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

Some Observations on the Reaction of Alkali Thiocyanates with Epoxides[1]

BY CHARLES C. PRICE AND PAUL F. KIRK[2]

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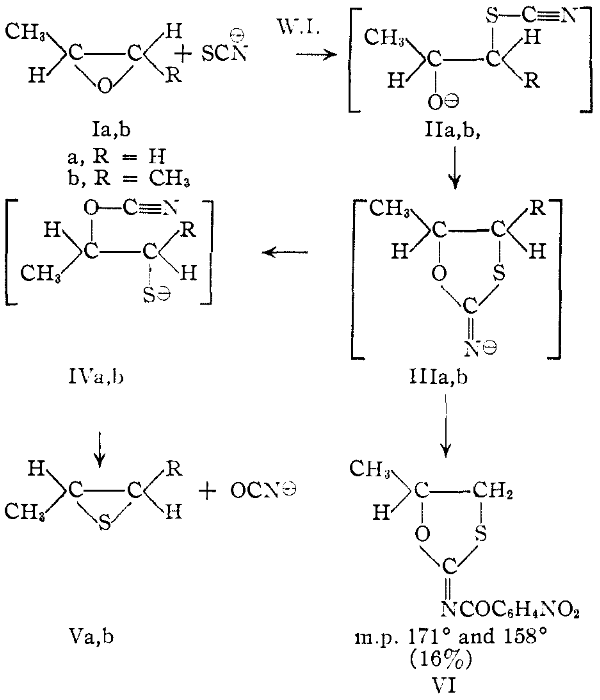
The mechanism proposed by Van Tamelen for the reaction of epoxides with thiocyanate ion to produce episulfides has been confirmed by isolation in 16% yield of 2-(*p*-nitrobenzimino)-5-methyl-1,3-oxathiolane from treatment of a mixture of propylene oxide and potassium thiocyanate with *p*-nitrobenzoyl chloride. The formation of optically active L(−)-2,3-epithiobutane from D(+)-2,3-epoxybutane oxide is in agreement with the mechanism proposed.

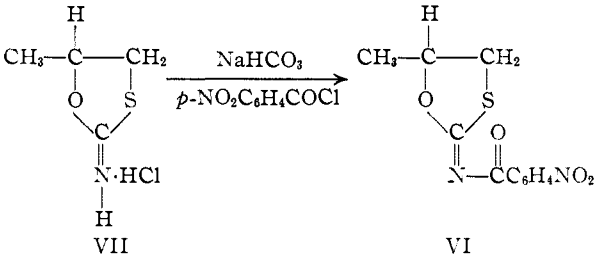
The reaction through which epoxides are converted to episulfides by alkali thiocyanates has received considerabe attention recently.[3-6] A plausible mechanistic scheme for this transformation has been proposed by Ettlinger[7a] and evidence for it obtained by van Tamelen.[3] Essentially this same mechanism was proposed independently by Miles and by Kirk.[7]



This mechanism implies two Walden inversions; the first, in the *trans* opening of the epoxide ring, and the second, in the *trans* closing of the episulfide ring (a step analogous to the formation of epoxide from 1,2-halohydrins). That the opening and closing of epoxide rings proceed with Walden inversion has been amply demonstrated.[8-10]

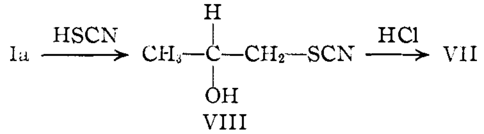
Van Tamelen[3] has shown that the episulfide does not form from cyclopentene oxide by treatment with alkali thiocyanates. This is in complete accord with the stereochemistry of the proposed mechanism since the formation of intermediate III would involve the fusion of two five-membered rings in the *trans* sense, a system involving considerable strain. Van Tamelen has shown, further, that cyclohexyl homologs corresponding to protonated derivatives of the anions II and III reacted with alkali to give the expected episulfide. It has been previously demonstrated[11] that the thiocyanate reaction proceeds with a considerable increase in *p*H.

The work reported herein has produced further evidence in support of this mechanism. First, the presence of the intermediate IIIa, was established by isolation of its N-(*p*-nitrobenzoyl) derivative (VII) in 16% yield. This was effected by treating an aqueous solution of propylene oxide and potassium thiocyanate with *p*-nitrobenzoyl chloride. A small time interval was allowed between the addition of the epoxide to the thiocyanate solution and the reaction with the chloride. Compound VI was then synthesized independently by treating the hydrochloride of IIIa (VII) with *p*-nitrobenzoyl chloride in a weakly basic medium.



VII VI

The identity of the two compounds was established by a mixed melting point determination and by comparison of their infrared spectra. VII was prepared by the reactions



$$\mathrm{Ia} \xrightarrow{\mathrm{HSCN}} \mathrm{CH_3}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{SCN} \xrightarrow{\mathrm{HCl}} \mathrm{VII}$$

VIII

The reaction of propylene oxide (Ia) with thiocyanic acid was carried out by the method of

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[1] Taken from the thesis of Paul F. Kirk, presented to the Graduate School of the University of Notre Dame in January, 1952, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented at the American Chemical Society Meeting, Milwaukee, Wis., April 1, 1952.

[2] A.E.C. Predoctoral Fellow 1949–1951.

[3] E. E. van Tamelen, THIS JOURNAL, **73**, 3444 (1951).

[4] J. S. Harding, L. W. C. Miles and L. N. Owen, *Chem. and Ind.*, 887 (1951).

[5] H. R. Snyder, J. M. Stewart and J. B. Ziegler, THIS JOURNAL, **69**, 2672 (1947).

[6] C. C. J. Culvenor, W. Davies and K. Pausacker, *J. Chem. Soc.*, 1050 (1946).

[7] (a) M. G. Ettlinger, THIS JOURNAL, **72**, 4792 (1950); (b) L. W. C. Miles, Ph.D. Thesis, University of London, 1950; (c) P. F. Kirk, Progress Report to the Atomic Energy Commission, April, 1951.

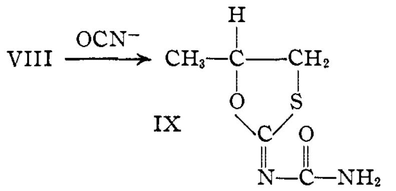
[8] For a recent review on epoxides see S. Winstein and R. B. Henderson, in R. C. Elderfield, "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 1.

[9] P. D. Bartlett and E. H. Rosenwald, THIS JOURNAL, **56**, 1990 (1934).

[10] H. J. Lucas and H. K. Garner, *ibid.*, **70**, 990 (1948).

[11] J. N. Brönsted, M. Kilpatrick and M. E. Kilpatrick, *ibid.*, **51**, 428 (1929).

Wagner-Jauregg,[12] who reported that the liquid propylene thiocyanohydrin decomposed to a white crystalline solid. A small amount of needle-like crystals was precipitated on standing overnight in our preparation. This solid, IX, showed an elemental analysis corresponding to one mole of VIII and one mole of cyanic acid. The infrared spectrum of IX gives no evidence for the presence of either a hydroxyl group or a thiocyano group (see Table II). IX was then synthesized in a very simple manner by reaction of VII with potassium cyanate.



IX

The identity of the two specimens (isolated and synthesized) was shown by their melting point behavior and by the identity of their infrared spectra which, incidentally, conform to that expected for structure IX. The compound is presumably formed from VIII through cyclization of some of the thiocyanohydrin (VIII) to the episulfide Va with elimination of cyanic acid. The latter reacts further with VIII to cyclize it to the oxathiolane which is then transformed into IX.

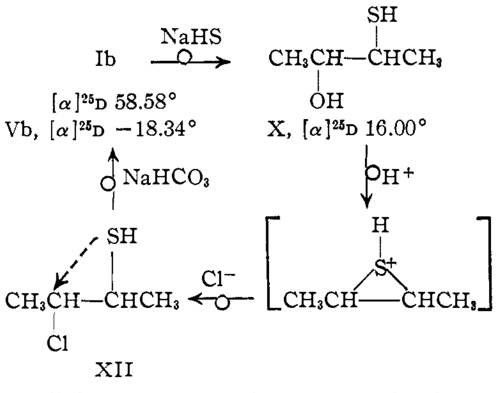
Further support for the proposed mechanism came from a study of the stereochemistry of the reaction. The thiocyanate reaction at room temperature with D(+)-2,3-epoxybutane, $[\alpha]^{25}\text{D}$ 59°[10] produced episulfide which was highly levorotatory, $[\alpha]^{25}\text{D}$ −94°, in 76% yield.

$$\text{Ib} \xrightarrow{\text{SCN}^-} \text{Vb}$$

D(+)-2,3-epoxybutane L(−)-2,3-epithiobutane

$[\alpha]^{25}\text{D}$ 58.58° $[\alpha]^{25}\text{D}$ −94.33°

An independent synthesis of the L(−)-episulfide was then performed by the scheme



It will be seen that this proposed scheme also involves a Walden inversion at each carbon of the three-membered ring. The reaction of the epoxide with the sodium hydrosulfide gave a fair (40%) yield of the hydroxythiol (X). By analogy with many other examples, the opening of the epoxide by the hydrosulfide ion is presumed to proceed with inversion of the carbon which the sulfur attacks. X reacted readily with concentrated hydrochloric acid, first dissolving, presumably, by the rapid formation of intermediate XI with subsequent separation of the chlorothiol XII. There is abundant evidence[13] that the great ease of replacement of hydroxy and halogen adjacent to sulfhydryl or sulfide groups involves participation of the sulfur in a cyclic sulfonium ion. The chlorothiol was extremely unstable and began to lose hydrogen chloride during the course of isolation. It was, therefore, treated immediately with bicarbonate solution to give Vb. The episulfide isolated by distillation was in an obviously impure state, chemically and optically, due to polymerization and extractant contamination and probably considerable racemization during the entire synthesis. Its rotation, although lower than that of the episulfide prepared by the thiocyanate reaction, was still highly negative, $[\alpha]^{25}\text{D}$ −18.34°. The infrared spectra of the two specimens compared well. All peaks found in the sample of greater negative rotation (presumably the purer) were observed in the other, although some differed in relative intensity. It was found that when the purer sample was treated with a very small amount of the *erythro*-chlorothiol (inactive) its rotation dropped about 10% and its infrared spectrum showed appreciable increases and decreases in intensity wholly in the direction of the spectrum of the sample prepared from the chlorothiol. The most marked changes were the diminution of absorption peaks at 9.8 and 10.27. These two peaks were entirely absent in the spectrum of the sample from the chloromercaptan. Presumably the explanation for this behavior is that contributions toward an infrared band of a given frequency are made unequally by the episulfide and its polymer. The less pure sample prepared from the chlorothiol had apparently been substantially polymerized. Its lower rotation is in agreement with this conclusion since the polymer, supposedly formed by successive Walden inversions, would be a *meso*-form and would have no appreciable rotation.

Finally, support for this mechanism was gained through simultaneous measurements of *p*H and optical rotation of a reaction mixture consisting of an aqueous alcoholic potassium thiocyanate solution and the optically active butene oxide. The results are shown in Table I. It will be seen that the *p*H rises rapidly, as expected, but does not then fall to any appreciable extent. It is assumed that the cyanate ion formed is hydrolyzed in the basic medium to carbon dioxide and ammonia, the latter in sufficient amount to maintain the high *p*H. The initial observed rotation of the solution, measured 30 seconds after mixing, was much lower than that calculated for the original mixture. Thereafter, the rotation fell evenly and slowly. This suggests that the initial attack of the thiocyanate ion, opening the ring, is extremely rapid. This is then followed by the rapid ring closure to the oxathiolane intermediate IIIb. The subsequent conversion of this heterocycle to the levorotatory

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[12] T. Wagner-Jauregg, *Ann.*, **561**, 87 (1949).

[13] See, *e.g.*, C. C. Price and L. B. Wakefield, *J. Org. Chem.*, **12**, 232 (1947); R. C. Fuson, C. C. Price and D. M. Burness, *ibid.*, **11**, 475 (1946).

episulfide is, then, comparatively slow. This stability of IIIb is in accord with the isolation of IIIa as its *p*-nitrobenzoyl derivative.

Experimental

We are most grateful to Dr. F. H. Stodola of the U. S. Department of Agriculture, Northern Regional Research Laboratories, Fermentation Division, Peoria, Illinois, for the sample of D(+)-butanediol used in this research. All melting and boiling points are uncorrected. A Beckman glass electrode *p*H meter was employed for *p*H measurements. Baird infrared spectrophotometers were used for the spectral analyses and we are indebted to Dr. C. L. Wilson at The Ohio State University for some of the infrared spectra. The data are summarized in Table II. The optical rotations were performed with a Schmidt & Haensch polarimeter from which readings were obtained with a reproducibility of ±0.02°. All elemental analyses were performed by Charles W. Beazley of the Micro-Tech Laboratories, Skokie, Illinois.

TABLE I

THE CHANGE IN *p*H AND OPTICAL ROTATION FOR A SOLUTION OF D(+)-2,3-EPOXYBUTANE AND POTASSIUM THIOCYANATE

t, min.	$\alpha_{\text{obsd.}}$	*p*H	*t*, min.	$\alpha_{\text{obsd.}}$	*p*H
0	+2.34°[a]	4.92[b]	100	0.99	11.86
1	1.01	6.34	125	.97	11.91
7	1.06	8.52	150	.95	11.97
17	1.06	11.02	200	.92	12.01
25	1.06	11.26	250	.90	12.00
35	1.04	11.43	300	.89	12.02
45	1.07	11.56	420	.79	12.02
55	1.05	11.62	2900	−1.04	11.92
65	1.02	11.69			

[a] Calculated. [b] Refers to aqueous ethanolic KSCN solution.

TABLE II

INFRARED SPECTRA CHARACTERISTICS

2,3-Epithiobutane (Vb)		Nitrobenzoate of iminoöxathiolane (VI)		Propylene thiocyanohydrin (VIII)		N-Carbamyl-iminoöxatholane (IX)	
λ, μ	Intensity	λ, μ	Intensity	λ, μ	Intensity	λ, μ	Intensity
3.36	V. str.	3.35	Med.	2.95	V. str.	2.86	Med.
3.43	Med.	6.06	Str.	3.37	Str.	2.95	Med.
6.72	Weak	6.21	Str.	3.45	Med.	3.42	Med.
6.91	Str.	6.57	V. str.	4.70	Str.	5.98	V. str.
7.24	V. str.	6.92	Weak	5.98	Str.	6.23	Med.
7.50	Weak	7.12	Weak	6.40	Str.	6.41	V. str.
7.70	Weak	7.21	Med.	6.87	Med.	6.93	Med.
9.00	Med.	7.42	Str.	7.10	Med.	7.23	Str.
9.20	Med.	7.65	Str.	7.24	Med.	7.48	Med.
9.35	Med.	8.03	Med.	7.48	Weak	8.04	Med.
9.48	Str.	8.45	Str.	7.70	Weak	8.47	Str.
9.80	Str.	8.80	Weak	8.00	Med.	8.83	Weak
10.10	Med.	9.10	Med.	8.41	Med.	9.1	Med.
10.25	Med.	9.24	Str.	8.84	Str.	9.2	Med.
10.55	Str.	9.86	Str.	9.20	Weak	9.65–9.90	Str.
11.27	Str.	10.67	V. str.	9.47	Med.	10.90	Weak
		11.1	Str.	10.68	V. str.	11.95	Med.
		11.45	Str.	12.15	Str.	14.3	Med.
		11.75	Str.	14.0–14.1	Med.		
		14.1	Med.				

Isolation of the Oxathiolane Intermediate (VI).—A solution of 58 g. (1 mole) of propylene oxide, 97 g. (1 mole) of potassium thiocyanate and 100 ml. of water was prepared according to the method of Snyder, Stewart and Ziegler.[5] After the odor of sulfide could be detected (strong, garlic-like odor) but before the organic layer had begun to separate (about 10 minutes after adding the oxide), 30 ml. of the mixture was removed and poured onto 4 g. of finely powdered *p*-nitrobenzoyl chloride in a 100-ml. beaker. The mixture was stirred rapidly with a glass rod. The powder immediately formed a yellow oil which became less viscous as the odor of sulfide became more prominent. The oil then turned pink and began to solidify into yellow curds which then became a vivid orange color. Much heat was generated. The color returned to a pinkish yellow as the reaction subsided. The solid was collected, dried in air and recrystallized from benzene. The resulting solid, 3.8 g. (66% based on *p*-nitrobenzoyl chloride, 4% based on propylene oxide), melted over the range 166–171°. It was found that if the sample were removed from the melting point apparatus and cooled rapidly in the air, the melting range of 166–171° was reproduced. However, if the sample were allowed to cool slowly within the apparatus and then reheated, the resulting melting point was 156–158°. This behavior would indicate that the compound exists in allotropic forms.

Anal. Calcd. for $C_{11}H_{10}O_4N_2S$: C, 49.76; H, 3.77; N, 10.49; S, 12.01. Found: C, 49.50; H, 3.61; N, 10.50; S, 11.97.

When larger amounts of *p*-nitrobenzoyl chloride were used (*e.g.*, half a mole of chloride to a mole of oxide) large amounts of crude product were obtained, but only a relatively small amount of oxathiolane intermediate could be isolated after chromatographing over alumina in benzene solution.[14]

The best conversion to the oxathiolane derivative was obtained by treating 0.1 mole of oxide reaction mixture with 0.027 mole of *p*-nitrobenzoyl chloride. Recrystallization of the crude product (6.1 g.) from benzene yielded 4.3 g., m.p. 163–168°. The infrared spectrum was identical to that of the sample analyzed. This represented a 60% conversion based on chloride used, 16% based on oxide.[14]

When the same procedure was repeated using benzoyl chloride in place of the *p*-nitro derivative, a colorless glass was obtained. Vacuum sublimation yielded a white solid melting at 126°, which proved to be benzamide.

Synthesis of 1-Thiocyano-2-propanol (VIII).—The method of Wagner-Jauregg[12] was used. A solution of 75 g. of potassium thiocyanate in 200 ml. of water was poured onto approximately 500 g. of shaved ice in a 2-liter separatory funnel and 200 ml. of ethyl ether was added with vigorous shaking to cool. To this was added slowly 100 g. of phosphoric acid (85%) with continued shaking. The red ethereal layer was separated and added to 14.5 g. (0.25 mole) of propylene oxide which had been cooled to 0° in a 500-ml. erlenmeyer flask. The resulting solution was allowed to remain in the ice-bath until the red color was discharged

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[14] The experiments described in these two paragraphs were carried out by Leon E. St. Pierre.

(about 15 minutes). A "pinch" of hydroquinone was added as stabilizer. The solution was dried with magnesium sulfate, the ether removed on a steam-bath, and the product distilled. The combined yield of product, boiling at 98–100° (0.2 mm.), for four such runs was 71 g. (61%), $n^{25}\text{D}$ 1.4976.

Anal. Calcd. for C_4H_7ONS: C, 41.02; H, 5.98; N, 12.02; S, 27.38. Found: C, 40.30; H, 5.91; N, 12.79; S, 27.00.

This analysis agrees with that calculated for 95% of VIII and 5% of cyanic acid. Indeed, on standing overnight, fine white needles separated out of the liquid, which solid was shown to be the reaction product of cyanic acid with VIII.

Isolation of N-Carbamyl-2-imino-5-methyl-1,3-oxathiolane (IX).—The white needles were filtered from the thiocyanohydrin above and recrystallized from hot methanol. The weight of the product was 3.1 g. The silvery needles exhibited extraordinary melting point behavior. The melting point was determined on a micro hot-plate equipped with a microscope. The needles began to melt internally while the outer portion remained intact. Small prismatic crystals appeared on the cover glass which then began to melt as did the outside of the original needles. The odor of a sulfide became noticeable as all portions began to decompose to an amorphous white solid (probably cyamelide). The whole process occurred from 173–174°.

Anal. Calcd. for $C_5H_8O_2N_2S$: C, 37.48; H, 5.03; N, 17.49; S, 20.01. Found: C, 37.60; H, 5.26; N, 17.26; S, 20.55.

Synthesis of IX.—To a solution of 0.1 g. of potassium cyanate in 5 ml. of water was added 0.2 of the hydrochloride (VII). The solution was heated at 60° for 10 minutes and poured onto a watch glass. As the water began to evaporate, fine white needles were precipitated. These were recrystallized from methanol. Both these needles, and a mixture of IX above, exhibited the same queer behavior on melting. The infrared spectra of the two were identical.

Preparation of 2-Imino-5-methyl-1,3-oxathiolane Hydrochloride (VII).—In a 250-ml. erlenmeyer flask fitted with gas inlet and outlet tube (both protected with calcium chloride drying tubes) was placed 15 g. (0.13 mole) of propylene thiocyanohydrin (VIII) which was cooled to ice temperature. Hydrogen chloride was passed in until the liquid became a glass. To this was added 100 ml. of absolute ether. The glass was broken up and crystallization induced by scratching. The ether suspension was then saturated with more hydrogen chloride, again at 0°. After standing for one hour, the ether was decanted and the crystals washed twice with 75-ml. portions of absolute ether. The solid was filtered and recrystallized from absolute methanol and absolute ether. The white solid was *very* hygroscopic, m.p. 112–115°.

Anal. Calcd. for C_4H_8ONSCl: C, 31.28; H, 5.25; N, 9.12; S, 20.87; Cl, 23.09. Found: C, 27.90; H, 5.65; N, 10.53; S, 19.00; Cl, 26.85.

While the analysis is unsatisfactory, it does agree well for a mixture of 90% VII and 10% ammonium chloride. Repeated attempts at recrystallization served only to increase the proportion of ammonium chloride as revealed by subsequent analysis. Doubtless the compound is easily hydrolyzed by atmospheric moisture to ammonium chloride, the organic product(s) remaining in the recrystallization solvents.

Synthesis of Oxathiolane Intermediate (VI).—In a 500-ml. beaker were placed 2.0 g. of the imine hydrochloride (VII) and 2.0 g. of *p*-nitrobenzoyl chloride. To this was added in four portions a solution of 8.0 g. of sodium bicarbonate in 110 ml. of water, the mixture being stirred as carbon dioxide was evolved. A 20-ml. portion of ether was added with vigorous stirring. The beaker was placed on a steam-bath for about 5 minutes, during which time the ether evaporated leaving behind a pale yellow oil which broke up into a fine powder with stirring. The solid was collected and recrystallized from benzene. This substance, compound VI, and a mixture of the two exhibited identical melting points (166–171° and 156–158° after slow cooling). The infrared spectrum of this compound was identical with that of VI.

When this same procedure was repeated using benzoyl chloride in place of the *p*-nitro derivative, a colorless glass was obtained which again yielded benzamide by vacuum sublimation.

Preparation of D(+)-2,3-Epoxybutane (Ib).—The method used was that given by Lucas and Garner.[10] This involves the preparation of the D(+)-diacetate of the D(+)-butane-2,3-diol. The diacetate is converted to the L(−)-chlorohydrin with subsequent conversion of this to the D(+)-oxide by the method of Wilson and Lucas.[15] Over-all yield of oxide from the glycol was 40%, $[\alpha]^{25}\text{D}$ 58.58°, $n^{25}\text{D}$ 1.3704. The constants reported[10] for the oxide are $[\alpha]^{25}\text{D}$ 59.05°, $n^{25}\text{D}$ 1.3705.

Synthesis of L(−)-2,3-Epithiobutane (Vb).—A solution of 1.5 g. of D(+)-2,3-epoxybutane and 2.5 g. of potassium thiocyanate in 3.0 ml. of water was sealed in a glass tube and agitated by slow rotation in a vertical plane for 36 hours. The tube was opened, the organic layer separated and dried with sodium sulfate at 0°. Distillation at room temperature at 30 mm. yielded 1.4 g. (76%) of 2,3-epithiobutane, $n^{25}\text{D}$ 1.4390, $[\alpha]^{25}\text{D}$ −94.33°.

Anal. Calcd. for C_4H_8S: C, 54.49; H, 9.15; S, 36.36. Found: C, 56.70, 62.17; H, 9.77, 10.87; S, 27.50, 10.89.

The first set of analytical figures was obtained a few days after preparation of the sample, the second set two weeks later.[16]

A solution composed of 0.225 g. of the sulfide diluted to 2.51 ml. with carbon tetrachloride was subjected to infrared analysis and its rotation measured ($\alpha_{\text{obsd.}}$ −8.44°). The solution was then sealed in a glass ampoule and heated in refluxing carbon tetrachloride for three days. The tube was opened after cooling and the spectral analysis and rotation measurement repeated. No change in spectra or rotation could be detected. However, when $^1/_2$ drop of inactive 3-chloro-2-butanethiol was added to the same solution and it was then again heated as before for 12 hours, infrared spectra changes were observed and the rotation changed to $\alpha_{\text{obsd.}}$ −7.67°.

L(+)-*erythro*-3-Mercapto-2-butanol (X) was prepared by the method of Culvenor.[17] A solution of 4.8 g. of potassium hydroxide in 64 ml. of absolute ethanol was saturated with hydrogen sulfide at 0°. To this was added 6.0 g. of the D(+)-2,3-epoxybutane. The solution was kept at 0° for half an hour and then was allowed to stand overnight at room temperature. It was acidified to litmus with 1 *N* sulfuric acid after diluting with 100 ml. of water. The mixture was extracted thrice with 50-ml. portions of chloroform. The extracts were combined, washed with 50 ml. of 5% sodium bicarbonate solution and dried over magnesium sulfate. The product was obtained by distillation, yielding 3.8 g. (43%) boiling at 73.5–74.0° (31 mm.), $n^{25}\text{D}$ 1.4783, $[\alpha]^{25}\text{D}$ 16.00°. Similar treatment of the inactive *trans*-oxide yielded hydroxythiol of $n^{25}\text{D}$ 1.4779.

Anal. Calcd. for $C_4H_{10}OS$: C, 45.24; H, 9.49; S, 30.19. Found: C, 44.30; H, 9.69; S, 28.60.

This substance is quite hygroscopic and the analysis indicates it contained about 4% water (Calcd.: C, 43.63; H, 9.54; S, 29.09.) Because the compound's odor induced nausea, no attempt at further purification was made.

Synthesis of L(−)-2,3-Epithiobutane (Vb).—To 20 ml. of concentrated hydrochloric acid in a glass-stoppered flask was added 3.6 g. of the active hydroxythiol. The thiol dissolved immediately in the acid and the mixture became cloudy in less than a minute, followed by rapid separation of a second layer. The flask was shaken occasionally for two hours.

The contents of the flask were extracted with three portions of chloroform. The combined extracts were washed twice with 50 ml. of water and dried with magnesium sulfate. The chloroform was distilled from a water-bath. Before

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[15] C. E. Wilson and H. J. Lucas, THIS JOURNAL, **58**, 2396 (1936).

[16] The explanation of this remarkable behavior may be related to the recent proposal by F. G. Bordwell and G. D. Cooper (THIS JOURNAL, **73**, 5187 (1951)) that episulfones would decompose readily to an olefin and sulfur dioxide. If the 2,3-epithiobutane were attacked by oxygen to produce first the sulfoxide and then the sulfone, the latter would then lose sulfur dioxide to give 2-butene. We are investigating this possible explanation for the observed changes in composition of this sample.

[17] C. C. J. Culvenor, W. Davies and M. S. Heath, *J. Chem. Soc.*, 278 (1949).

the last small amount of chloroform could be distilled, the substance began to release hydrogen chloride rapidly. Heating was discontinued and the crude chlorothiol added immediately to a solution of 5.0 g. of sodium bicarbonate in 70 ml. of water and shaken until the evolution of carbon dioxide ceased. The mixture was extracted with two 15-ml. portions of ether. The combined extracts were dried with sodium sulfate. The ether was evaporated from a water-bath and the product was distilled at reduced pressure. The fraction boiling at 22–28° at 40 mm. (obviously impure) had a specific rotation of −18.34°. Its infrared spectrum was taken.

Simultaneous Measurements of *p*H and Optical Rotation on the Thiocyanate Reaction.[18]—In a 50-ml. volumetric flask was placed 1.0 g. (1.25 ml.) of the active butene oxide. After dilution to volume with a 50% aqueous ethanolic solution of potassium thiocyanate (0.28 *N*), the flask was shaken rapidly for 10 seconds. A 2-decimeter polarimeter tube was filled, stoppered to prevent evaporation and thermostated at 25.0°. The readings of *p*H and rotation for these samples appear in Table I.

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[18] Edwin C. Mertz assisted in these measurements.

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

The Reaction of Dinitrogen Tetroxide with Tolane

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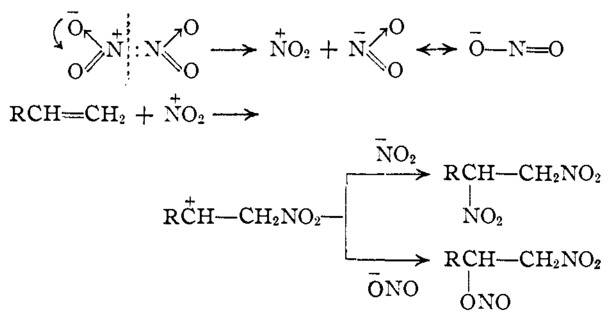
Dinitrogen tetroxide has been shown to react with tolane to form *cis*-1,2-dinitrostilbene, *trans*-1,2-dinitrostilbene and 5-nitro-2-phenylisatogen. A free radical mechanism has been proposed to account for the formation of *cis*-1,2-dinitrostilbene, and possible mechanisms for the formation of the isatogen have been discussed.

In recent years several detailed investigations have been carried out, chiefly by Levy, Scaife and their associates[2] on the addition of dinitrogen tetroxide to olefins. In general, two types of addition products have been isolated, the dinitroalkanes and the nitroalkanol nitrite (or nitrate) esters, and the ratio of these two types of products does not appear to be affected by the presence of catalysts or by minor alterations in the experimental conditions. When unsymmetrical olefins are used, the nitroalkyl nitrite obtained has the nitro group attached to the carbon atom carrying the greater number of hydrogen atoms. These results led Levy and Scaife[3] and the Ingolds[4] to postulate an ionic mechanism for the addition.



The object of the present work was to investigate the addition of dinitrogen tetroxide to substituted olefins and to acetylenes, in the hope of isolating the dinitro products for testing as explosives. Although dinitrogen tetroxide reacted readily (at 0° in anhydrous ether) with allyl chloride, methyl vinyl ether, ethyl allyl ether and acrylonitrile, it was not found possible to isolate any homogeneous product as the dark red oils decomposed rapidly at room temperature. Under the same conditions addition of dinitrogen tetroxide to acetylene occurred very slowly, and no definite reaction product could be isolated. Attention was then turned to tolane, in the hope that it would give more stable products.

Schmidt[5] and Wieland and Blumick[6] studied the addition of dinitrogen tetroxide to tolane and obtained as major products the two isomers of 1,2-dinitrostilbene; the *trans* form, m.p. 186–187° and the *cis* form, m.p. 107–108°.[7] They also obtained small amounts of a third compound, which was red, melted at about 234° and which from its empirical formula, $C_{14}H_8N_2O_4$, they considered to be a dinitrotolane. Neither Wieland nor Schmidt found any substance which would correspond to nitronitrite addition. The work of Schmidt and of Wieland was done before the importance of anhydrous conditions and of highly purified dinitrogen tetroxide was recognized, and in view of the experiences of Scaife and others with olefins, it was considered worthwhile to reinvestigate the reaction.

A solution of tolane in anhydrous ether was added to anhydrous, redistilled dinitrogen tetroxide in ether at about 0°, and the mixture was then allowed to stand at 0–25° for varying periods of time. When one mole of N_2O_4 was used per mole of tolane, an appreciable amount of the hydrocarbon was recovered unchanged, so in later work an excess of dinitrogen tetroxide was used. The reaction products were purified by crystallization and by chromatography over alumina and silica gel. The highest yield of crystalline material obtained was about 40% based on the tolane not

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[1] Abstracted from the Ph.D. thesis of John Shavel, Jr., Notre Dame, August, 1951. This work was done in part under contract Nord-10273 between the University of Notre Dame and the Bureau of Naval Ordnance. Presented at the Milwaukee A.C.S. Meeting, April, 1952.

[2] N. Levy and J. D. Rose, *Quart. Rev.*, **1**, 358 (1948); N. Levy, C. W. Scaife and A. E. Wilder-Smith, *J. Chem. Soc.*, 52 (1948); H. Baldock, N. Levy and C. W. Scaife, *ibid.*, 2627 (1949); E. I. du Pont de Nemours and Co., British Patent 603,344, *C. A.*, **43**, 665 (1949); K. N. Campbell and R. S. Towne, O.S.R.D. Report 3984.

[3] N. Levy and C. W. Scaife, *J. Chem. Soc.*, 1093 (1946).

[4] C. K. Ingold and E. H. Ingold, *Nature*, **159**, 743 (1947).

[5] J. Schmidt, *Ber.*, **34**, 619 (1901).

[6] H. Wieland and E. Blumick, *Ann.*, **424**, 100 (1921).

[7] Schmidt and Wieland showed that the nitro groups were attached to the side chain by reduction to piperazines. They did not, however, establish the geometrical configurations, although Schmidt suggested that the higher-melting form was the *trans*. E. Bergmann, *J. Chem. Soc.*, 402 (1936), confirmed Schmidt's suggestion by showing that the higher melting form had a zero dipole moment.