## THE FORMATION OF 1-ARYL-3,3-DISUBSTITUTED TRIAZENES IN THE REACTION OF 1-ACYL-1-ALKYL- AND 1-ALKOXYCARBONYL-1-ALKYLHYDRAZINES WITH NITROSOBENZENE

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The reaction of aromatic nitroso compounds with 1,1-dialkyl-, 1-aryl-1-alkyl-, and 1,1-diarylhydrazines is the standard method for the synthesis of 1-aryltriazene 1-oxides [1-3]. We have shown that the reaction of 1-acyl-1-alkyl- and 1-alkoxycarbonyl-1-alkylhydrazines (I)-(III) with nitrosobenzene proceeds by a different path, leading to the formation of 1-phenyl-3,3-disubstituted triazenes (IV)-(VI) in moderate yields.



Such a reaction course was previously noted in the reaction of nitrosoarenes with semicarbazide and p-nitrophenylhydrazine [4] and in the reaction of perfluoronitrosoalkanes with mono- [5] and disubstituted hydrazines [6]. Our results along with the literature data indicate that the formation of triazenes from nitroso compounds and substituted hydrazines is rather general in nature and is observed when one of the reaction components has strongly electron-withdrawing groups.

Hydrazines (I) and (II) were obtained according to Peet [7] and Zinner [8]. 1-Cyanoethyl-1-ethoxycarbonylhydrazine (III) was synthesized in 60% yield from cyanoethylhydrazine and  $ClCO_2C_2H_5$ in dry CH<sub>2</sub>Cl<sub>2</sub> at -20°C, bp 120°C (2 mm Hg),  $n_D^{19}$  1.4615. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1120 (C—O—C), 1700 (CO), 2250 (CN). PMR spectrum in CDCl<sub>3</sub> ( $\delta$ , ppm, J, Hz): 1.11 t (CH<sub>3</sub>, J = 7.5), 2.5 t (CH<sub>2</sub>CN, J = 7.5), 3.51 t (NCH<sub>2</sub>, J = 7.5), 3.8-4.2 br,s (NH<sub>2</sub>).

Products (IV)-(VI) were obtained by the reaction of 4.67 mmoles nitrosobenzene with 1.20 mmoles (I)-(III) in 10 ml acetic acid at 20°C.

3-Acetyl-3-methyl-1-phenyl-1-triazene (IV) was obtained in 60% yield, mp 32-33°C (from 2:1 hexane—acetone).

**3-Methyl-3-ethoxycarbonyl-1-phenyl-1-triazene** (V) was obtained in 50% yield, mp 31-32°C (from ethanol). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1105 (C–O–C), 1690 (CO). PMR spectrum in CDCl<sub>3</sub> ( $\delta$ , ppm, J, Hz): 1.43 t (CH<sub>3</sub>, J = 7.5), 3.48 s (NCH<sub>3</sub>), 4.42 q (CH<sub>2</sub>, J = 7.5), 7.25-7.71 m (C<sub>6</sub>H<sub>5</sub>). Mass spectrum, m/z: M<sup>+</sup> 207. Found: C, 57.47; H, 6.31; N, 20.48%. Calculated for C<sub>10</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>: C, 57.97; H, 6.28; N, 20.29%.

**3-Cyanoethyl-3-ethoxycarbonyl-1-phenyl-1-triazene (VI)** was obtained in 30% yield, mp 49-50°C (from 1:1 hexane—chloroform). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1160 (C—O—C), 1720 (CO), 2240 (CN). PMR spectrum in CDCl<sub>3</sub> ( $\delta$ , ppm, J, Hz): 1.38 t (CH<sub>3</sub>, J = 7.5), 2.67 t (CH<sub>2</sub>CN, J = 7.5), 4.4 t (NCH<sub>2</sub>, J = 7.5), 4.43 q (OCH<sub>2</sub>, J = 7.6), 7.23-7.7 m (C<sub>6</sub>H<sub>5</sub>). Found: C, 58.03; H, 5.88; N, 22.50%. Calculated for C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>O: C, 58.64; H, 5.69; N, 22.76%.

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## THE LOW-TEMPERATURE MATRIX STABILIZATION AND IR SPECTRUM OF DIMETHYLGERMANONE, Me<sub>2</sub>Ge=O

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The formation of germanones  $R_2Ge=O$ , which are unstable species under ordinary conditions, has been postulated on the basis of indirect evidence for many reactions [1]. However, direct spectroscopic data for these shortlived intermediates has been limited to the IR spectra of inorganic molecules, GeO, GeO<sub>2</sub>, and F<sub>2</sub>Ge=O [2] and the photoelectron spectrum of Me<sub>2</sub>Ge=O (I) [3]. We are the first to report the low-temperature matrix stabilization and IR spectrum of germanone (I), which is the first example of organic intermediates with a Ge=O double bond.

Germanone (I) was obtained by vacuum pyrolysis of two independent sources, namely, 3,3-dimethyl- (IIa) and 1,3,3,5-tetramethyl-6-oxa-3-germabicyclo[3.1.0]hexanes (IIb)[4], in a quartz flow system attached to an optical cryostat. The pyrolysis products were frozen on a copper mirror base at 12 K along with excess argon (~1000:1) and studied by IR spectroscopy.

The spectrum of the products of the pyrolysis of (IIa) at 800-850°C and  $10^{-3}-5\cdot10^{-4}$  torr showed bands for butadiene, weak bands for cyclogermoxanes (Me<sub>2</sub>GeO)<sub>n</sub> (n = 3 and 4) (IIIa) at 865-805 cm<sup>-1</sup>, and bands for GeO (976 cm<sup>-1</sup> [2]), methyl radicals (616 cm<sup>-1</sup>), and new species at 1241, 1231, 972, 874, 796, 606, 524, and 465 cm<sup>-1</sup>, which disappeared upon warming the matrix from 12 to 40-45 K, which indicated their relationship to an unstable species. An increase in the intensity of the bands for (III) and retention of the bands of butadiene and unchanged (IIa) were also observed.



The bands, which disappeared upon warming of the matrix, were also observed along with bands for dimethylbutadiene in the matrix spectra of the products of the pyrolysis of (IIb) under analogous conditions.

All these bands were not retained in the spectrum after warming of the matrix to 20°C and repeated spraying of the products of the pyrolysis of (IIa) and (IIb) along with argon at 12 K. The pyrolysis of (II) above  $850^{\circ}$ C at  $5 \cdot 10^{-4}$ 

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