
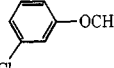

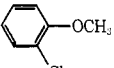

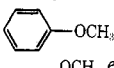

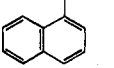

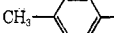


Table I  
Reaction of Aryl Chlorides with Sodium Methoxide in HMPA

Registry no.	Aryl chloride	Reaction conditions			Product	Yield, <sup>b</sup> %	Registry no.
		Temp, °C	Time, h	Molar/ equiv <sup>a</sup> CH <sub>3</sub> ONa			
541-73-1		90	20	1.2		87	2845-89-8
		90	19	1.1 <sup>c</sup>			
95-50-1		90	19.5	1.1		78 <sup>d</sup>	766-51-8
108-90-7		120	18.5	1.5		50	100-66-3
90-13-1		120	19	1.5		54	2216-69-5
106-43-4		120	24	1.5		13	104-93-8

<sup>a</sup> Commercial sodium methoxide used in all cases except where noted. <sup>b</sup> Yields determined by GLC. <sup>c</sup> Sodium methoxide generated in reaction mixture from methanol and sodium hydride. <sup>d</sup> Addition of 0.1 molar equiv of *p*-dinitrobenzene had no effect on yield. <sup>e</sup> Trace of 2-methoxynaphthalene also present.

and an infrared spectrum identical with that of an authentic sample. An alternative procedure involved generation of sodium methoxide from methanol and sodium hydride. A mixture of 0.71 g (22 mmol) of methanol, 1.06 g of a 50% dispersion of sodium hydride in mineral oil (22 mmol), and 40 ml of dry HMPA was stirred at room temperature for 1.5 h before addition of 2.94 g (20 mmol) of *m*-dichlorobenzene and heating at 90° for 19 h. Completion of the reaction as in the above procedure gave a 79% yield of *m*-chloroanisole.

***o*-Chloroanisole.** A magnetically stirred mixture of 2.94 g (20 mmol) of *o*-dichlorobenzene, 1.19 g (22 mmol) of sodium methoxide, and 40 ml of dry HMPA was heated at 90° for 19.5 h in a flask equipped with a condenser and drying tube. A work-up procedure the same as that described for *m*-chloroanisole gave 2.66 g of liquid. Analysis of the liquid by GLC (SE-30, 120°, or methyl silicone, 145°) revealed that it consisted of *o*-chloroanisole and a small amount of unreacted *o*-dichlorobenzene and that the yield of *o*-chloroanisole was 78%. *m*-Chloroanisole had a shorter retention time than *o*-chloroanisole and was completely absent. Product purified by GLC gave a refractive index of  $n_D^{20}$  1.5440 (lit.<sup>10</sup>  $n_D^{20}$  1.5445) and an infrared spectrum identical with that of an authentic sample. When the above reaction was run in exactly the same manner except that 0.34 g (2 mmol) of *p*-dinitrobenzene was also added, there was no change in the yield of *o*-chloroanisole.

**Anisole.** A magnetically stirred mixture of 2.25 g (20 mmol) of chlorobenzene, 1.62 g (30 mmol) of sodium methoxide, and 40 ml of dry HMPA was heated at 120° for 18.5 h in a flask equipped with a condenser and drying tube. A work-up procedure the same as that described for *m*-chloroanisole gave 1.71 g of liquid. Analysis of the liquid by GLC (methyl silicone, 127°) revealed that it consisted of anisole and unreacted chlorobenzene and that the yield of anisole was 50%. Product purified by GLC gave an infrared spectrum identical with that of an authentic sample.

**1-Methoxynaphthalene.** A magnetically stirred mixture of 3.25 g (20 mmol) of 1-chloronaphthalene, 1.62 g (30 mmol) of sodium methoxide, and 40 ml of dry HMPA was heated at 120° for 19 h in a flask equipped with a condenser and drying tube. A work-up procedure identical with that described for *m*-chloroanisole gave 2.80 g of liquid. Comparison of GLC (Carbowax 20M, 165°) retention times with those of authentic samples revealed that the liquid consisted of 1-methoxy- and 2-methoxynaphthalene (97:3 ratio), some unreacted 1-chloronaphthalene, and an unidentified product of short retention time. The yield of 1-methoxynaphthalene, which had only a slightly shorter retention time than the 2-methoxy isomer, was 54%. Product purified by GLC gave a refractive index of  $n_D^{20}$  1.6219 (lit.<sup>10</sup>  $n_D^{20}$  1.6220) and an infrared spectrum identical with that of an authentic sample of 1-methoxynaphthalene.

***p*-Methylanisole.** A magnetically stirred mixture of 2.53 g (20 mmol) of *p*-chlorotoluene, 1.62 g (30 mmol) of sodium methoxide, and 40 ml of dry HMPA was heated at 120° for 24 h in a flask equipped with a condenser and drying tube. A work-up similar to that previously described for *m*-chloroanisole gave 1.98 g of liquid. Analysis of the liquid by GLC (SE-30, 122° or Carbowax 20M,

120°) revealed that it consisted of *p*-methylanisole and much unreacted *p*-chlorotoluene and that the yield of *p*-methylanisole was 13%. Product purified by GLC gave an infrared spectrum identical with that of an authentic sample.

Registry No.—HMPA, 680-31-9; methoxide ion, 3315-60-4.

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#### An Oxime to Nitro Conversion. A Superior Synthesis of Secondary Nitroparaffins

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Received August 12, 1975

We have devised a convenient oxime to nitro conversion which constitutes an improved synthesis of secondary ni-

Table I  
Selective Reduction of *gem*-Chloronitro Compounds

Registry no.	Compd	Reagent	Yield, % of nitro compd
598-92-5	1-Chloro-1-nitroethane	(Bu <sub>3</sub> Sn) <sub>2</sub> O-PMS	50 <sup>a</sup>
600-25-9	1-Chloro-1-nitropropane	Bu <sub>3</sub> SnH	30 <sup>a</sup>
		H <sub>2</sub> -cat.	65 <sup>b</sup> (28) <sup>c</sup>
594-71-8	2-Chloro-2-nitropropane	Bu <sub>3</sub> SnH	56 <sup>a</sup>
		H <sub>2</sub> -cat.	50 <sup>b</sup>
22236-53-9	2-Chloro-2-nitrobutane	Bu <sub>3</sub> SnH	73 <sup>a</sup>
		NaBH <sub>4</sub>	0
873-92-7	1-Chloro-1-nitrocyclohexane	Bu <sub>3</sub> SnH	67 <sup>d</sup>
		H <sub>2</sub> -cat.	65
		RaNi-NaOH-H <sub>2</sub> O	50

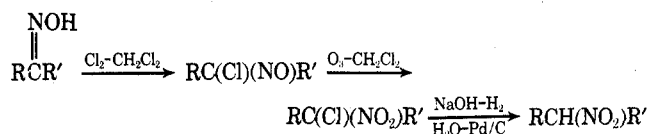
<sup>a</sup> Identified by GC retention times. Yields based on GC analysis. <sup>b</sup> Water solvent. <sup>c</sup> Ethanol solvent. <sup>d</sup> Isolated yield 28%.

Table II  
Preparation of Secondary Nitroparaffins, RCH(NO<sub>2</sub>)R'

R	R'	Yields, % <sup>a</sup>				Registry no.
		This <sup>b</sup>	Direct oxidn <sup>16</sup>	Iffland <sup>16</sup>	Nitrite <sup>16</sup>	
Me	Me	67		0	26	79-46-9
Me	Et	75	47			600-24-8
Me	<i>t</i> -Bu	37	0	30	0	599-02-0
Me	<i>n</i> -Hex	95		10	23	4609-91-0
Et	<i>n</i> -Am	77				4609-92-1
<i>n</i> -Pr	<i>n</i> -Bu	77				4609-93-2
	(CH <sub>2</sub> ) <sub>4</sub>	69	60	55	57	2562-38-1
	(CH <sub>2</sub> ) <sub>5</sub>	70	62	50	0	1122-60-7

<sup>a</sup> Yields are distilled product. <sup>b</sup> Products were identified by comparison of infrared spectra and/or index of refraction to those of authentic samples or published data (ref 5, 18, 19). Where spectra were not published, the spectra were consistent with assigned structure.

troparaffins. The method involves treatment of an oxime with chlorine to give chloronitroso compound; oxidation with ozone to the chloronitro compound; and, finally, catalytic hydrogenation in the presence of 2 equiv of sodium hydroxide to the nitro compound.



The method is essentially a two-pot operation. It is carried out without purification of intermediates and the final product is easily isolated, usually in high purity.

Each of the individual steps was studied before arriving at the optimum conditions. The chlorination of oximes to *gem*-chloronitroso compounds is a well-known one and has been carried out by numerous reagents, using a variety of conditions and solvents.<sup>1</sup>

The most suitable reagent from the standpoints of expense, yield, and convenience was elemental chlorine with CH<sub>2</sub>Cl<sub>2</sub> as solvent.<sup>2,3</sup>

It was felt initially that the oxidation step would be quite easily accomplished, since it had been described in several different places in the literature.<sup>4</sup> Those reagents that have been reported such as HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub>,<sup>5</sup> HNO<sub>3</sub>,<sup>6</sup> or O<sub>2</sub> in the presence of illumination<sup>7</sup> gave, at best, only moderate yields and were contaminated with various unidentified side products. Other reagents such as *m*-chloroperbenzoic acid, peracetic acid, activated manganese dioxide, or nickel peroxide likewise either failed outright or did not give satisfactory yields.

It was finally found that treating a *gem*-chloronitroso compound in methylene chloride solvent with a stream of ozonized oxygen gave the corresponding chloronitro compound in quantitative yield free of side products. The only example of oxidation of a *gem*-chloronitroso compound with ozone was reported in a patent and then only in a poor

yield.<sup>8</sup> This may have been due to the acetic acid solvent that was employed.

Several unsuccessful attempts to selectively reduce *gem*-chloronitro compounds to nitro compounds with various reagents such as sodium borohydride, chromous chloride, or "various catalytic procedures" have been noted in the literature.<sup>9,10</sup> We found only one successful example of such a reduction; in a study of the reduction of *gem*-chloronitro compounds to oximes, it was noted that nitrocyclohexane could be obtained on hydrogenation of 1,1-chloronitrocyclohexane in the presence of aqueous base, followed by acidification.<sup>11</sup> We verified this result and extended it to other compounds. This proved to be a convenient, effective method. Uptake of hydrogen ceases at the theoretical amount. The nitro compound is easily isolated by acidification of the aqueous solution with hydroxylamine hydrochloride and extraction with ether.<sup>12</sup>

Reducing agents that were less successful, but which could prove useful in special cases, were tributyltin hydride,<sup>13</sup> tributyltin oxide-polymethylhydrogen siloxane,<sup>14</sup> and Raney alloy in aqueous base. In these instances, isolation of product proved to be difficult. We also verified that sodium borohydride is ineffective in this reaction. The results of our reduction experiments are shown in Table I.

Having thus delineated optimum conditions for each step of the sequence, we applied it to a series of ketoximes. As can be seen in Table II, this method gives better yields than the other methods of synthesizing secondary nitroparaffins; these other methods are direct oxidation of ketoximes with trifluoroperacetic acid,<sup>15</sup> the Iffland oxidation of ketoximes,<sup>5</sup> and nitrite displacement reactions on secondary halides.<sup>16</sup>

Other advantages of this method are that work-ups are simpler, reagent costs are lower, scale-ups are easier, and by-products are virtually eliminated (e.g., nitrite esters). Disadvantages are that not all ketoximes will react with chlorine<sup>17</sup> and not all functionalities would survive the reaction conditions.

With minor modifications this sequence can be applied to aldoximes to yield primary nitro compounds. The chlorination of the aldoxime is carried out at  $-60^{\circ}$  to prevent the chloronitroso compound from rearranging to the hydroxymoyl chloride.<sup>20</sup> The ozonization is then carried out while allowing the solution to warm up gradually. The final hydrogenation step is carried out at slightly higher hydrogen pressure (3 vs. 2 atm) than is necessary to produce secondary nitro compounds.

In this manner yields of 1-nitrobutane, 1-nitroheptane, and phenylnitromethane were 50, 44, and 65%, respectively. However, as a method of synthesizing primary nitro compounds it must be pointed out that this method is probably inferior to the nitrite displacement of primary aliphatic halides.

### Experimental Section

Boiling points are uncorrected. Ir spectra were determined using a Perkin-Elmer 421 instrument. GLC analyses were performed with a Beckman GC/2 instrument employing an SE-30 on Chromosorb W column.

**Materials.** The oximes employed except 3-octanone oxime and 4-octanone oxime were commercial materials and used without purification. 3-Octanone oxime and 4-octanone oxime were prepared by standard oximation of the corresponding ketones with hydroxylamine hydrochloride and excess sodium hydroxide in ethanol-water solvent. All other reagents used were commercial materials and used as received. The methylene chloride solvent was distilled before use.

**General Procedure for Synthesis of Secondary Nitroparaffins. Nitrocyclopentane from Cyclopentanone Oxime.** To a solution of 5.0 g (0.05 mol) of cyclopentanone oxime in 50 ml of methylene chloride cooled to  $0-5^{\circ}$  with an ice bath was added a slow stream of chlorine gas until the initially blue solution took on a distinct greenish cast.<sup>21</sup> This solution was then flushed with a stream of oxygen for approximately 15 min to remove excess chlorine and then was treated with an ozone-oxygen stream<sup>22</sup> until the blue color was completely discharged. The methylene chloride solvent was removed in vacuo on a rotary evaporator to leave a residue of 7.75 g (100%) of 1-chloro-1-nitrocyclopentane. The residue was added to a solution of 5.0 g of sodium hydroxide in 50 ml of water in a hydrogenation bottle. To this mixture was added 1.0 g of 5% palladium on charcoal catalyst. It was then hydrogenated on a Parr hydrogenation apparatus with an initial pressure of 26 psi until uptake of hydrogen ceased. The mixture was filtered to remove catalyst and then cooled to  $0^{\circ}$  and acidified at this temperature with 13 g (0.19 mol) of hydroxylamine hydrochloride. The mixture was allowed to stir overnight,<sup>23</sup> saturated with sodium chloride, and extracted with  $3 \times 50$  ml of diethyl ether. The ether solution was dried over sodium sulfate, the ether removed in vacuo on a rotary evaporator, and the residue distilled to give 4.0 g (69%) of nitrocyclopentane, bp  $82-84^{\circ}$  (30 mm),  $n^{25}_{\text{D}}$  1.4525 [lit.<sup>5</sup> bp  $90^{\circ}$  (40 mm),  $n^{25}_{\text{D}}$  1.4518]. The infrared spectrum had bands at 1540 and  $1370 \text{ cm}^{-1}$  ( $\text{RNO}_2$ ) and no other complicating features.

**General Procedure for the Synthesis of Primary Nitroparaffins. 1-Nitroheptane from Heptaldoxime.** To a solution of 5.0 g (0.038 mol) of heptaldoxime in 75 ml of methylene chloride cooled to  $-60^{\circ}$  with a dry ice-acetone bath was added a slow stream of chlorine gas for approximately 5 min. At the end of this time the mixture was distinctly green. This solution was then flushed with a stream of oxygen for approximately 15 min at  $-60^{\circ}$  and then was treated with an ozone-oxygen stream while allowing the mixture to warm up gradually to room temperature over a period of ca. 4 h. As the solution warmed up, the green color faded to yellow and then again turned to blue. When the blue color was completely discharged, the methylene chloride was removed in vacuo to leave a residue of 7.0 g (100%) of 1-chloro-1-nitroheptane. This residue was added to a solution of 5.0 g of sodium hydroxide in 50 ml of water and 1.0 g of 5% palladium on charcoal was then added. The mixture was then hydrogenated on a Parr hydrogenation apparatus with an initial pressure of 50 psi until uptake of hydrogen ceased. The solution was worked up as previously described to give 2.5 g (44%) of 1-nitroheptane, bp  $42-45^{\circ}$  (0.001 mm),  $n^{25}_{\text{D}}$  1.4310 [lit.<sup>19</sup> bp  $66^{\circ}$  (2 mm),  $n^{25}_{\text{D}}$  1.4285]. The infrared spectrum of the product was identical with that published for 1-nitroheptane.<sup>19</sup>

**Tributyltin Hydride Reduction of 1-Chloro-1-nitrocyclohexane.** Into a flask equipped with a reflux condenser, stopcock

with septum inlet, nitrogen inlet, and magnetic stirrer were placed 5 g of 1-chloro-1-nitrocyclohexane and 50 mg of azobisisobutyronitrile. After flushing with prepurified nitrogen for 1 h, 9 g of tributyltin hydride (prepared from tributyltin chloride<sup>13</sup>) was added all at once through the septum, using a syringe. The mixture was heated at  $90^{\circ}$  until the Sn-H band at  $1815 \text{ cm}^{-1}$  disappeared and the nitro band shifted from  $1570 \text{ cm}^{-1}$  to  $1540 \text{ cm}^{-1}$  (ca. 2 h). Gas chromatographic analysis showed a 65% conversion to nitrocyclohexane. Distillation of the reaction mixture yielded 1.0 g (26%) of product, bp  $106-108^{\circ}$  (40 mm) [lit.<sup>5</sup> bp  $106-108^{\circ}$  (40 mm)].

**Tributyltin Oxide-Polymethylhydrogen Siloxane Reduction of 1-Chloro-1-nitroethane.** In a large Pyrex test tube were mixed successively 5 g (0.05 mol) of 1-chloro-1-nitroethane, 4.6 g (0.75 equiv) of polymethylhydrogen siloxane, and 22.8 g (0.038 equiv) of tributyltin oxide. On the addition of the tributyltin oxide, a red color developed. The tube was stoppered and the contents were photolyzed in a Hanovia photochemical reactor for 5 h total time. After 1 h the red color had disappeared and GLC analysis showed approximately 15% conversion. After 5 h, analysis showed approximately 50% conversion which did not increase with further irradiation. Attempted isolation by distillation failed to yield any 1-nitroethane.

**Registry No.**—Nitroethane, 79-24-3; 1-nitropropane, 108-03-2; 2-propanone oxime, 127-06-0; 2-butanone oxime, 96-29-7; 3,3-dimethyl-2-butanone oxime, 2475-93-6; 2-octanone oxime, 7207-49-0; 3-octanone oxime, 7207-50-3; 4-octanone oxime, 7207-51-4; cyclopentanone oxime, 1192-28-5; cyclohexanone oxime, 100-64-1; 2-chloro-2-nitrosopropane, 2421-26-3; 2-chloro-2-nitrosobutane, 681-01-6; 2-chloro-3,3-dimethyl-2-nitrosobutane, 677-58-7; 2-chloro-2-nitrosooctane, 690-91-5; 3-chloro-3-nitrosooctane, 57484-12-5; 4-chloro-4-nitrosooctane, 57484-13-6; 1-chloro-1-nitrosocyclopentane, 694-63-3; 1-chloro-1-nitrosocyclohexane, 695-64-7; 2-chloro-3,3-dimethyl-2-nitrobutane, 57484-14-7; 2-chloro-2-nitrooctane, 57484-15-8; 3-chloro-3-nitrooctane, 57484-09-0; 4-chloro-4-nitrooctane, 57484-10-3; 1-chloro-1-nitrocyclopentane, 931-93-1; methylene chloride, 75-09-2; 1-nitroheptane, 693-39-0; heptaldoxime, 629-31-2; 1-chloro-1-nitroheptane, 57484-11-4.

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- (21) We found an ordinary gas wash bottle to be a convenient reaction vessel.
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- (23) In some instances the regeneration of the nitro compound from the salt is very slow, as is the case for nitrocyclopentane. Other nitro compounds were usually generated more rapidly. This phenomenon has been noted elsewhere.<sup>5</sup>