further investigation will add numerous examples.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF NOTRE DAME]

Methyl Vinyl Sulfoxide. Copolymerization and Spectra

BY CHARLES C. PRICE AND RICHARD D. GILBERT[1,2]

Although methyl vinyl sulfoxide retards copolymerization, data with styrene indicate values for the resonance stabilization factor $Q = 0.10$ and for the electrical factor $e = 0.9$. The latter is as expected. The conjugative properties of a sulfoxide group are unexpectedly low, as indicated by the value of Q, by ultraviolet absorption and by infrared spectra.

As reported in a previous publication,[3] the copolymerization properties and ultraviolet spectra of methyl vinyl sulfide and sulfone indicated strong conjugative properties for the sulfide group, very weak conjugative properties for the sulfone group. The evidence was interpreted as supporting the view that the sulfur–oxygen bond is best represented as a semi-polar bond. The purpose of the present investigation was to extend this investigation to methyl vinyl sulfoxide.

Experimental[4]

Methyl Vinyl Sulfoxide. A. From β-Chloroethyl Methyl Sulfoxide.—Although efforts to dehydrohalogenate this chloro sulfoxide with sodium methoxide gave only displacement products, the methoxyl and hydroxyl derivatives,[3] experiments showed that sodium *t*-butoxide was a satisfactory reagent for dehydrohalogenation. β-Chloroethyl sulfide[5] was oxidized with one equivalent of hydrogen peroxide in glacial acetic acid and the reaction mixture was stripped to 62° at 25 mm. To the residue (161.9 g., 1.28 moles) maintained below 40°, a well-stirred suspension of sodium *t*-butoxide (122.9 g., 1.28 moles) in 1000 ml. of *t*-butyl alcohol was added in small portions over three hours. After stirring overnight, the mixture was filtered and the residue distilled, yielding three fractions: (1) *t*-butyl alcohol, b.p. 81–83°, *ca.* 1000 ml.; (2) methyl vinyl sulfoxide, b.p. 46–47° (0.8 mm.), $n^{25}D$ 1.4938, 48 g.; (3) β-chloroethyl methyl sulfoxide, b.p. 102–103° (4 mm.), 7.2 g.

Redistillation of fraction 2 yielded 44.5 g. (38.6%) of **methyl vinyl sulfoxide**, b.p. 43.5° (0.5 mm.), $n^{25}D$ 1.4925. It decolorized bromine in carbon tetrachloride rapidly.

Anal. Calcd. for C_3H_6SO: C, 39.97; H, 6.71; S, 35.57. Found: C, 39.56; H, 6.97; S, 35.16.

B. From Methyl Vinyl Sulfide.—Methyl vinyl sulfide (12 g., 0.16 mole) (prepared in 56% yield according to Brown and Moggridge,[6] b.p. 67.3°, $n^{25}D$ 1.4802) in 25 ml. of methanol was treated with 186 ml. of commercial "Clorox" (a 1.7 *N* solution of sodium hypochlorite) added so that the reaction mixture was maintained below 5°. After three hours, the homogeneous reaction mixture was extracted with two 100-ml. portions of chloroform. After drying over magnesium sulfate, the chloroform was removed and the residue distilled through a small Vigreux column.

Methyl vinyl sulfoxide (4.6 g., 32%) was collected at 52° (3 mm.), $n^{25}D$ 1.4921.

Anal. Found: C, 39.70; H, 6.77; S, 35.80.

Copolymerization experiments with styrene and methyl methacrylate were carried out by the previously reported procedure.[3] The sulfoxide seemed to have mild retarding properties, especially evident in the copolymerization experiments with methyl methacrylate. The results are summarized in Tables I and II.

TABLE I

COPOLYMERIZATION OF STYRENE (M_1) WITH METHYL VINYL SULFOXIDE (M_2)

M_2[a]	Time, hr.	Conversion, %	Percentages S	C	H	dM_2[b] (S)	dM_2[c] (C)
0.125	3.5	3.18	0.94	91.10	7.75	0 0.30	0.026
.250[d]	5.0	1.13	1.90	89.84	7.87	.059	.053
.375[d]	6.0	1.83	2.27	88.78	7.43	.073	.077
.500[d]	7.6	0.42	2.80	87.70	7.78	.089	.099
.625[d]	10.5	.28	3.84	..[e]	..	.123	
.750	22.0	..	..	...	..		
.875	47.0	..	..	...	..		

[a] Mole fraction of methyl vinyl sulfoxide in original monomer mixture. [b] Mole fraction of methyl vinyl sulfoxide in copolymer, calculated from sulfur analysis. [c] Mole fraction of methyl vinyl sulfoxide in copolymer, calculated from carbon analysis. [d] Analysis corrected for ash content. [e] Yield too small for analysis.

TABLE II

COPOLYMERIZATION OF METHYL METHACRYLATE (M_1) WITH METHYL VINYL SULFOXIDE (M_2)

M_2[a]	Time, hr.	Conversion, %	Percentages S	C	H	dM_2[b] (S)
0.225[d]	3.0	2.42	0.24	59.08	8.04	0.007
.250[d]	6.0	0.45	.77	60.98	8.36	.024
.375	45.0	..[e]	..	...	..	
.500	48.0	..	..	...	..	

[a] Mole fraction of methyl vinyl sulfoxide in original monomer mixture. [b] Mole fraction of methyl vinyl sulfoxide in copolymer, calculated from sulfur analysis. [d] Analysis corrected for ash content. [e] Yield too small for analysis.

Ultraviolet Absorption Measurements.—The measurements were made using 95% ethanol as the solvent. A Beckman quartz spectrophotometer was employed, the spectrum was examined from 225 to 250 mμ at 1.0 mμ intervals, and from 250 to 320 mμ at 5.0 mμ intervals.

The molar extinction coefficient (ϵ) was calculated from the equation $\epsilon = D/cd$; where D is the density of transmission, d is the length of the cell in centimeters, and c is the concentration of the solution in mole/liter. The concentration of methyl vinyl sulfoxide was 0.0001368 mole/liter in the case of the product from the dehydrohalogenation of β-chloromethyl methyl sulfoxide, and 0.0001497 mole/liter in the case of the product from the hypochlorite oxidation of methyl vinyl sulfide. The curves were identical and showed a maximum at 229 mμ, log ϵ 3.32.

Infrared Absorption Measurements.—The measurements were made using a Beckman spectrophotometer Model IR-2; the spectrum was examined from 6.8 to 8.5 μ, employing the pure compounds (*i.e.*, no solvent was used). The β-chloroethyl methyl sulfoxide was recovered material from one dehydrohalogenation experiment, and it was redistilled and collected at 96° (0.9 mm.), but still had a trace

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[1] American Cyanamid Fellow, 1948–1950.

[2] Abstracted from a Ph.D. thesis submitted to the Graduate School of the University of Notre Dame. Presented at the XII International Congress, New York, September 11, 1950.

[3] C. C. Price and J. Zomlefer, THIS JOURNAL, 72, 14 (1950).

[4] Analyses by Micro-Tech Laboratories, Skokie, Ill.

[5] W. R. Kirner and W. Windus, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 136.

[6] R. Brown and R. C. G. Moggridge, *J. Chem. Soc.*, 816 (1946).

of color. Both methyl vinyl sulfoxide and β-chloroethyl methyl sulfoxide showed one strong band in this region; the former a sharp band at 7.19 μ, the latter a broad band at 7.17–7.20 μ.

Discussion

Analysis of the copolymerization data for the pair styrene (M_1)–methyl vinyl sulfoxide (M_2) according to the equation[7]

$$r_2 = \frac{M_1}{M_2}\left[\frac{dM_2}{dM_1}\left(1 + \frac{M_1}{M_2} - r_1\right) - 1\right]$$

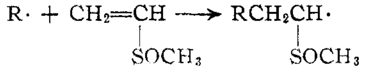
gave values of $r_1 = 4.2 \pm 0.2$ and $r_2 = 0.01 \pm 0.01$. From these values of the copolymerization ratios for this system, the values of the resonance stabilization factor, Q_2, and the electrical factor, e_2, were calculated from the equations of Alfrey and Price.[8]

$$r_1 = Q_1/Q_2\, e^{-e_1(e_1-e_2)}$$
$$r_2 = Q_2/Q_1\, e^{-e_2(e_2-e_1)}$$

Using the values of $Q_1 = 1.0$ and $e_1 = -0.8$ for styrene[9] we obtain the values of $Q_2 = 0.10$ and $e_2 = 0.9$.

The value of 0.9 for e for methyl vinyl sulfoxide, somewhat smaller in magnitude than $e = 1.2$ for methyl vinyl sulfone,[3] is reasonable in view of the smaller σ constant for the methyl sulfoxide group (0.5) compared to the methyl sulfonyl group (0.7).[10]

The Q-value for methyl vinyl sulfoxide (0.10) is low, like methyl vinyl sulfone ($Q = 0.07 - 0.15$) as compared to methyl vinyl sulfide ($Q = 0.33 - 0.34$), indicating little resonance interaction between the sulfoxide group and the carbon free radical intermediate in polymerization.



$$R\cdot + \underset{\displaystyle SOCH_3}{CH_2{=}CH} \longrightarrow \underset{\displaystyle SOCH_3}{RCH_2CH\cdot}$$

Since the sulfoxide group retains an unshared pair of electrons on the sulfur and in this way resembles the sulfide more than the sulfone, it was surprising to find such a low Q factor. However, the data on the ultraviolet spectra are in agreement since they too indicate little conjugation between the sulfoxide group and the carbon–carbon double bond for methyl vinyl sulfoxide; λ_{max} 229 mμ, log ε 3.32. Mohler[11] reports that β-chloroethyl sulfoxide shows λ_{max} 220 mμ, log ε 3.1.

This is a relatively small change in spectra when compared with the shift occurring for the sulfide: β-chloroethyl sulfide,[11] λ_{max} 205 mμ, log ε 3.5; methyl vinyl sulfide,[3] λ_{max} 240 mμ, log ε 4.0.

The ineffective resonance interaction between the sulfur–oxygen bond and the carbon–carbon bond is further indicated by the identity of the 7.19 μ bands for the saturated and unsaturated sulfoxides.[12] This contrasts with the shift of the carbonyl frequency from 5.81 μ in methyl ethyl ketone[13] to 5.95 μ in methyl vinyl ketone.[14]

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[7] F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs and F. R. Mayo, This Journal, **70**, 1519 (1948).

[8] T. Alfrey and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947).

[9] C. C. Price, *ibid.*, **3**, 772 (1948).

[10] C. C. Price and J. J. Hydock, This Journal, **74**, 1943 (1952).

[11] H. Mohler, *Helv. chim. acta*, **20**, 1188 (1937).

[12] It is not certain whether this 7.19 μ band is that of the sulfur-oxygen or the sulfur-carbon bond. If the former, resonance interaction should shift it to longer wave length, if the latter, to shorter wave length.

[13] H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 166.

[14] C. Cherrier, *Compt. rend.*, **225**, 997 (1947).

NOTRE DAME, INDIANA RECEIVED NOVEMBER 23, 1951

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

A New Reaction: The Rearrangement of the Hydrochloride of *cis*-2-Aminocyclopentyl *p*-Nitrobenzoate

BY EUGENE E. VAN TAMELEN

The hydrochloride of *cis*-2-aminocyclopentyl *p*-nitrobenzoate rearranges when heated to *trans*-N-*p*-nitrobenzoyl-2-chlorocyclopentylamine. Experimental evidence is presented which points to an oxazoline intermediate. The scope of this reaction is reported and discussed.

During an investigation concerned with the mechanism of acyl migrations, the author had occasion to attempt a N ⟶ O acyl transfer with *cis*-2-*p*-nitrobenzamidocyclopentanol (I). After the latter substance was refluxed for three hours in dry dioxane which had been previously saturated with dry hydrogen chloride, a 19% yield of the expected hydrochloride of *cis*-2-aminocyclopentyl *p*-nitrobenzoate (II) crystallized on cooling. In an attempt to account for the remainder of the material, the solvent was evaporated from the filtrate and a solid isolated. The product was found, however, to be neither II nor starting material, but a new substance (III), whose melting point (125–126°) was raised to 127.0–127.5° by crystallization from benzene. Compound III (i) was insoluble in water, (ii) gave a positive Beilstein halogen test but no precipitate with alcoholic silver nitrate, and (iii) exhibited strong absorption in the infrared at 6.04 microns, characteristic of the amide function. The analysis corresponded to the empirical formula $C_{12}H_{13}O_3N_2Cl$. These data are consistent with the formulation of III as N-*p*-nitrobenzoyl-2-chlorocyclopentylamine. The ready conversion of III to the known[1] (*cis*) oxazoline (IV) through the agency of alcoholic sodium hydroxide confirms this assignment; the type of ring closure exemplified here characterizes N-acyl-2-haloalkylamines. In addition, the transformation provides evidence for the stereochemistry of III. Winstein[2] and Carter[3] have amply demonstrated the generality of ring closure of N-acyl-2-amino-

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[1] G. E. McCasland and D. A. Smith, This Journal, **72**, 2190 (1950).

[2] S. Winstein and R. Boschan, *ibid.*, **72**, 4669 (1950).

[3] G. E. McCasland, R. K. Clark and H. E. Carter, *ibid.*, **71**, 637 (1949).