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Monohalogenation of Primary Nitroparaffins

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Received May 10, 1977

Treatment of the salts of primary nitroparaffins with halogens generally gives the monohalonitro compound contaminated with greater or lesser amounts of the dihalonitro compound and the starting nitroparaffin. In 1960 Trippett and Walker[1] reported that pure 1-bromo-1-nitroalkanes could be prepared by addition of the dry, finely powdered, sodium or ammonium salt of the nitro compound to bromine at 0 °C; they obtained 65–70% yields of pure products. Several years later, Levering[2] devised a procedure for chlorinating the sodium salt of nitroethane, which gives excellent yields of pure 1-chloronitroethane. Unfortunately, his procedure depends on density differences between the monochloronitro compound and the solution of nitroparaffin salt; these differences quickly become relatively small as the molecular weight increases, so that even the preparation of pure 1-chloro-1-nitrobutane is no longer a simple matter. And still more recently, Novikov et al.[3] proposed the use of *N*-halo-*N*-nitroamines or *N*-halosuccinimides as reagents for monohalogenating the salts of primary nitroparaffins, but the purity of their products cannot be regarded as established.

We now report a simple, convenient procedure for chlorinating, brominating, and iodinating primary nitroparaffins; the yields of pure products range from 82 to 94%. All that is required is addition of a methylene chloride solution of the halogen, precooled to −78 °C, to a slurry of the nitroparaffin salt and ice. The reaction is complete in 1–2 min, the methylene chloride phase is dried, the solvent is removed, and the residue is subjected to a simple distillation. This gives analytically pure monohalonitro compound in the yields shown in Table I.

Experimental Section

Chlorination is exemplified by the preparation of 1-chloro-1-nitropropane.

1-Chloro-1-nitropropane. A solution of 22.2 g (337 mmol) of 85% potassium hydroxide in 120 mL of water is prepared under nitrogen in a 500-mL flask fitted with an efficient stirrer.[4] When this solution comes to room temperature 30.0 g (337 mmol) of 1-nitropropane is added all at once and the mixture is stirred under nitrogen until the nitro compound dissolves (ca. 15 min). Following this, the solution is cooled until it just starts to freeze (ca. −15°C), at which point ca. 300 mL of crushed ice is added, and then a solution of 20 mL (ca. 60 g) of liquid chlorine in 100 mL of methylene chloride, which has been cooled to −78 °C, is added all at once with vigorous stirring.[4] In about 1 min the reaction is over. After separation of the two layers, the aqueous phase is extracted with 50 mL of methylene chloride; the combined methylene chloride solutions are washed once with 50 mL of a saturated sodium chloride solution, and then dried over anhydrous magnesium sulfate. The methylene chloride and excess chlorine are removed by distillation through a short column, the column is removed, and the residue is distilled in vacuo. This gives 37.8 g (93% yield) of 1-chloro-1-nitropropane, bp 55 °C (26 mm). On VPC analysis only a single peak is obtained and elemental analysis (Table I) confirms the purity of this material.

Bromination may be carried out as for chlorination. Alternatively, a slightly modified procedure also works well, especially when small batches are being prepared. Instead of adding ice, it suffices to cool a larger volume of methylene chloride than would otherwise be used. The following procedure is illustrative.

1-Bromo-1-nitrooctane. In a 100-mL flask fitted with an efficient stirrer[4] a solution of 2.08 g (31.4 mmol) of 85% potassium hydroxide in 40 mL of 25% aqueous methanol[5] is prepared under nitrogen. At room temperature 5 g (31.4 mmol) of 1-nitrooctane is added, and the mixture is stirred under nitrogen until the nitro compound dissolves (ca. 40 min). The resulting solution is cooled until it just starts to freeze, and then 4.93 g (30.8 mmol) of bromine in 50 mL of methylene chloride (precooled to −78 °C) is added, all at once, with vigorous stirring.[4] After about 1 min the reaction is over; the layers are separated and the aqueous phase is extracted with 20 mL of methylene chloride. The combined methylene chloride solutions are washed with 20 mL of H_2O and dried over anhydrous magnesium sulfate, and then the solvent is removed. Distillation of the residue gives 6.64 g (89% yield) of analytically pure 1-bromo-1-nitrooctane; bp 75 °C (0.4 mm).

1-Iodo-1-nitroethane. To a solution of 4.40 g (66.7 mmol) of 85% KOH in 40 mL of water at 20–25 °C is added 5 g (66.7 mmol) of nitroethane all at once; the mixture is stirred under nitrogen until the nitro compound dissolves (ca. 10 min). With minimal exposure to light, the aqueous solution is cooled until freezing begins, and then 50 mL of CH_2Cl_2 (cooled to −78 °C) is added followed by 16.6 g (65.3 mmol) of powdered iodine (nitrogen atmosphere; vigorous stirring). In about 3 min the reaction is complete. After separating the layers, the aqueous phase is extracted with 20 mL of CH_2Cl_2, the combined methylene chloride solutions are dried (anhydrous $MgSO_4$), and then the solvent is removed by distillation through a short Vigreux column, first at atmospheric pressure and, finally, at 50 mm. The column is removed and the residue is distilled at 0.4 mm, whereupon 10.95 g (82% yield) of analytically pure 1-iodo-1-nitroethane is obtained (bp 42 °C). This compound soon develops a pink color.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Table I. Monohalonitroparaffins

Compd	Registry no.	Yield, %	Bp, °C (mm)	Anal. Calcd	Anal. Found
1-Chloro-1-nitroethane	598-92-5	92	52 (45)	C, 21.94; H, 3.66; Cl, 32.36	C, 21.86; H, 3.73; Cl, 32.42
1-Chloro-1-nitropropane	600-25-9	94	55 (26)	C, 29.17; H, 4.86; Cl, 28.69	C, 29.38; H, 4.89; Cl, 29.00
1-Chloro-1-nitrooctane	63599-45-1	92	60 (0.4)	C, 49.74; H, 8.29; Cl, 18.34	C, 50.00; H, 8.25; Cl, 18.19
1-Bromo-1-nitroethane	563-97-3	89	48 (11)	C, 15.59; H, 2.60; Br, 51.92	C, 15.63; H, 2.68; Br, 51.79
1-Bromo-1-nitropropane	5447-96-1	92	50 (4)	C, 21.44; H, 3.57: Br, 47.59	C, 21.61; H, 3.65; Br, 47.39
1-Bromo-1-nitrooctane	63569-74-4	89	75 (0.4)	C, 40.35; H, 6.72; Br, 33.59	C, 40.48; H, 6.86; Br, 33.80
1-Iodo-1-nitroethane	51771-09-6	82	42 (0.4)	C, 11.94; H, 1.99; I, 63.18	C, 11.87; H, 1.87; I, 63.03

Registry No.—1-Nitropropane, 10903-2; methylene chloride, 75-09-2; 1-nitrooctane, 629-37-8; nitroethane, 79-24-3.

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(4) A mechanical stirrer is required.
(5) With the higher nitroparaffins it is advantageous to employ 25% methanol–75% water to achieve rapid solution.

Bicyclo[3.3.0]octane-2,6-dione and Bicyclo[3.3.0]octa-3,7-diene-2,6-dione

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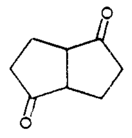
Received October 8, 1976

Several projects in this laboratory[1] have required substantial quantities of bicyclo[3.3.0]octane-2,6-dione (**1**) and the related dienedione **2**. Although these compounds have been known since 1934[2] and 1953,[3] respectively, the original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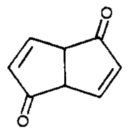
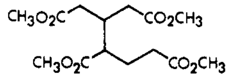

2

preparations, as well as some more recent procedures,[4] are unwieldy for large-scale operation. Therefore, we present here the details of our modified preparation of these versatile intermediates in molar quantities.

The synthetic sequence is outlined in Figure 1, and, as mentioned above, is based on the methods worked out by the Dauben group.[3,4] The free-radical induced coupling of dimethyl glutarate (**3**) to give tetraester **4** proceeds in only modest yield (ca. 50% based on recovered **3**), but is well suited for large (ca. 1 mol) runs. It is advisable to recrystallize the tetraester after distillation to remove some 15% of an impurity (presumably the isomeric ester **6**) which otherwise interferes in Dieckmann cyclization.



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The cyclization of **4** is best carried out with sodium methoxide in dimethyl sulfoxide (Me_2SO). Provided that all sources of hydroxide ion are excluded, this combination gives yields superior to those obtained previously with potassium *tert*-butoxide in *tert*-butyl alcohol.[4] Hydrolysis and decarboxylation of the resulting bisketo ester **5** are accomplished by heating with aqueous acid followed by extraction; because of an unfavorable partition coefficient, ether is a very poor solvent for this extraction, but the dione **1** is readily recovered using chloroform. If necessary, the dione may be purified by sublimation in vacuo; recrystallization is not recommended, as **1** tends to oil out, even when very pure.

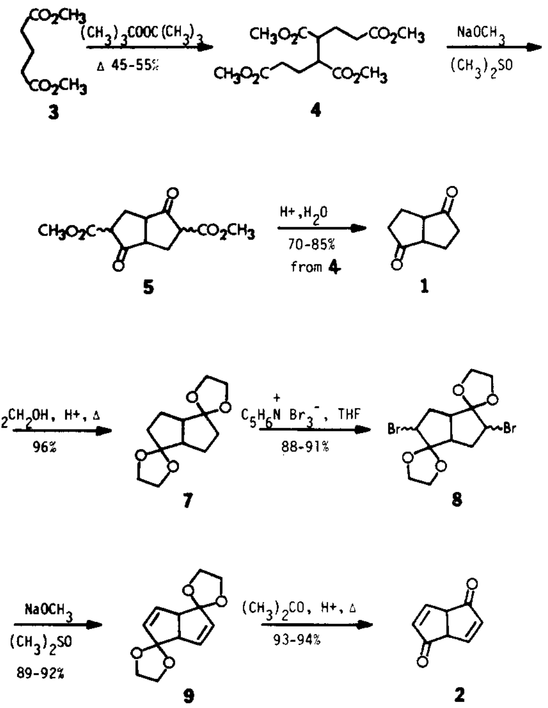

Figure 1. Improved synthesis of bicyclo[3.3.0]octa-3,7-diene-2,6-dione (**2**).

The conversion of the saturated dione **1** into dienedione **2** was originally[3] carried out by chlorination, ketalization with ethylene glycol, double dehydrochlorination, and deketalization. The last procedure of the Dauben group[4b] paralleled this, employing the bromoketal. We experienced considerable difficulty with this route, finding bromination of the bisenol acetate capricious, and the ketalization and elimination steps very slow. We have employed instead the sequence used by Eaton in some related systems,[5] and found it very satisfactory.

Ketalization of dione **1** with ethylene glycol proceeds smoothly and in nearly quantitative yield. The oily diketal is then brominated with pyridinium tribromide in tetrahydrofuran at low temperature (if the reaction is carried out at or near room temperature considerable polymer is formed, and the product can be purified only with difficulty). The dibromo diketal **8** may also be obtained directly by brominating **1** in ethylene glycol,[6] but this method is suitable for small-scale runs only. Although double dehydrobromination of **8** with ethanolic potassium hydroxide[4] requires refluxing for several days for complete reaction, the elimination may be effected in several hours with sodium methoxide in Me_2SO. Finally, ketal exchange with acetone afforded dienedione **2**.

By means of these procedures we have obtained quantities of both diketones sufficient to permit their use as starting materials for other syntheses. The preparations are reasonably rapid and efficient and, provided the usual precautions are taken, free from hazard. There is no reason to suppose that they could not be scaled up several fold over the amounts specified in the Experimental Section, provided suitably sized equipment is at hand.

Experimental Section

General. All melting points were measured in open capillaries with a Thomas-Hoover apparatus and are uncorrected; boiling points are also uncorrected. Combustion analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Unless noted otherwise, reagents and solvents were reagent-grade materials used as received.

Proton nuclear magnetic resonance (NMR) spectra were run on Varian A-60, A-56/60, and T-60 instruments (60 MHz). Chemical shifts are reported in parts per million downfield of internal tetramethylsilane (δ 0.0). Infrared spectra were measured on a Perkin-Elmer Model 137 spectrophotometer. Liquid samples were examined as neat films, and solids as Nujol mulls. All gas chromatographic separations were achieved using an F and M Model 700 chromatograph equipped with a thermal conductivity detector. Helium was used as the carrier gas at flow rates of 70–80 mL/min; an injector temperature of 240 °C and a detector temperature of 270 °C were used