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A NEW SYNTHESIS OF NITRO COMPOUNDS USING DIMETHYLDIOXIRANE[1]

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Abstract: Dimethyldioxirane oxidizes primary amines to nitro compounds in a facile, mild, high yield process.

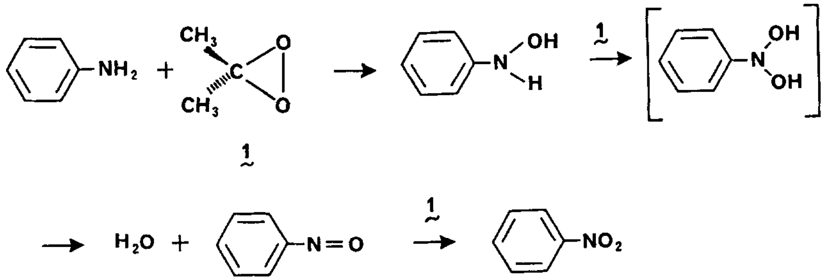
As part of our ongoing studies on the relationship between ozone chemistry and chemical carcinogenesis we have been examining the chemistry of carbonyl oxides and the isomeric dioxiranes. Here we report that aliphatic and aromatic primary amines are rapidly and efficiently oxidized to nitro compounds by dimethyldioxirane, **1**. Indeed a survey of some general methods for the preparation of nitro compounds[2] suggests to us that the use of **1** may be the method of choice. The conditions used are exceedingly mild and give the nitro compound as a solution in acetone. Table 1 summarizes our results with some representative amines.[3]

Table 1. Oxidation of Amines with Dimethyldioxirane.

Amine	Product	Yield(%)[a]	Product m.p.(°C)
Aniline	Nitrobenzene	97	
p-Anisidine	*p*-Nitroanisole	94	54
n-Butylamine	1-Nitrobutane	84	
sec-Butylamine	2-Nitrobutane	87	
tert-Butylamine	2-Methyl-2-nitrobutane	90	
1-Aminoadamantane	1-Nitroadamantane	95	159
Cyclohexylamine	Nitrocyclohexane	95	
trans-Azobenzene[b]	Azoxybenzene	96	36

a. Yields were determined by gas chromatography using the cut and weigh method with prior calibration except for 1-nitroadamantane which is the isolated yield.
b. Included as additional example of oxidation by **1**.

In a typical reaction *n*-butylamine (0.052g; 0.7 mmol) in 5 ml of acetone was treated with 95 ml of **1** in acetone solution (*ca* 0.05 M)[4]. The solution was kept at room temperature for 30 min. with the exclusion of light. Analysis of the reaction mixture by capillary GC[6] indicated the presence of 1-nitrobutane only. The oxidations are believed to occur by means of successive oxidations by **1**. The overall process is shown for the case of aniline in Eqn. (1). In the aniline case the blue color of the nitroso compound is observed immediately upon adding the solution of **1**. In separate experiments we have shown that both phenylhydroxylamine and nitrosobenzene are readily oxidized to nitrobenzene by **1**. The blue color of intermediate nitroso compound was observed in all of the amine oxidations. Thus it seems likely that all are following the reaction path shown in Eqn. (1).



(1)

Dimethyldioxirane is a powerful oxygen atom donor which oxidizes a variety of substrates[7] including hydrocarbons[1]. Work is continuing on the oxidation of nitrogen-containing compounds by **1**.

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3. The products were identified by comparing physical, chromatographic, and spectral properties with those of the authentic materials.

4. The concentration of **1** in acetone was determined by titrating an aliquot with phenylmethyl sulfide. The synthesis of **1** has been described[5].

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6. The capillary GC was carried out on a Perkin-Elmer Sigma 2000 Gas Chromatograph interfaced with a Model 3390-A Hewlett-Packard Integrator. The column used was a DB 210, 0.5 μM thickness, 30M X 0.311 mm capillary column using a flame ionization detector. The initial column temperature was 50°C (5 min.) then changed to 120°C (4 min.) at a rate of 10°C/min. The retention time of 1-nitrobutane was 9.16 min.

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