Anal. Calcd. for $C_{10}H_{12}O_3N_2S$: N, 11.7. Found: N, 11.8.

(B).—When the ethylene oxide in the above experiment was replaced by an equivalent of propylene oxide, 27.7 g. (83%) of 3-phenylmercaptopropanol-2, b.p. 133° (9 mm.), $n^{25}D$ 1.5715, was the only product obtained. The melting points of the *p*-nitrobenzoate (64–65°) and sulfone *p*-nitrobenzoate (164°) agree closely with values reported by Fuson and Koehnecke,[11] who used an unambiguous synthesis. Thus the direction of cleavage of propylene oxide by this reagent is determined.[12]

3,3'-Dihydroxydipropyl Sulfide.—A solution of 6 g. of trimethylene oxide, 25 g. of sodium sulfide nonahydrate and 25 ml. of water was allowed to stand 3 days at about 30°. After the reaction mixture was acidified and concentrated *in vacuo*, the precipitated sodium chloride was filtered and washed with alcohol. Evaporation of the solvent then gave 8.2 g. (95%) of a pale yellow, viscous, non-distillable oil. The phenylurethan melted at 120° (from alcohol).[13]

The use of twice as much sodium sulfide led to the same result, and an attempt to isolate 3-hydroxypropylmercaptan by steam distillation of the reaction mixture was unsuccessful.

Reaction of Potassium Bisulfite with Trimethylene Oxide. A solution of 5 g. of the oxide with 10 g. of potassium metabisulfite in 15 ml. of water previously saturated with sulfur dioxide was allowed to stand 3 days at about 30°. After removal of the solvent *in vacuo* the white residue was extracted with 95% alcohol in a Soxhlet apparatus. White platelets separated from the alcoholic extract, m.p. 195–198° dec.

Anal. Calcd. for $C_3H_7O_4SK$: K, 22.4. Found: K, 23.1, 23.2.

Reaction of Sodium Thiosulfate with Ethylene and Trimethylene Oxides.—The Ross procedure[4] for following the reaction kinetically was modified to reduce the extent of evaporation of these volatile oxides: The oxide (0.002 mole) was added to 50 ml. of aqueous 0.1 *M* sodium thiosulfate, well stirred and thermostated at 35°, and 0.1 *N* hydrochloric acid was added from a microburet at a rate such that the *p*H of the solution remained constant (within ± 0.2 *p*H, as determined by a Beckman model H *p*H meter).

The data gave a linear relationship between the time and log $(V_\infty)/(V_\infty - V)$, where V and V_∞ are the volumes of acid added at time t and t_∞, in agreement with the first order rate law, and the first order rate constant, k, was evaluated graphically. The theoretical volume of acid was used in the reaction of ethylene oxide but not in that of the slower reacting trimethylene oxide. Since the direct reaction of this compound with water is extremely slow and since its odor was quite discernible over the solution, it seems likely that the difference was caused by evaporation. This was taken into consideration by treating the data as a case of two simultaneous first order equations. The constant k evaluated graphically thus is k_{thio} plus $k_{\text{evap.}}$, and k_{thio} was evaluated by solving[14]

$$\frac{V \times k}{[A]_0 \times k_{\text{thio}}} = 1 - e^{-kt}$$

(where $[A]_0$ is the initial oxide concentration) for individual sets of V and t values and then averaged.

TABLE III

FIRST ORDER RATE CONSTANTS FOR REACTION OF OXIDES IN 0.2 *M* THIOSULFATE AT 35°

*p*H	Ethylene oxide, min.$^{-1}$	Trimethylene oxide, min.$^{-1}$
8	0.20	0.013
5.0		.017
4.5	.22	.025
3.4	.35	

From the specific rate constants observed at three *p*H values (Table III) the constants k_w and k_a, for the "uncatalyzed" and acid-catalyzed reactions, respectively, were evaluated from the relation

$$k = k_w + k_a/[H^+]$$

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[11] Fuson and Koehnecke, *J. Org. Chem.*, **14**, 706 (1949).

[12] NOTE ADDED IN PROOF.—The same conclusion was reported recently by R. D. Schuetz, THIS JOURNAL, **73**, 1881 (1951).

[13] McGinnis and Robinson, *J. Chem. Soc.*, 406 (1941), reported m.p. 122–123°.

[14] F. H. MacDougall, "Physical Chemistry," revised ed., The Macmillan Co., New York, N. Y., 1943, p. 425, eq. 51.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

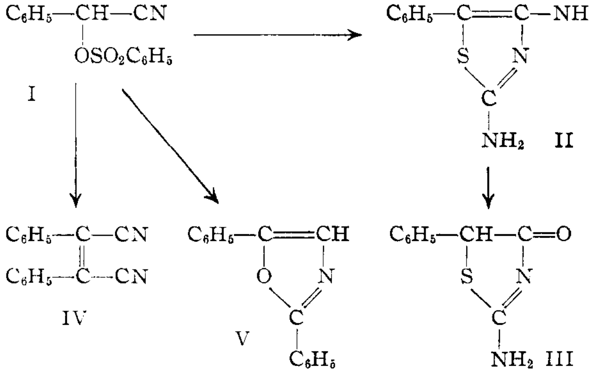
α-Cyanoalkyl Sulfonates. I. The Reactions of α-Cyanobenzyl Benzenesulfonate

BY R. M. DODSON AND HARRY W. TURNER[1]

2,4-Diamino-5-phenylthiazole benzenesulfonate was prepared in excellent yield by the reaction of α-cyanobenzyl benzenesulfonate with thiourea. The structure of the 2,4-diamino-5-phenylthiazole was established by its hydrolysis to the known 2-amino-5-phenyl-4(5)-thiazolone. Treatment of α-cyanobenzyl benzenesulfonate with a suspension of potassium cyanide in alcohol yielded α,α¹-dicyanostilbene. When the α-cyanobenzyl benzenesulfonate was treated with benzaldehyde and sodium cyanide in dilute dioxane, 2,5-diphenyloxazole was obtained.

Even though the chemistry of cyanohydrins has been extensively studied, the α-cyanoalkyl sulfonates have been neglected. Because of the similarity of alkyl sulfonates and alkyl halides in chemical reactions, one would expect the α-cyanoalkyl sulfonates to be similar to the α-halonitriles in their reactions. In the work reported in this paper, this has been found to be true.

α-Cyanobenzyl benzenesulfonate (I) was prepared in 84% yield by the reaction of sodium cyanide and benzenesulfonyl chloride with benzaldehyde.[2] The compound is rather unstable; it slowly decomposes at room temperature but can be stored at 0°. When an acetone solution of α-cyanobenzyl benzenesulfonate was treated at room temperature with an equivalent amount of thiourea and then diluted with water until cloudy, the



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[1] Abstracted from the Ph.D. thesis of Harry W. Turner.

[2] F. Francis and O. C. M. Davis, *J. Chem. Soc.*, **95**, 1403 (1909).

benzenesulfonate of 2,4-diamino-5-phenylthiazole[3] (II) slowly precipitated from the solution. While 2,4-diamino-5-phenylthiazole benzenesulfonate and 2,4-diacetamido-5-phenylthiazole are stable, the free base is unstable; it hydrolyzes readily and darkens on exposure to air. Nitrogen analyses on the free base were not completely satisfactory. These properties are in agreement with those previously reported for 4-aminothiazoles and 2,4-diaminothiazoles.[4]

The structure of II was verified by its hydrolysis with dilute hydrochloric acid to the known 2-amino-5-phenyl-4(5)-thiazolone (III).[5] This synthesis of 2,4-diamino-5-phenylthiazole (II) from α-cyanobenzyl benzenesulfonate is analogous to the synthesis of 2,4-diaminothiazole from chloroacetonitrile.[4a,b,c] The hydrolysis of II to the thiazolone (III) was expected, since 2,4-diaminothiazole was hydrolyzed in a similar manner to 2-amino-4(5)-thiazolone.[4a,d]

2,4-Diamino-5-phenylthiazole (II) was also prepared in excellent yield by first treating potassium cyanide and benzenesulfonyl chloride with benzaldehyde in a water suspension and then treating this crude mixture with a solution of thiourea in alcohol. In this case, however, a small quantity of α-cyanobenzyl phenyl sulfone was also isolated. The structure of this sulfone was established by its hydrolysis to the known benzyl phenyl sulfone.[6] The preparation and properties of α-cyanobenzyl sulfones will be discussed in a later publication.

In analogy with the reaction of α-bromophenylacetonitrile[7] α-cyanobenzyl benzenesulfonate (I) yielded the lower melting isomer of α,α'-dicyanostilbene (IV) in 35% yield when treated in alcoholic solution with potassium cyanide. In view of the ease of preparation of α-cyanobenzyl benzenesulfonate, these reactions provide a very simple method for the preparation of α,α'-dicyanostilbene. When α-cyanobenzyl benzenesulfonate and benzaldehyde in dilute dioxane were treated with sodium cyanide, 2,5-diphenyloxazole (V) resulted.

Experimental[8]

α-Cyanobenzyl Benzenesulfonate (I).—A mixture of 53.0 g. (0.50 mole) of benzaldehyde, 88.0 g. (0.50 mole) of benzenesulfonyl chloride, 24.5 g. (0.50 mole) of sodium cyanide and 100 ml. of water was allowed to stand for three hours at 0–5° with occasional shaking. The cream-colored solid was separated by filtration, then dissolved in 250 ml. of a cold mixture of acetone, alcohol and ether (2:2:1). The undissolved material was separated from this solution by filtration and discarded. The addition of 150 g. of ice to the cold filtrate precipitated an oil which solidified on standing at 0°. In this way 114 g. (84%) of α-cyanobenzyl benzenesulfonate, m.p. 54.5–56.5°, was obtained. The analytical sample, m.p. 57.5–58.5°, was prepared by crystallization of the compound from ethanol. We have never succeeded in obtaining material melting at 66° as previously reported.

Anal. Calcd. for $C_{14}H_{11}NO_3S$: C, 61.52; H, 4.06. Found: C, 61.50; H, 4.10.

2,4-Diamino-5-phenylthiazole Benzenesulfonate.—A mixture of 60.0 g. (0.22 mole) of α-cyanobenzyl benzenesulfonate (I), 16.8 g. (0.22 mole) of thiourea and 100 ml. of acetone was stirred at room temperature until solution was achieved (15–30 minutes). The resulting solution was allowed to stand overnight at room temperature and was then diluted with water until slightly cloudy. 2,4-Diamino-5-phenylthiazole benzenesulfonate, 61 g. (80%), m.p. 254–257° (dec.), slowly precipitated from this solution during the next 24 hours. The analytical sample, m.p. 261–262° (dec.), was obtained by the precipitation of the salt from alcohol solution by the addition of ether. This salt is slightly soluble in alcohol but is insoluble in the other common organic solvents and in water.

Anal. Calcd. for $C_{15}H_{15}N_3O_3S_2$: C, 51.56; H, 4.33; N, 12.03. Found: C, 51.66; H, 4.42; N, 11.90.

2,4-Diacetamido-5-phenylthiazole.—The 2,4-diamino-5-phenylthiazole benzenesulfonate (2.0 g.) was thoroughly mixed with 10 ml. of a 15% aqueous potassium hydroxide solution. The residual solid was separated by filtration and was washed twice with 15-ml. portions of water. The slightly moist solid was dissolved in five ml. of acetic anhydride. The clear colorless solution on standing at room temperature for two hours set to a thick paste. By filtration of this material, 1.20 g. (76%) of 2,4-diacetamido-5-phenylthiazole, m.p. 232–233.5°, was obtained. Crystallization of the product from a mixture of acetone and ether raised its melting point to 233.5–234°.

Anal. Calcd. for $C_{13}H_{13}N_3O_2S$: C, 56.72; H, 4.76; N, 15.26. Found: C, 56.50; H, 4.85; N, 15.38.

2,4-Diamino-5-phenylthiazole (II) was obtained from the 2,4-diamino-5-phenylthiazole benzenesulfonate by thoroughly mixing the salt with dilute (1:1) ammonium hydroxide. The residual solid was separated by filtration, washed thoroughly with anhydrous ether and dried in a stream of air; m.p. *ca.* 157° (dec.).

Anal. Calcd. for $C_9H_9N_3S$: C, 56.66; H, 4.75; N, 21.98. Found: C, 56.24; H, 4.83; N, 20.92.

All attempts to prepare an analytical sample by crystallization of this material resulted in less pure material.

α-Cyanobenzyl phenyl sulfone was isolated in low yield from a preparation of 2,4-diamino-5-phenylthiazole in which a suspension of crude α-cyanobenzyl benzenesulfonate (obtained by shaking equivalent amounts of benzaldehyde, benzenesulfonyl chloride and sodium cyanide for 0.5 hour with a little water) was treated with thiourea in dilute alcohol. Since the α-cyanobenzyl phenyl sulfone was insoluble in dilute hydrochloric acid, soluble in ether and soluble in dilute sodium hydroxide solution, it was easily separated from the 2,4-diamino-5-phenylthiazole. Pure α-cyanobenzyl phenyl sulfone, m.p. 149.5–150°, was easily obtained by crystallization of the compound from dilute methanol.

Anal. Calcd. for $C_{14}H_{11}NO_2S$: C, 65.35; H, 4.31; N, 5.44. Found: C, 65.39; H, 4.30; N, 5.21.

Hydrolysis of the α-cyanobenzyl phenyl sulfone with aqueous sodium hydroxide yielded benzyl phenyl sulfone, m.p. 146.5–147.5°. A mixture of this material with an authentic sample of benzyl phenyl sulfone[6] showed no depression in melting point.

2-Amino-5-phenyl-4(5)-thiazolone (III).—2,4-Diamino-5-phenylthiazole benzenesulfonate (10.0 g.) was mixed thoroughly with 40 ml. of dilute (1:1) ammonium hydroxide. The remaining solid was separated by filtration and washed with 50 ml. of water. This material was heated with 150 ml. of dilute (1:2) hydrochloric acid at the boiling point for 10 minutes. The resulting clear solution was quickly cooled by the addition of 50 g. of ice and by the application of an ice-bath to the outside of the flask. Neutralization of this solution with concentrated ammonium hydroxide precipitated 4.5 g. (82%) of 2-amino-5-phenyl-4(5)-thiazolone, m.p. 239–241° (dec.). Crystallization of the compound from methanol raised its melting point to 243.5–244.5° (dec.). A comparison of the infrared spectrum of this compound with that of a sample of 2-amino-5-phenyl-4(5)-

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[3] After this work was completed, the preparation of 2,4-diamino-5-phenylthiazole from α-bromobenzyl cyanide was reported: W. Davies, J. A. Maclaren and L. R. Wilkinson, *J. Chem. Soc.*, 3491 (1950).

[4] (a) W. Zeweck and M. Schubert, German Patent 729,853; *C. A.*, **38**, 382 (1944); (b) K. Ganapathi and A. Venkataraman, *Proc. Indian Acad. Sci.*, **22A**, 359 (1945); *C. A.*, **40**, 4059 (1946); (c) H. Erlenmeyer and D. Markees, *Helv. Chim. Acta*, **29**, 1229 (1946); (d) A. H. Land, C. Ziegler and J. M. Sprague, *J. Org. Chem.*, **11**, 617 (1946).

[5] P. N. Rylander and E. Campaigne, *ibid.*, **15**, 252 (1950).

[6] R. L. Shriner, H. C. Struck and W. J. Jorison, THIS JOURNAL, **52**, 2060 (1930).

[7] C. L. Reimer, *Chem. Ber.*, **14**, 1797 (1881).

[8] Microanalyses by Messrs. Amidon, Buckley, Davis, Errede and Turner. All melting points were taken on a Fisher-Johns melting point apparatus.

thiazolone prepared from ethyl α-chlorophenylacetate and thiourea,[5,9] showed the compounds to be identical.[10]

Anal. Calcd. for $C_9H_8N_2OS$: C, 56.23; H, 4.20; N, 14.58. Found: C, 56.25; H, 4.04; N, 14.19.

2-Acetamido-4-acetoxy-5-phenylthiazole, m.p. 183–184°, was obtained in 80% yield by heating the 2-amino-5-phenyl-4(5)-thiazolone with excess acetic anhydride under reflux. The compound is easily crystallized from alcohol. Identical treatment of an authentic sample[5] of the thiazolone yielded the same diacetate, m.p. and mixed m.p. 183–184°.

Anal. Calcd. for $C_{13}H_{12}N_2O_3S$: C, 56.50; H, 4.38; N, 10.14. Found: C, 56.78; H, 4.63; N, 10.33.

α,α′-Dicyanostilbene (IV).—A solution of 4.00 g. (0.015 mole) of α-cyanobenzyl benzenesulfonate (I) in 25 ml. of alcohol was shaken vigorously with 1.0 g. (0.015 mole) of potassium cyanide and then allowed to stand at room temperature for six hours with intermittent shaking. The mixture became darker in color and slowly deposited a plate-like solid. This water-soluble solid was separated by filtration, then discarded. Addition of water to the filtrate precipitated the dicyanostilbene, which, after crystallization from alcohol, weighed 0.58 g. (35%) and melted at 161.5–163°. The compound is reported to melt at 158° and at 160°.[11]

Anal. Calcd. for $C_{16}H_{10}N_2$: C, 83.45; H, 4.38. Found: C, 83.76; H, 4.70.

2,5-Diphenyloxazole (V).—A mixture of 10.0 g. (0.036 mole) of α-cyanobenzyl benzenesulfonate (I), 4.0 g. (0.036 mole) of benzaldehyde, and 2.0 g. (0.05 mole) of sodium cyanide in 50 ml. of dilute (1:1) dioxane was stirred for 24 hours at room temperature. The mixture was diluted with water; the oil, which separated, solidified on standing. Trituration of this solid with 50 ml. of cold ethanol yielded 1.8 g. (22%) of 2,5-diphenyloxazole, m.p. 69–71°. Crystallization of the compound from dilute alcohol gave an analytically pure sample, m.p. 74.0–74.5°. The compound is reported to melt at 74°.[12]

Anal. Calcd. for $C_{15}H_{11}NO$: C, 81.42; H, 5.01. Found: C, 81.40; H, 5.09.

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[9] We are grateful to Dr. E. Campaigne for supplying us with a sample of this compound. His sample was reported to melt at 234° with decomposition[5]; it decomposed at 239–241° on our Fisher–Johns melting point block.

[10] We are indebted to Dr. Inskeep and Mr. Schwabacher for these infrared spectra.

[11] C. L. Reimer, *Ber.*, **13**, 742 (1880); J. v. Braun, *ibid.*, **36**, 2651 (1903).

[12] E. Fischer, *ibid.*, **29**, 205 (1896).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY]

Preparation of Stereoisomeric Alkenyllithium Compounds. II. *cis*- and *trans*-1,2-Diphenylvinyllithium and α- and β-Styryllithium[1]

BY DAVID Y. CURTIN AND ELBERT E. HARRIS

cis-Bromostilbene undergoes an exchange reaction with butyllithium to give an organolithium intermediate which reacts with Dry Ice to give only *cis*-α-phenylcinnamic acid and with methanol to give only *cis*-stilbene. *trans*-Bromostilbene similarly gives only *trans*-α-phenylcinnamic acid or *trans*-stilbene. Although ω-bromostyrene with butyllithium in ether, even at −55°, gives only phenylpropiolic acid, α-bromostyrene with butyllithium, followed by treatment with Dry Ice gives α-carboxystyrene as the only acidic product.

In the first paper in this series,[2] *cis*- and *trans*-1-*p*-chlorophenyl-1,2-diphenylvinyllithium were prepared and their reactions with carbon dioxide and methanol reported. Since other lithium–halogen exchanges of alkenyl halides have been little investigated it was desirable to extend the previous work.

Compounds with the general formula, RCH=CLiR′ (R and R′ = Ph or H), seemed to be of particular interest in view of the fact that earlier attempts to prepare such compounds have met with limited success. Thus vinyl bromide has been found to react with phenyllithium[3] or butyllithium[4] in ether or petroleum ether to give only products derived from dilithium acetylide. β-Chloro- and β-bromostyrene with either butyllithium or phenyllithium under a variety of conditions in ether have been found to give only derivatives of phenylacetylene.[3,5,6]

Marvel, Hager and Coffman,[7] however, found that when ω-bromostyrene was treated with butyllithium for thirty-eight days in petroleum ether rather than ether solution, the principal products were 1-phenyl-1-hexene and *trans*–*trans*-1,4-diphenylbutadiene. Gilman, Langham and Moore[8] later reported that carbonation of a similar reaction mixture after only 20 hours gave a 23% yield of *trans*-cinnamic acid.

Wright[9] was able to prepare alkenyllithium compounds from *cis*- or *trans*-β-bromostyrene by a direct reaction with lithium metal in ether. The lithium reagent from each isomer gave, on carbonation, *trans*-cinnamic acid (4 parts) and phenylpropiolic acid (1 part) in a combined yield of 35%. Recently, Braude, Timmons and Coles[10] have prepared isobutenyllithium and cyclohexenyllithium from the corresponding halides (neither of which can undergo elimination to an acetylene) and lithium metal in ether.

In spite of the unpromising results quoted above we have investigated the lithium–halogen exchange of *cis*- and *trans*-α-bromostilbene[11] (*cis*- and *trans*-I) with butyllithium in benzene–ether at temperatures below zero degrees. *cis*-I, after treatment with butyllithium at −35° for seven minutes and carbonation of the lithium reagent, gave as the only

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[1] This paper contains a portion of a Ph.D. thesis submitted by Elbert E. Harris to Columbia University.

[2] D. Y. Curtin and E. E. Harris, THIS JOURNAL, **73**, 2716 (1951).

[3] G. Wittig and G. Harborth, *Ber.*, **77B**, 306 (1944).

[4] H. Gilman and A. H. Haubein, THIS JOURNAL, **67**, 1420 (1945).

[5] G. Wittig and H. Witt, *Ber.*, **74B**, 1474 (1941).

[6] G. Wittig and G. Harborth, *ibid.*, **77B**, 315 (1944).

[7] C. S. Marvel, F. D. Hager and D. D. Coffman, THIS JOURNAL, **49**, 2323 (1927).

[8] H. Gilman, W. Langham and F. W. Moore, *ibid.*, **62**, 2327(1940).

[9] G. F Wright, *J. Org. Chem.*, **1**, 457 (1936).

[10] E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 2000, 2007 (1950); E. A. Braude and J. A. Coles, *ibid.*, 2012, 2014 (1950).

[11] For evidence for the configurations of the α-bromostilbenes see P. Pfeiffer, *Z. physik. Chem.*, **48**, 40 (1904). This assignment is based on the assumption that the elimination reaction proceeds in a *trans* fashion. A recent discussion of this point is given in the paper by S. J. Cristol, N. F. Hause and J. S. Meek, THIS JOURNAL, **73**, 674 (1951).