

Anal. Calcd for  $C_{22}H_{21}N_2P$ : N, 8.13; P, 9.00. Found: N, 8.17; P, 8.98.

$\alpha$ -Dithiocarboxy- $\alpha$ -cyanomethylene(*p*-dimethylaminophenyl)-diphenylphosphorane (IX).—A solution of 1.50 g (0.00435 mole) of cyanomethylene(*p*-dimethylaminophenyl)diphenylphosphorane in 25 ml of chloroform, to which had been added 40 ml of carbon disulfide, was allowed to stand at room temperature for 24 hr. Upon evaporation of the solvents under vacuum 1.79 g (98%) of the yellow dithiocarboxylic acid IX was obtained, mp 125–135° dec. An analytical sample recrystallized from benzene-ether melted at 136–139° dec.

Anal. Calcd for  $C_{23}H_{21}N_2PS_2$ : N, 6.66; P, 7.37; S, 15.25. Found: N, 6.65; P, 7.30; S, 15.39.

**Acknowledgment.**—The authors wish to express their gratitude to Professor Nathan Kornblum, Purdue University, for reading and commenting upon the original manuscript. We are also greatly indebted to Mrs. Barbara Artman of the Analytical Chemistry Department for the microanalyses.

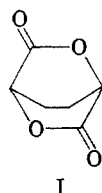
### On the Ring Closure of Some 2,5-Dibromoadipic Acids

R. B. SANDIN, W. J. REBEL,<sup>1a</sup> AND S. LEVINE<sup>1b</sup>

Department of Chemistry, University of Alberta,  
Edmonton, Alberta, Canada

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Le Sueur<sup>2</sup> heated *meso*-2,5-dihydroxyadipic acid and obtained water and a lactone-lactide. However, heating racemic-2,5-dihydroxyadipic acid afforded the racemic dilactone (I). Marvel and collaborators<sup>3</sup> also

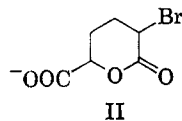


I

prepared I by heating the racemic acid.

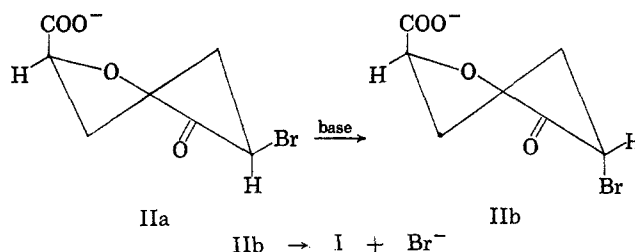
In connection with some biological studies of derivatives of the 2,5-dibromoadipic acids, the behavior of these acids with sodium carbonate in refluxing acetonitrile has been examined. It has been found that, irrespective of the acid (racemic, *meso*, active), the reaction mixture affords as one of the end products the dilactone I in 43% yield.

These results can be rationalized by a reaction scheme which must involve the intermediate  $\delta$ -lactone (II)<sup>4</sup>



II

which would probably adopt the half-chair conformation<sup>5</sup> to give the final product. By a backside dis-



placement with inversion of configuration, IIb is changed into I. Epimerization at the brominated carbon in IIa *via* base-catalyzed enolization could give rise to IIb. Such an epimerization is conformationally reasonable and involves quasi-axial Br  $\rightarrow$  quasi-equatorial Br in a half-chair ring. Experimentally it was found that dilactone formation is slower for the *meso* acid.

Freudenberg and collaborators<sup>6</sup> heated (+)-2,5-dihydroxyadipic acid and obtained the (+)-dilactone. In view of this work it was of interest to carry out reactions with the active dibromoadipic acids. We have found that (+)-2,5-dibromoadipic acid yields some (+)-dilactone and, similarly, (-)-2,5-dibromoadipic acid affords some (-)-dilactone. Based on the *assumption* that the dibromo acids and the dihydroxy acids with the same sign of optical rotation have the same configuration an interesting mechanism can be considered for the formation of the active dilactones from the active dibromo acids. It would involve a double inversion (the first inversion brought about by neighboring group participation by the carboxylate ion to form an  $\alpha$ -lactone) with retention of configuration<sup>7</sup> to give the  $\delta$ -lactone IIb. The active dilactone is then formed from IIb through a backside displacement. The *meso* acid would also undergo a double inversion (the first inversion brought about by neighboring group participation by the carboxylate ion to form an  $\alpha$ -lactone) with retention of configuration to give the  $\delta$ -lactone IIa. By means of a base-catalyzed enolization and epimerization at the brominated carbon, IIa is converted to IIb. Experimentally it happens that there is also retention of the sign of rotation for the optically active dibromo acids.

For the active dihydroxy acid two intramolecular esterifications afford the active dilactone. No inversion of configuration is possible because bonds to the asymmetric carbon atoms are not involved and again there is retention of the sign of rotation. This also explains the fact that the *meso*-dihydroxy acid is not a suitable material for making the dilactone, since inversion would be necessary.

#### Experimental Section

**Materials.**—The racemic and *meso*-2,5-dibromoadipic acids were prepared by the procedure of Holmberg and Muller.<sup>8</sup> The resolution of *rac*-2,5-dibromoadipic acid was carried out according to Holmberg and Muller.<sup>8</sup> The acetonitrile was certified reagent from Fisher Scientific Co.

**Dilactone from *rac*-2,5-Dibromoadipic Acid.**—Powdered, anhydrous sodium carbonate (1.75 g) was slowly added to a solu-

(5) It has been suggested that  $\delta$ -lactones will adopt a half-chair conformation whenever possible [K. K. Cheung, K. H. Overton, and R. A. Sim, *Chem. Commun.*, 634 (1965)], permitting the resonance of OC(=O) system.

(6) K. Freudenberg, W. F. Bruce, and E. Gauf, *Ann.*, **510**, 209 (1934).

(7) W. A. Cowdrey, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1208 (1937); E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 841 (1958).

(8) B. Holmberg and E. Muller, *Ber.*, **58B**, 1601 (1925); see also, C. K. Ingold, *J. Chem. Soc.*, **119**, 951 (1921).

(1) (a) To whom correspondence should be addressed at the Union Carbide Corp., Chemicals Division, Tarrytown, N. Y.; (b) Department of Chemistry, University of Saskatchewan, Regina Campus.

(2) H. R. Le Sueur, *J. Chem. Soc.*, **93**, 718 (1908).

(3) C. S. Marvel, E. D. Weil, L. B. Wakefield, and C. W. Fairbanks, *J. Am. Chem. Soc.*, **75**, 2327 (1953).

(4) This lactone was not isolated. The infrared spectrum of the reaction mixture supports the structure of an intermediate  $\delta$ -lactone.

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<sub>8</sub>H<sub>8</sub>O<sub>4</sub>: C, 50.71; H, 4.26. Found: C, 50.49; H, 4.23.

A longer period of refluxing did not improve the yield.<sup>9</sup>

**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), [ $\alpha$ ]<sub>D</sub><sup>25</sup> -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°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -3.38 ± 0.17°.

*Anal.* Calcd for C<sub>8</sub>H<sub>8</sub>O<sub>4</sub>: C, 50.71; H, 4.26. Found: C, 50.73; H, 4.32.

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

*Anal.* Calcd for C<sub>8</sub>H<sub>8</sub>O<sub>4</sub>: 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 Rudolph 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

ROBERT E. BOYLE

Department of the Army, Fort Detrick, Frederick, Maryland

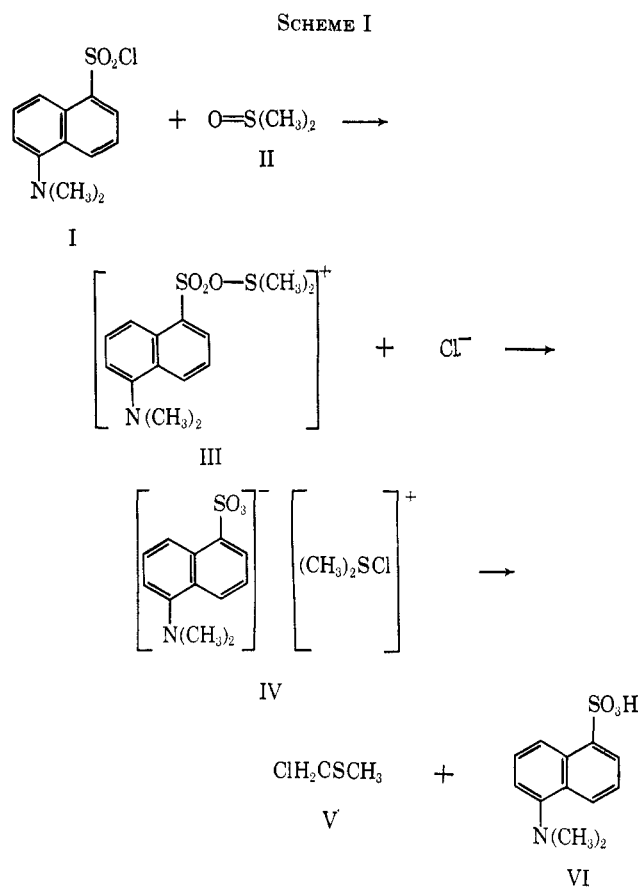
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Dimethyl sulfoxide (DMSO) has been used extensively in recent years because of its unique solvent and reaction characteristics.<sup>1–3</sup> In the course of testing

(1) T. Sato, *Yuki Gosei Kagaku 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).



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.

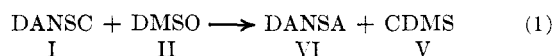


Figure 1 is a reproduction of a repetitive scan spectrum for a single kinetic experiment. From this set of curves and others the absorbance at 360 and 316 m $\mu$  was determined, and plotted as a function of time, and the slopes were determined. The logarithms of these slopes were plotted against the 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  $1.1 \pm 0.2 \times 10^{-3} \text{ sec}^{-1}$  and for the appearance of DANSA was  $1.4 \pm 0.2 \times 10^{-3} \text{ sec}^{-1}$  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