisfactory. In fact these methods had disadvantages such as low temperature, low yield and presence of undesired products. This lead us to develop a simple and inexpensive route from cyclooctanone which is now described here. The route consists of the nitration of 1-acetoxy-1-cyclooctene [obtained from cyclooctanone] with acetyl nitrate.



I II III

EXPERIMENTAL SECTION

1-Acetoxy-1-cyclooctene (II).- Cyclooctanone (22.42 g, 178 mmol) was added to a solution of acetic anhydride (36.4 g, 357 mmol) and TosOH (0.103 g, 0.6 mmol). The solution was heated at 175° (bath temperature) and at the same time, the acetic acid generated was removed by distillation. After 3 hrs, the solution was cooled at room temperature, and dichloromethane (100 ml) was added; the resulting solution was washed with water (2x60 ml), 5% Na_2CO_3 (2x60 ml) and dried over magnesium sulfate. The solvent was removed under vacuum to leave a residue which after distillation (60-62°/0.4 mm) yielded 22.7 g (76%) of 1-acetoxy-1-cyclooctene (II). IR(neat): 1683 and 1745 cm^{-1}. NMR($CDCl_3$): δ 1.25-2.60 (m+s, 15H); 5.25(t, 1H, J = 8.25 Hz).

2-Nitrocyclooctanone (III).- To a solution of 1-acetoxy-1-cyclooctene (10.9 g, 649 mmol), acetic anhydride (19.5 ml), dichloromethane (20 ml) and three drops of conc. sulphuric acid cooled at 0°, a mixture of glacial acetic acid (3.25 ml) and concentrated nitric acid (4.55 ml, 0.07 mol) was added over a period of 30 min. The inner temperature was maintained below 6° by external cooling. The resulting mixture was stirred at 0-5° for 1 hr, then at room temperature for 2 hrs. Acetic acid was removed as completely as possible under vacuum at 40° and the residue was dissolved in ether (100 ml); the solution was washed with water (2x60 ml). The ethereal solution was dried over $MgSO_4$, the solvent removed under vacuum to yield 8.76 g (79%) of an oily residue, pure by tlc (Silica gel, 8:2 hexane/ethyl acetate). A sample of the product was distilled, bp. 58-60°/0.08 mm, lit.[3] bp. 73-74°/0.2 mm. IR(neat): 1720 (C=O), 1555 (NO_2) cm^{-1}; NMR ($CDCl_3$): δ 1.00-3.00 (m, 12H); 5.32-5.55 (dd, 1H, J = 6.0 Hz); n_D^{20} = 1.5036.

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