tion of *rac*-2,5-dibromoadipic acid (5.00 g) in 50 ml of boiling acetonitrile. The mixture was heated at reflux for 2.0 hr. After cooling to room temperature the reaction mixture was filtered with suction and afforded unreacted carbonate, sodium bromide, and a filtrate which contained the dilactone. The solvent was removed at room temperature and the residue after two recrystallizations from ethanol gave 1.01 g (43%) of dilactone (I), mp 135°.

Anal. Calcd for $C_6H_6O_4$: C, 50.71; H, 4.26. Found: C, 50.49; H, 4.23.

A longer period of refluxing did not improve the yield.[9]

Dilactone from *meso*-2,5-Dibromoadipic Acid.—In a similar manner the *meso* acid afforded the dilactone, mp 135°. However, a longer period of refluxing (7.0 hr) was required to give a yield of 43%. Refluxing for 3 hr gave a 34% yield and refluxing for 72 hr gave a 43% yield. The infrared and nmr spectra and melting points of the dilactones derived from the racemic and *meso* isomers were identical.

Reaction of (−) and (+) Acids with Sodium Carbonate in Acetonitrile.—To (−)-2,5-dibromoadipic acid (0.75 g), $[\alpha]^{25}D$ −60.1 ± 1°, dissolved in acetonitrile (25 ml) was added sodium carbonate (0.29 g), and the reaction mixture was refluxed for 48 hr. The final product was recovered in the above manner and after two recrystallizations from ethanol afforded 0.13 g (38%) of dilactone, mp 129–131°, $[\alpha]^{25}D$ −3.38 ± 0.17°.

Anal. Calcd for $C_6H_6O_4$: C, 50.71; H, 4.26. Found: C, 50.73; H, 4.32.

The retained optical activity was 24.2% and was based on $[\alpha]^{18}D$ −66.3° for the (−) acid[8] and on $[\alpha]D$ −15.5° for (−) dilactone.[6] The melting point of the active dilactone is 120–121°.[6] In a similar manner (+)-2,5-dibromoadipic acid, $[\alpha]^{25}D$ +15.9 ± 1°, afforded a dilactone, $[\alpha]^{25}D$ +0.89 ± 0.29°, mp 132–133.5°, 37.8% yield, and with 25.5% retained optical activity.

Anal. Calcd for $C_6H_6O_4$: C, 50.71; H, 4.26. Found: C, 50.67; H, 4.22.

Racemization, which accounts for the loss in optical rotation, may be due to the equilibration (+) acid ⇄ *meso* acid ⇄ (−) acid. It is also possible that competing intramolecular displacements with inversions may give a dilactone of opposite optical rotation. All rotations were obtained with a Ruldolph Model 80 polarimeter, and using 5% in acetone solutions. Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill.

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(9) The low yield may be due to the unavoidable formation of 1 mole of water. This may render the starting material at some stage in the reaction sequence to become unproductive from the standpoint of I. The reaction is also not homogeneous and there is the added possibility of intermolecular reactions taking place.

The Reaction of Dimethyl Sulfoxide and 5-Dimethylaminonaphthalene-1-sulfonyl Chloride

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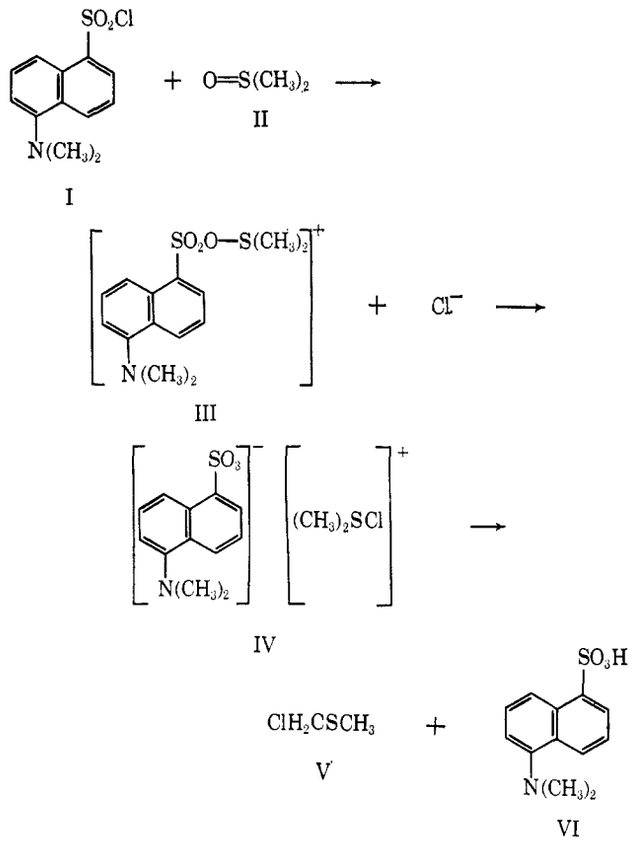
Dimethyl sulfoxide (DMSO) has been used extensively in recent years because of its unique solvent and reaction characteristics.[1-3] In the course of testing DMSO as a solvent and stabilizer for 5-dimethylaminonaphthalene-1-sulfonyl chloride (DANSC) in protein staining we have observed a rapid reaction at room temperature that resulted in a change in the absorption characteristics and produced a fluorescence emission. This paper presents a simple kinetic analysis of the reaction and a proposed mechanism for the formation of 5-dimethylaminonaphthalene-1-sulfonic acid (DANSA) and chlorodimethyl sulfide (CDMS) *via* a sulfoxonium salt intermediate. The reaction can be formulated empirically as shown in eq 1.

SCHEME I



$$\underset{\text{I}}{\text{DANSC}} + \underset{\text{II}}{\text{DMSO}} \longrightarrow \underset{\text{VI}}{\text{DANSA}} + \underset{\text{V}}{\text{CDMS}} \qquad (1)$$

Figure 1 is a reproduction of a repetitive scan spectrum for a single kinetic experiment. From this set of curves and others the absorbance at 360 and 316 mμ was determined, and plotted as a function of time, and the slopes were determined. The logarithms of these slopes were plotted against the logarithms of the concentration of DANSC to establish the order of the reaction as a function of the concentration of DANSC. Figure 2 shows the results for the appearance of DANSA and the disappearance of DANSC. Both slopes are approximately 1, indicating first-order dependence. Further first-order dependence was confirmed using the integrated rate equations, half-life dependence, and by the differential method. The first-order rate constant for the disappearance of DANSC was 1.1 ± 0.2 × 10^{-3} sec^{-1} and for the appearance of DANSA was 1.4 ± 0.2 × 10^{-3} sec^{-1} as a function of the initial concentration of the DANSC.

The adherence of the results of the reaction to the pseudo-unimolecular kinetics as a function of the concentration of DANSC and the constancy of the rate as

(1) T. Sato, *Yuki Gosei Kaguku Kyokai Shi*, **23**, 768 (1965); *Chem. Abstr.*, **63**, 13062b (1965).

(2) "DMSO, Reaction Medium and Reactant, A Survey of the Literature," Crown Zellerbach Corp., 1962.

(3) N. Kharasch and B. S. Thyagarajan, *Quart. Rep. Sulfur*, **1**, 1 (1966).

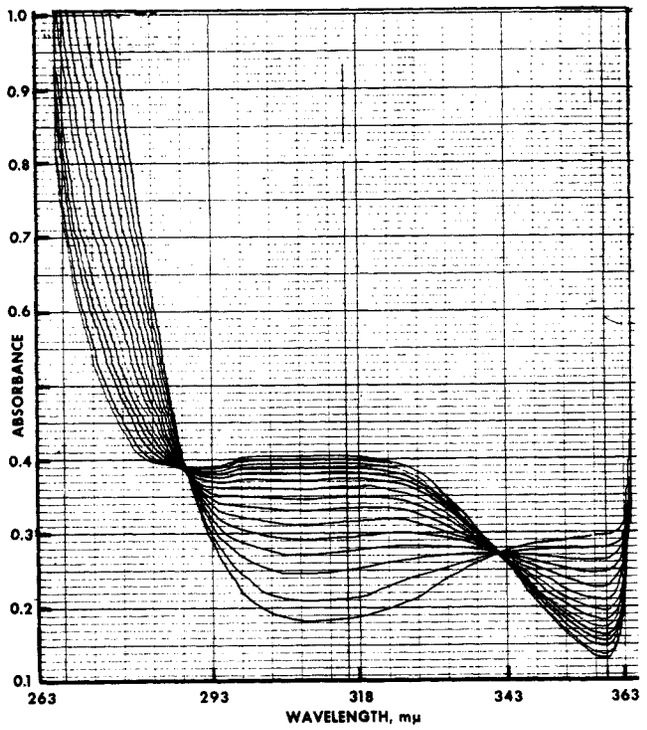


Figure 1.—Repetitive scan spectra; concentration of DANSC = 0.92×10^{-4} M, DMSO = 6.15 M; solvent ethyl ether; total reaction time 870 sec.

a function of the DMSO are indicative of a bimolecular reaction. The presence of an isosbestic point in Figure 1 at 340 mμ, although not absolute proof, indicates only two reactants; the identification of only two products of the reaction is additional evidence for the formulation of the reaction as shown in eq 1. Further, Bordwell and Pitt[4] have shown CDMS and benzoic acid and CDMS and HCl to be products of the reaction of DMSO with benzoyl and thionyl chloride, respectively. With silicon tetrachloride, Lappert[5] has shown the products to be CDMS and HCl. DMSO has also been shown to react with a variety of materials such as aromatic sulfonic acid esters,[6] sulfonamides,[7] alcohols,[8] phenols,[9,10] and acetic anhydride.[11]

A suggested mechanism for the reaction is given in Scheme I, beginning with a nucleophillic attack by the DMSO (II) on the sulfur containing the chloride in DANSC (I) with the formation of a sulfoxonium intermediate III. The chloride ion then displaces the oxygen-containing group in III by attack at the sulfur ion to give the sulfonium compound IV, which rearranges to give CDMS (V) and DANSA (VI). This proposed mechanism, which is not the only reasonable one which satisfies the data, is consistent with that proposed for the reaction of the DMSO with organic and inorganic acyl halides,[4,6] anhydrides,[11-13] and alkyl halides.[14]

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(5) M. F. Lappert and J. K. Smith, *J. Chem. Soc.*, 3224 (1961).
(6) S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).
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(10) K. E. Pfitzner, J. P. Marino, and R. A. Olofson, *ibid.*, **87**, 4658 (1965).
(11) S. Oae, T. Kitao, S. Kanamura, and Y. Kitaoka, *Tetrahedron*, **19**, 817 (1963).
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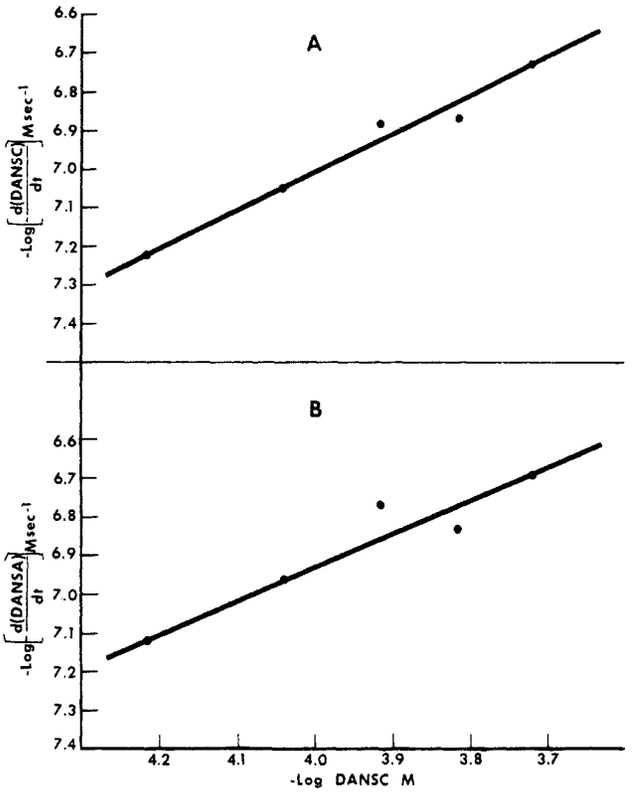

Figure 2.—Logarithm of the rate of disappearance of DANSC as a function of the logarithm of the initial concentration of DANSC (A). Logarithm of the rate of appearance of DANSA as a function of the logarithm of the initial concentration of DANSC (B).

The reaction and mechanism can be considered as Pummerer type which has been thoroughly discussed by Becker, Nickol, and Russell.[15]

Although the reaction in ether at room temperature proceeded moderately and gas chromatographic and spectrophotometric analyses of the reaction mixture gave no indication of other products, it was noted that when the DANSC was added directly to DMSO the solution became warm and passed through several color changes from red to yellow to colorless. This change in color was not investigated but it might possibly be related to the intermediates formed.

Experimental Section

Materials.—DANSC, DANSA, and CDMS were obtained from the K & K Laboratories, Inc., and the DMSO and ether were reagent grade from Fisher Scientific Co. The materials were used without further purification. The molar absorptivities were determined as follows: DANSC in ether, 360 mμ (ϵ 3.62×10^3); DANSA in DMSO, 322 mμ (ϵ 4.77×10^3). In a mixture of DMSO and ether the wavelength of maximum absorbance for DANSA shifted to 316 mμ but ϵ remained the same.

Kinetics.—The decrease in absorbance at 360 mμ for DANSC and increase at 316 mμ for DANSA were followed simultaneously on a Beckman DK-2[16] spectrophotometer equipped with an automatic repetitive scanning attachment using 1.0-cm quartz cuvettes. The spectrum was scanned from 365 to 265 mμ with a scanning time of approximately 90 sec. The reaction was followed for approximately 20 min; the exact times were recorded for each experiment. The order of addition of reagents was always the same. Starting with a given volume and concentration of DANSC in ether, ether and DMSO were added in the pro-

(15) H. D. Becker, G. J. Nikol, and G. A. Russell, *ibid.*, **85**, 3410 (1963).
(16) The citation of commercial equipment and manufacturers by name does not constitute an official endorsement or approval by the U. S. Army.

portions required to give the final desired concentrations. All reaction times were measured from the time of addition of the DMSO. The DANSC concentration ranged from 0.6 to 1.8 × 10^{-4} *M*. The DMSO concentration was 6.2 *M* to give a large excess consistent with a pseudo-unimolecular reaction. All of the kinetic studies were made at room temperature, 27 ± 2°. Ether was chosen as a reaction solvent to prevent complicated side reactions.[5]

Identification of Reaction Products.—The increase in the absorbance at 316 mμ served to identify the DANSA formed in the reaction. It was further identified in a preparative experiment described later. The CDMS was identified by gas chromatography using a 4 ft × 6 mm column of Carbowax-20 M (5%), Haloport F (30–60 mesh) with programming at 11°/min from 60 to 170° on an F and M Model 500[16] gas chromatograph. The CDMS identification was confirmed by comparison of the peak and retention time with an authentic sample.

In a preparative experiment, the reaction mixture was allowed to stand for 24 hr at room temperature. A sample was removed and gas chromatographed as before. Only two peaks were observed and these were confirmed to be DMSO and CDMS with authentic samples treated the same way. The ether was removed from the remaining reaction mixture by gentle heating on a water bath and 1.0 ml of the residual solution was removed, diluted to 100 ml with DMSO, and examined spectrophotometrically. A single peak was observed at 322 mμ as evidence of the presence of DANSA. The remaining solution was treated according to the procedure of Laurence.[17] A solid material was obtained that when recrystallized from 0.1 HCl had a decomposition point of 292° uncor compared with 294° uncor for an authentic sample. Quantitative recovery of the DANSA was not made because of its extreme solubility in DMSO. The isolated material redissolved in DMSO showed only one absorbance peak at 322 mμ, substantiating the presence of DANSA. No "material" balance for the reaction was obtained.

Acknowledgment.—The author wishes to acknowledge the assistance of Mr. Robert A. Saperstein and to thank Mr. Phillip Albro and Dr. Charles K. Huston for the gas chromatography analyses.

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Deoxygenation of Nitro Groups. The Question of Nitrene Formation

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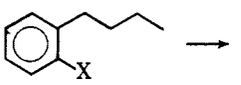
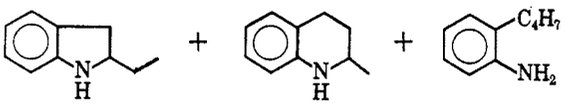
Reductive cyclization of aromatic nitro compounds has been achieved by a number of workers using several different reagents. Cadogan and co-workers,[1] and more recently Sundberg,[2] prepared heterocyclic compounds by heating the appropriate nitro compound in triethyl phosphite. Other investigators have accomplished similar reactions using such reagents as ferrous oxalate[3,4] or iron pentacarbonyl.[5] It has been postulated that all three reagents deoxygenate the nitro group to a nitrene intermediate,[1,3,5] though polar mechanisms have also been suggested[1a,2] for the triethyl phosphite reactions. Our present studies show that nitrenes are involved in the triethyl phosphite reactions but not in the ferrous oxalate case.

Apparently, the only support for the argument that a nitrene was involved in the above reactions was the fact that pyrolysis of the corresponding aromatic azides gave analogous products. It is generally agreed that nitrenes are involved in many azide decomposition reactions.[6] Since nitrenes formed from azides have been shown[6] to insert into the C–H bond of a saturated carbon atom, we believe that the most convincing evidence for intervention of a nitrene in the deoxygenation of a nitro group would be the formation of a carbon–nitrogen bond at a saturated carbon atom.

Sundberg has recently reported[7] that heating a solution of *o*-nitro-*n*-butylbenzene (Ia) in triethyl phosphite formed, in approximately 10% total yield,

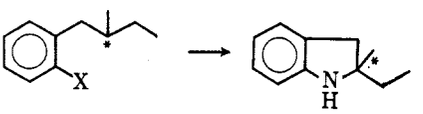


Ia, X = NO_2
b, X = N_3



II III IV

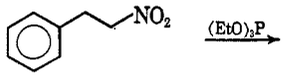
a mixture of compounds consisting of II, III, and IV in almost the same ratio as was formed from the solution phase decomposition[8] of the azide Ib. We wish to report that heating (+)-(*S*)-2-nitro-1-(2-methylbutyl)benzene (Va)[9] in triethyl phosphite resulted in a 25% yield of partially active (~50%) indoline VI. This compares favorably with our earlier finding[9]



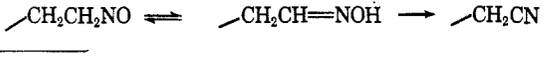
Va, X = NO_2
b, X = N_3 VI

that solution-phase pyrolysis of azide Vb gave VI (60%) of 65% optical purity. Both of the above deoxygenation reactions meet our criterion for a nitrene reaction.

Heating the aliphatic nitro compound, 1-nitro-2-phenylethane (VII), in triethyl phosphite resulted in the formation of phenylacetonitrile presumably *via* the oxime since the nitrile could also be obtained by starting with the oxime (eq 1).



VII



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