restricted in $PhSO_2\cdot$ radical. Our entropy of activation ($\Delta S^{\ddagger}$) of -7 eu is in good accord with Bartlett's[5] observation of lowering of $\Delta S^{\ddagger}$ in *tert*-butyl perester decomposition.

Experimental Section

Kinetics.—The sulfur dioxide was expelled from the melted reaction mixture (243-297°) by a stream of nitrogen which was purified by passing through alkaline alcoholic solution of pyrogallol. The SO_2 was then absorbed in aqueous sodium hydroxide and titrated in the presence of 1% H_2O_2. The reaction mixture consisted of 0.0025 mol of phenyl sulfone and 0.05 g-atom of sulfur.

Mass Spectrometry.—A Nier-type double collector mass spectrometer, MS-6, produced at the Institute Jožef Stefan, Ljubljana, Yugoslavia, was used. For the isotope effect determination natural abundance of sulfur-34 was utilized. Samples of SO_2 gas from the reaction carried out to about 2% completion, and to complete decomposition of phenyl sulfone, respectively, were collected in a liquid air trap and purified in a vacuum line, and the $^{32}S/^{34}S$ mass ratios were determined as previously described.[6]

Registry No.—Phenyl sulfone, 127-63-9; sulfur, 7704-34-9.

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A Mannich-Type Condensation of Ethylenedinitramine with Carbethoxyhydrazine and Formaldehyde

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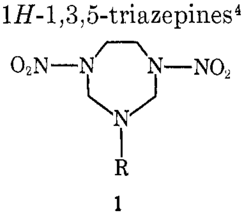
Primary nitramines have an active hydrogen atom on nitrogen and readily undergo the Mannich reaction with amines and formaldehyde.[1,2] Reaction conditions generally are milder than in the condensation of compounds which have the active hydrogen on carbon. The reaction of amines and formaldehyde with ketones which have active hydrogen atoms requires heating,[3] whereas the reaction with nitramines generally occurs at 0-25°.

Ethylenedinitramine ($O_2NNHCH_2CH_2NHNO_2$, EDNA) forms a linear condensation product, *N,N'*-bis(*N*-piperidinomethyl)ethylenedinitramine, $[C_5H_{10}NCH_2N(NO_2)CH_2]_2$, with piperidine and formaldehyde.[1] With primary amines the condensation reaction yields cyclic products, 3-alkyl-1,5-dinitrohexahydro-1*H*-1,3,5-triazepines[4] (**1a**).



a, R = alkyl
b, R = $NHCO_2C_2H_5$

1

In a recent investigation we required a sample of 3-carbethoxyamino-1,5-dinitrohexahydro-1*H*-1,3,5-triazepine (**1b**) as an intermediate. The condensation reaction of ethyl carbazate[5] ($NH_2NHCO_2C_2H_5$) with EDNA and formaldehyde was examined as a route to this compound.

The use of hydrazines in place of amines in a Mannich-type condensation reaction has received very little attention. We found only four references to reactions of this type.[6] No examples of a Mannich-type condensation of nitramines with hydrazines have been reported.

The reaction of ethyl carbazate with EDNA[7] and formaldehyde proceeded readily to afford a good yield of **1b**. Undoubtedly, the method could be employed for the condensation of other hydrazine derivatives with various nitramines, but our current research interests do not lie in this area. We plan no further experiments of this type.

Experimental Section

A mixture of 7.0 g (46.6 mmol) of EDNA, 9.8 g (121 mmol) of 37% formaldehyde, and 24.5 ml (49.0 mmol) of 2.0 *N* sodium hydroxide in 42 ml of water was magnetically stirred at ambient temperature for 45 min to obtain a somewhat cloudy solution (A). Potassium acid phthalate (10.5 g, 51.5 mmol) was dissolved with warming in 47 ml of water, and ethyl carbazate (4.9 g, 47.1 mmol) was added after allowing the solution to cool to 55°. This solution was immediately added to A in one portion with magnetic stirring, and 5 ml of water was used to rinse the flask and complete the addition. Product began to precipitate after 6 min. The mixture was stirred overnight to complete the reaction. The white solid was filtered off, washed with water, and dried *in vacuo* over phosphorus pentoxide. The yield was 10.4 g (80%). Recrystallization from an acetone-carbon tetrachloride mixture yielded 8.8 g (68%) of **1b**: mp 181° (frothing) at 1°/min; ir (Nujol) 2.98 (m, NH), 5.72 (vs, C=O), 6.52 and 6.58 (vs, NNO_2), 7.66 (vs), 7.84 (vs), 9.11 (ms), and 10.65 μ (s); $\lambda_{\rm EtOH}^{\rm max}$ 243 mμ (ϵ 11,000); nmr (acetone-d_6) τ 1.53 (NH, broad s), 4.71 (NCH_2N, s), 5.69 (NCH_2CH_2N, s), 5.98 (q, $J = 7$ cps), 8.84 (t, $J = 7$ cps).

Anal. Calcd for $C_7H_{14}N_6O_6$: C, 30.21; H, 5.07; N, 30.21; mol wt, 278. Found: C, 30.44; H, 5.23; N, 30.20; mol wt, 280.

Substantially lower yields were obtained when potassium acid phthalate was not employed. This was due to an increase in pH which resulted from the liberation of sodium hydroxide as EDNA was used up. An attempt to use hydrochloric acid in place of potassium acid phthalate resulted in the formation of a sticky, viscous material. Another experiment in which 33% more potassium acid phthalate was used gave an impure product. The infrared spectrum of this crude product was very similar to that of the pure material except that an additional N-H band occurred at 3.09 μ. A similar type of impure product resulted when exactly 2 mol of formaldehyde were employed for each mole of EDNA instead of the 30% excess described above.

Registry No.—**1b**, 32121-18-9; EDNA, 505-71-5; carbethoxyhydrazine, 4114-31-2; formaldehyde, 50-00-0.

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