Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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1-NITROCYCLOÖCTENE

[Cycloöctene, 1-nitro-]

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Checked by E. Lewars, P. H. McCabe, and Peter Yates.

1. Procedure

Caution! Dinitrogen tetroxide is very toxic (Note 1), and nitro nitrites are unstable. The reaction must be carried out in a well-ventilated hood with an adequate shield.

Benzene has been identified as a carcinogen; OSHA has issued emergency standards on its use. All procedures involving benzene should be carried out in a well-ventilated hood, and glove protection is required.

Sodium-dried diethyl ether (150 ml.) is placed in a 1-l., four-necked flask equipped with a fritted gas-inlet extending to its bottom, a sealed mechanical stirrer (Note 2), a 100-ml., pressure-equalizing dropping funnel, a thermometer, and a dry ice condenser protected with a phosphorus pentoxide drying tube. Cycloöctene (44.4 g., 53.5 ml., 0.404 mole) (Note 3) is placed in the dropping funnel, and the system is swept with dry oxygen. Dinitrogen tetroxide (39.3 g., 27.1 ml. at −9°, 0.427 mole) (Note 4) is condensed (Note 5) in a graduated, calibrated trap that is protected with a phosphorus pentoxide drying tube and has been swept with dry oxygen.

The flask is cooled to −10°, and the dinitrogen tetroxide is distilled with a warm water bath from the trap into the ether, with slow stirring; the transfer is aided by a minimal flow of dry oxygen. The solution is allowed to warm to 0–5°, and the oxygen flow rate is increased to 10 ml. per minute (Note 6). The cycloöctene is dropped into the dinitrogen tetroxide solution, with vigorous stirring, over a 30-minute period. The reaction is exothermic, and the temperature is kept at 9–12° by cooling with a methanol–dry ice bath at −20°. The dropping funnel is rinsed with 25 ml. of ether, and the yellow solution (Note 7) is stirred for an additional 30 minutes at 10° with continued oxygen flow. Triethylamine (121 g., 1.20 moles) (Note 8) is added, with stirring, over a 12-minute period; the temperature of the reaction mixture is kept at 4–12° by maintaining the bath at −4° (Note 9). The mixture is kept at room temperature for an additional 30 minutes, diluted with 150 ml. of ether, and cooled to 0–5°. The excess triethylamine is neutralized with an ice-cold solution of 72 g. of acetic acid in 200 ml. of water, with stirring. The reaction mixture is transferred to a 2-l. separatory funnel and extracted with three 400-ml. portions of ether. The combined ethereal extracts are washed with two 200-ml. portions of water, three 150-ml. portions of saturated aqueous sodium hydrogen carbonate, and again with water (Note 10).

Most of the ether is removed at room temperature with a rotary evaporator. The water that separates is removed with the aid of a small separatory funnel, and the remaining ether, traces of water, and cycloöctane (Note 11) are distilled at room temperature (10 mm.) over 3 hours, yielding 59–61 g. of crude 1-nitrocycloöctene as a yellow oil (Note 12) and (Note 13). Chromatography on silica gel (Note 14) with successive elution with *n*-hexane and benzene gives 39–40 g. (63–64%) of 1-nitrocycloöctene (Note 15). Distillation (Note 16) gave an analytically pure sample, b.p. 60° (0.2 mm.), n_D^{20} 1.5116 (Note 17).

2. Notes

1. Concentrations of dinitrogen tetroxide of 100–150 p.p.m. are dangerous for exposures of 30–60 minutes, and concentrations of 200–700 p.p.m. may be fatal after even very short exposures.
2. The checkers found that magnetic stirring could be used in place of mechanical stirring.
3. Cycloöctene (95% pure) from Columbia Carbon Co., a division of Cities Service, was used without

further purification.
4. A slight excess of dinitrogen tetroxide over olefin is necessary for maximum yields.
5. For good yields all reagents must be absolutely dry. For condensation of dry dinitrogen tetroxide free of dinitrogen trioxide, streams of dry oxygen (run through a flow meter, a calcium chloride tube, and concentrated sulfuric acid) and dinitrogen tetroxide (99.5% pure from the Matheson Company), are combined and run slowly through a phosphorus pentoxide tube before condensation. The freezing point of dinitrogen tetroxide is −9.3°, and a convenient cooling bath for condensation is methanol–dry ice at −8° to −10°.
6. The use of oxygen in this reaction prevents formation of undesirable by-products, *e.g.*, nitro nitroso compounds.[2] For the preparation of 1-nitro-1-octadecene the optimum mole ratio of olefin to oxygen was found[3] to be 1/50 to 1/150, compared with 1/30 in this procedure.
7. Nitro nitrites are unstable, and it is safe practice to keep them in solution until they are converted to nitro alcohols[2] or nitro olefins.[3]
8. Commercial triethylamine (Eastman Kodak Co.) was used without further purification. Stoichiometric amounts of triethylamine based on olefin produced poor yields of nitro olefins, owing to the slow rate of elimination of the nitro nitrite compounds.[3] A twofold molar ratio of triethylamine to olefin was sufficient to produce 1-nitro-1-octadecene from 1-nitro-2-octadecyl nitrite in 92% yield.[3] The same excess applied to the crude reaction product from cycloöctene and dinitrogen tetroxide resulted in only an 80% yield of 1-nitrocycloöctene.
9. At the end of the exothermic elimination reaction the color turns brown with simultaneous precipitation of the triethylammonium salts.
10. The checkers washed the ethereal extracts with saturated brine and dried them over anhydrous magnesium sulfate before removal of ether.
11. Cycloöctane is the major impurity in the starting material.
12. The submitter estimated the crude product to be 95% pure by IR spectroscopy: $\varepsilon_{6.59\mu}/\varepsilon_{3.40\mu} = 3.00$ (CCl_4: matched 0.1-mm. cells; analytical absorbances, 0.2–0.7).
13. For further reactions involving reduction,[4] the crude product can be used.
14. The silica gel column was 14 × 2.5 in. I.D.; a shorter column may suffice.
15. The checkers found for this product: n_D^{26} 1.5106; ^{1}H NMR ($CDCl_3$), δ 1.6 (m, 8 H), 2.3 (m, 2 H), 2.7 (m, 2 H), and 7.24 (t, $J \equiv 9$ Hz., 1 H).
16. It is safe practice to remove the peroxide that may be formed in this free radical reaction by chromatography before distillation. The submitter distilled an aliquot (12.7 g.) of the hexane eluate, giving 9.9 g. of product, $\varepsilon_{6.59\mu}/\varepsilon_{3.40\mu} = 3.12$ (Calcd. for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.84; H, 8.27; N, 8.80).
17. Slow decomposition with simultaneous precipitation of a solid occurred on standing for several weeks at 23°. Immediate analysis and use of the product are advised.

3. Discussion

The major advantage of the present method, the only method reported[3] for the preparation of 1-nitrocycloöctene, is the convenience of converting an olefin to a 1-nitro olefin in good yield without isolation of any intermediate. The submitter has also used this method[3] successfully for the preparation of 1-nitro-1-octadecene from 1-octadecene.

In the past the products from the addition of dinitrogen tetroxide to olefins have been hydrolyzed and converted to 1-nitro olefins by various methods, *e.g.*, acetylation of the isolated nitro alcohol and elimination of acetic acid with potassium carbonate,[5,6] dehydration of the nitro alcohol with phthalic anhydride[7] or potassium hydrogen sulfate,[8] and base-catalyzed elimination of nitrous and nitric acid from dinitro compounds and nitro nitrates, respectively.[2] Besides representing longer syntheses, these routes require separation of the nitro alcohol from the dinitro compound and, since these substances occur in approximately equal amounts, 50% of the yield is lost in the first step. Furthermore, in the case of the higher 1-olefins, this separation is difficult[9,10] and tedious.[3] 1-Nitro 1-olefins have been employed in the preparation of saturated nitro compounds and oximes.[4]

References and Notes

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

silica gel

dinitrogen tetroxide

dinitrogen trioxide

nitrous and nitric acid

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

Benzene (71-43-2)

ether,
diethyl ether (60-29-7)

sodium hydrogen carbonate (144-55-8)

oxygen (7782-44-7)

phthalic anhydride (85-44-9)

potassium hydrogen sulfate (7646-93-7)

magnesium sulfate (7487-88-9)

hexane,
n-hexane (110-54-3)

triethylamine (121-44-8)

cyclooctene

cyclooctane (292-64-8)

1-nitro-1-octadecene

1-nitro-2-octadecyl nitrite

1-octadecene (112-88-9)

1-NITROCYCLOOCTENE,
Cyclooctene, 1-nitro- (1782-03-2)