0.1 mol) was added dropwise with rapid stirring. Vigorous evolution of a gas (CH_3Cl) was noted. After addition was complete the reaction mixture was allowed to warm to room temperature and then vacuum distilled. Dimethyl benzoylphosphonate (18.2 g, 85%) was collected as a yellow oil, bp 130–134° (3 Torr). A ^{31}P nmr spectrum of the product showed a single resonance at +1 ppm.

Hydrogen dimethyl phosphite (5.16 g, 0.047 mol) was placed in a reaction flask to which 100 ml of diethyl ether had been added. Following the addition of di-*n*-butylamine (0.5 g, 0.0026 mol), the solution was cooled to 0°. Dimethyl benzoylphosphonate (10.0 g, 0.047 mol) was introduced slowly with rapid stirring. The reaction was moderately exothermic; external cooling was required to maintain the temperature at 0°. A white solid began to form almost immediately. After all the dimethyl benzoylphosphonate had been introduced the reaction mixture was allowed to warm to room temperature. Filtration yielded 14.6 g (96%) of the title compound.

The tetramethyl ester of phenylmethanehydroxydiphosphonic acid was hydrolyzed by refluxing for 3 hr with an excess of concentrated HCl. The monosodium salt was crystallized by the method of Pflaumer and Filcik.[9] A ^{31}P nmr spectrum consisted of a single resonance at −15.5 ppm.

Anal. Calcd for $C_7H_9O_7P_2Na$: C, 29.0; H, 3.1; P, 21.2; Na, 7.9. Found: C, 28.6; H, 3.0; P, 21.0; Na, 8.3.

Registry No.—Phenylmethane hydroxydiphosphonic acid (monosodium salt), 32247-16-8.

[9] P. F. Pflaumer and J. P. Filcik, Belgian Patent 712,159 (1968).

On the Mechanism of the Desulfonylation of Phenyl Sulfone in Molten Sulfur

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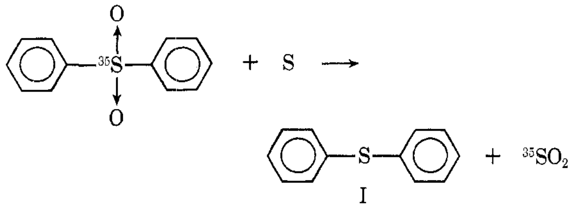
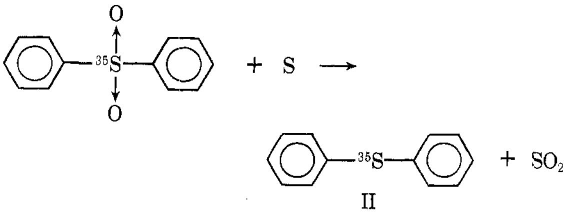
The reaction between sulfur-35 labeled phenyl sulfone and ordinary sulfur has been studied[1] at temperature above 300°. It has been found that, in addition to reaction 1, the reduction process 2 also takes place in about 25% yield. This work has some serious limitations since it is based upon 80% recovery of products.



I (1)



II (2)

Suggestions have been made that thermal decomposition of sulfones normally occurs by homolytic cleavage of RSO_2R into R· and RSO_2· radicals, followed by loss of sulfur dioxide and subsequent recombination of the two R· radicals.[2]

Since the reaction studied in these laboratories proceeds in molten sulfur, the attack by sulfur radical should also be considered. If the rate-determining step were to be a concerted displacement by sulfur radical, then a very small sulfur-34 isotope effect should be found. On the other hand, in a homolytic cleavage into RSO_2· and R· radicals a substantial isotope effect should be observed.

The kinetics of the overall process in nitrogen atmosphere at 243, 262, 288, and 297° were studied, and the corresponding first-order rate constants, $k \times 10^6$ sec^{-1}, found to be 5.21 ± 0.12, 19.2 ± 0.3, 120 ± 1, and 209 ± 9, respectively (uncertainties are standard deviations of the mean). Using the technique of least squares the energy of activation for the overall reaction was found to be 41 ± 1 kcal mol^{-1}, and the frequency factor 1.0 $\times 10^{12}$ sec^{-1}. The entropy of activation was found to be −7 eu. Oae, *et al.*,[1] determined that the ratio of product yields from reactions 1 and 2 (I/II) remain unchanged even at the boiling point of sulfone (379°). This observation indicates that the energies of activation of both reactions must be similar and approximately equal to the energy of activation determined by us for the overall process (41 kcal mol^{-1}).

The maximum isotope effect in breaking a C–S bond can be calculated from Bigeleisen theory.[3] Assuming the C–S stretching frequency[4] of 700 cm^{-1} the maximum isotope effect for decomposition of the hypothetical C–S molecule was calculated to be 1.07% ($^{32}k/^{34}k$ = 1.0107) at 243°.

The sulfur-34 isotope effect for the overall reaction at 243° was determined with $^{32}k/^{34}k$ = 1.0043 ± 0.0012. On the assumption that about 75% of SO_2 is formed by reaction 1 with an isotope effect (IE), and 25% of SO_2 by reaction 2 with an isotope effect (IE′), it follows that 0.43 = 0.75 IE + 0.25 IE′. The isotope effect (IE) of reaction 1 can only be estimated, since the isotope effect of reaction 2 (IE′) is not known. Reaction 2 may occur by a bimolecular attack of sulfur radicals from the melt. In this case a positive isotope effect related to the formation of sulfur radicals by sulfur–sulfur bond breaking will be reduced by the negative isotope effect caused by the bimolecular attack of sulfur radicals on the substrate. The resulting isotope effect of reaction 2, IE′, is therefore most probably not far from zero. If zero, IE is about 0.6%. It can be concluded that the measured isotope effect is primarily that due to reaction 1, and that its value is roughly one-half of the maximum isotope effect for breaking a C–S bond. This substantial isotope effect for reaction 1 indicates appreciable C–S bond weakening in the transition state, suggesting dissociation as a rate-determining step, followed by loss of sulfur dioxide and subsequent recombination of Ph· and S· radicals. The negative entropy of activation of −7 eu can be explained by assuming almost free rotation about the two C–S bonds in starting material, while this rotation may be quite

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[1] S. Oae and S. Kawamura, *Bull. Chem. Soc. Jap.*, **36**, 163 (1963).

[2] W. K. Busfield and K. J. Ivin, *Trans. Faraday Soc.*, **57**, 1044 (1961); W. K. Busfield, K. J. Ivin, H. Mackle, and P. A. G. O'Hare, *ibid.*, **57**, 1054 (1961); E. M. Lacombe and B. Stewart, *J. Amer. Chem. Soc.*, **83**, 3457 (1961).

[3] J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947); J. Bigeleisen, *ibid.*, **17**, 675 (1949).

[4] W. O. George, R. C. W. Goodman, and J. H. S. Green, *Spectrochim. Acta*, **22**, 1749 (1966).

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.

Acknowledgment.—The authors thank Professor Maurice Kreevoy for helpful discussion.

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A Mannich-Type Condensation of Ethylenedinitramine with Carbethoxyhydrazine and Formaldehyde

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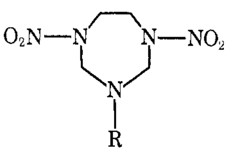
Primary nitramines have an active hydrogen atom on nitrogen and readily undergo the Mannich reaction with amines and formaldehyde.[1,2] Reaction conditions generally are milder than in the condensation of compounds which have the active hydrogen on carbon. The reaction of amines and formaldehyde with 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); $\lambda_{\mathrm{EtOH}}^{\max}$ 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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