REACTION OF NITROSOBENZENE WITH 1,1-DIALKYLDIAZENIUM SALTS AS A NEW METHOD FOR THE SYNTHESIS OF 3,3-DIALKYLTRIAZENE 1-OXIDES

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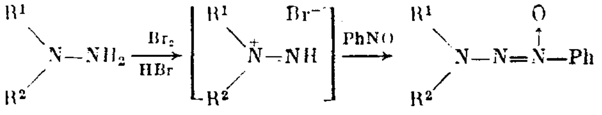
Compounds containing a triazene 1-oxide group have anti-inflammatory [1] and immunosuppressant properties [2]. The standard methods for the synthesis of 3,3-dialkyltriazene 1-oxides entail the reaction of nitroso compounds with asymmetrical dialkylhydrazines in the presence of oxidizing agents [1,3,4] or excess nitroso compound [5,6] in inert organic solvents.

We propose a new approach for obtaining the triazene 1-oxide group based on the previously unreported reaction of nitrosoarenes with 1,1-dialkyldiazenium salts. Thus, the reaction of 1,1-dimethyldiazenium hydrobromide, generated in situ according to Urry et al. [7] from 1,1-dimethylhydrazine and bromine in 16% hydrobromic acid, with nitrosobenzene leads to the formation of 3,3-dimethyl-1-phenyltriazene 1-oxide (I). Under somewhat more vigorous conditions, 1-methyl-1-(β-cyanoethyl)hydrazine, bromine, and nitrosobenzene in 40% hydrobromic acid gave 3-methyl-1-phenyl-3-(β-cyanoethyl)triazene 1-oxide (II). The yields of (I) and (II) are 75 and 63%, respectively, and exceed the yield of these compounds according to the procedure of Miesel [1] and our method [4].



(I), (II)

$R^1 = R^2 = CH_3$ (I); $R^1 = CH_3$, $R^2 = CH_2CH_2CN$.

Carrying out the reaction in a two-phase system containing hydrobromic acid and ether, which facilitates the rapid removal of acid-sensitive (I) and (II) from the reaction sphere, improves the product yield.

3,3-Dimethyl-1-phenyltriazene 1-Oxide (I). A sample of 2.1 g (0.013 mole) bromine was added dropwise with stirring to a mixture of 0.8 g (0.013 mole) 1,1-dimethylhydrazine, 1.4 g (0.013 mole) nitrosobenzene, 35 ml 16% hydrobromic acid, and 35 ml diethyl ether at −10°C. The reaction mixture was maintained for 10 h, gradually raising the temperature to 15°C. The reaction mixture was poured into a mixture of 40 g ice, 6.5 g (0.077 mole) $NaHCO_3$, and 100 ml ether. After 15 min, the organic layer was separated. The aqueous layer was extracted with three 100-ml portions of ether. The combined extracts were dried over $MgSO_4$. The solvent was removed in vacuum. Product (I) was isolated by thin-layer chromatography to give 1.65 g (75%) (I) as a brown oil. This product was found to be identical to a sample of (I) obtained according to Miesel [1] by IR and PMR spectroscopy.

3-Methyl-1-phenyl-3-cyanoethyltriazene 1-Oxide (II). A sample of 1.9 g (0.012 mole) bromine was added dropwise with stirring to a mixture of 1.2 g (0.012 mole) 1-methyl-1-cyanoethylhydrazine, 1.3 g (0.012 mole) nitrosobenzene, 30 ml 40% hydrobromic acid, and 30 ml diethyl ether at −20°C. The reaction mixture was maintained for 4.5 h, gradually raising the temperature to 20°C. The reaction mixture was treated with base according to the above procedure to give 1.55 g (63%) (II) as a brown oil. The IR and PMR spectral data of this sample were identical to those reported in our previous work [4].

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A SIMPLE SYNTHESIS OF 2-METHYL-1,4-DITHIACYCLOHEPTANE FROM DIALLYL SULFIDE AND HYDROGEN SULFIDE

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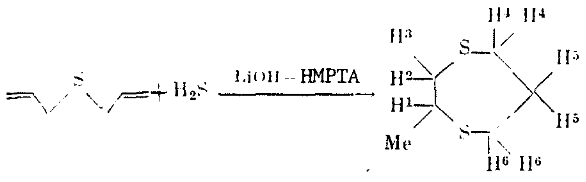
Diallyl sulfide reacts with hydrogen sulfide in LiOH/DMSO with the formation of 4-thia-1-heptane-6-thiol (I) and 3,7-dimethyl-1,2,5-trithiacycloheptane (II) [1].

We have discovered that the reaction of hydrogen sulfide with diallyl sulfide in LiOH/HMPTA leads to 2-methyl-1,4-dithiacycloheptane (III) in addition to the expected products, (I) and (II). The yield of (III) is about 20%.



(III)

A mixture of 10 g LiOH, 100 ml HMPTA, and 10.1 g diallyl sulfide was prepared and hydrogen sulfide was introduced at 50°C for 6 h. Then, the mixture was diluted with water and extracted with ether. The ethereal extracts were washed with water and dried over $CaCl_2$. Ether was distilled off. Distillation at 40-90°C (1 mm) gave a fraction (9.6 g) containing 22.2% (18.8% yield) (I), 36% (24.8% yield) (II), and 27.8% (19.7% yield) (III) as indicated by gas-liquid chromatographic analysis. The conversion of diallyl sulfide was 97.1%. Repeated distillation at 75-80°C (1 mm) gave a fraction, from which a sample of (III) was isolated by preparative gas-liquid chromatography.

PMR spectrum of (III) in benzene-d_6 (δ, ppm, J, Hz): 2.29 q (1H, H^2), 2.56 q (H^3, $^2J_{3,2}$ = 14.5), 2.55-2.75 m (1H, H^1, $^3J_{1,2}$ = 9.5, $^3J_{1,3}$ = 3.0), 2.95-2.55 m (4H, H^4, H^6), 1.45-1.65 m (2H, H^5), 0.96 d (3H, Me).

The elemental analysis data correspond to the calculated values. Mass spectrum: $M^{+\cdot}$ 148 m/z, n_D^{20} 1.5441.

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