The pure L-**lysine salt** (monohydrate) had m.p. 166–168° (dec.), $[\alpha]^{25}D$ +36.8 ± 0.3° (*c* 4, water); yield 45.5 g. (84%).

Anal. Calcd. for $C_{17}H_{25}O_6N_3Br_2.H_2O$: C, 37.43; H, 4.99. Found: C, 37.49; H, 4.98.

L-Lysine Monohydrochloride.—A sample of the pure L-lysine salt (31.5 g.) was dissolved in 10 parts of hot water and 12 cc. of concentrated hydrochloric acid was added. The resolving agent (hemihydrate) then crystallized on cooling (97%) in condition suitable for re-use. The filtrate was evaporated to dryness *in vacuo*, the residue was taken up in 80 cc. of 95% ethanol and L-lysine monohydrochloride was precipitated by adding 5.9 g. of pyridine and keeping overnight at 5°. The salt was taken up in 10 cc. of water and reprecipitated with 40 cc. of ethanol.[11] After washing with absolute ethanol and ether and drying it weighed 8.75 g. (80%) and had $[\alpha]^{25}D$ +10.1° (*c* 4, water); +18.7° (*c* 4, 0.6 *N* HCl); +19.9° (*c* 4, 6 *N* HCl). Doherty and Popenoe[4] report $[\alpha]^{24}D$ +20.5° (*c* 3, 6 *N* HCl). The combined rotation samples were recovered as the dihydrochloride which had $[\alpha]^{25}D$ +16.0° (*c* 4, water).

The resolving agent and crude D-lysine hydrochlorides were recovered from the combined resolution liquors as for the L-form. The di- and monohydrochlorides had, respectively, $[\alpha]^{25}D$ −12.9° and −8.1° (*c* 4, water) and accordingly contained about 90% of the D-form.

(B) **Half-equivalent Salt Procedure.**—Acetyldibromo-L-tyrosine (0.10 mole) was dissolved in 100 cc. of hot water containing 0.12 mole of ammonia. DL-Lysine monohydrochloride (0.20 mole) was added and the L-lysine salt (monohydrate) obtained as before (three crops). After systematic recrystallization from aqueous methanol it weighed 42.5 g. (78%) and was identical with the salt previously described. In a further simplification L-lysine monohydrochloride was obtained directly from this salt by decomposition with exactly one equivalent of hot dilute hydrochloric acid; the resolving agent was filtered off after cooling, the filtrate was evaporated to small volume and the hydrochloride precipitated with ethanol. The salt (13.2 g.) had $[\alpha]^{25}D$ +20.2° (*c* 4, 6 *N* HCl). Crude D-lysine hydrochloride (20.3 g.) isolated similarly from the resolution liquors had $[\alpha]^{25}D$ −7.2° (*c* 4, water).

Supplementary Experiments (a).—Equivalent amounts (0.01 mole) of N-acetyl-3,5-dibromo-D-tyrosine[8] (ammonium salt) and the *ca.* 90% D-lysine monohydrochloride from (A) above gave the expected pure D-lysine salt. Except for sign of rotation the salt was identical with its antipode; m.p. 166–168° (dec.), $[\alpha]^{25}D$ −37.0° (*c* 4, water).

(b).—Attempted resolution of N-acetyl-3,5-dibromo-DL-tyrosine[8] (ammonium salt) with D-lysine (monohydrochloride) failed. The corresponding partially racemic double salt crystallized from water as the dihydrate in transparent thin plates, rapidly converted in air to the anhydrous form, m.p. 265–270° (charring). The salt was not resolved in methanol.

(c).—Attempts to obtain pure active lysine derivatives by fractional crystallization of partially active mixtures were not successful with the hydrochlorides, picrates and salicylidene derivatives. In each instance the DL-form was considerably less soluble; the active form was enriched in foot fractions but not completely purified.

NASHVILLE, TENN. RECEIVED JUNE 9, 1951

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Unsaturated Sulfonic Acids. I. Diels–Alder Reactions[1]

BY CHRISTIAN S. RONDESTVEDT, JR., AND JAMES C. WYGANT[2]

The methyl esters of 2-phenylethene-1-sulfonic acid and 2-*p*-nitrophenylethene-1-sulfonic acid form adducts with cyclopentadiene. These esters were inert to butadiene. Other derivatives, such as the sodium salts, the sulfonyl chlorides and the N,N-dialkylamides did not react with typical dienes. The adduct from methyl 2-*p*-nitrophenylethene-1-sulfonate and cyclopentadiene consists of stereoisomers, one of which can be converted to a bromosultone. This observation supplies supporting evidence for the *trans*-configuration of 2-phenylethene-1-sulfonic acid derivatives.

A qualitative similarity between the sulfonyl group in sulfones and sulfonic acids and the carbonyl group was first demonstrated by Kohler.[3,4] The ability of the sulfonyl group to participate in conjugation with a carbon–carbon double bond[3,5] leads to a prediction that α,β-unsaturated sulfones and sulfonic acids should be able to function as dienophiles. A recent survey[6] uncovered only two unsaturated sulfones—2,3-dihydrothiophene-1,1-dioxide and *p*-tolyl vinyl sulfone—which have undergone the Diels–Alder reaction. More recently, methyl ethylenesulfonate was coupled with cyclopentadiene at 140–150° to form a normal adduct.[7] As part of our investigation of unsaturated sulfonic acids and their derivatives, we have explored the condensation of derivatives of 2-phenyl- and 2-*p*-nitrophenylethene-1-sulfonic acid with typical dienes.

When methyl 2-*p*-nitrophenylethene-1-sulfonate was refluxed with cyclopentadiene in bromobenzene solvent for one hour, an adduct was formed in 68% yield. Variations in time or temperature reduced the yield, either increasing tar formation or returning more starting material. The product was identified as methyl 6-*p*-nitrophenyl-2,5-endomethano-1,2,5,6-tetrahydrobenzenesulfonate by analysis of the adduct and several derivatives, and by analogy to the host of well-known Diels–Alder adducts.

The adduct is not sterically homogeneous, however. If methyl 2-*p*-nitrophenylethene-1-sulfonate were in the *cis* configuration, the Alder rules[8] predict a single adduct, with an *endo* configuration. Since more than one adduct is formed, the *trans* configuration of the dienophile is more probable. Further evidence for the *trans* assignment can be deduced from the failure of 2-phenylethene-1-sulfonyl chloride (starting material for the nitro derivatives) to be cyclized to benzothiophene-1,1-dioxide,[9] whereas 2,2-diphenylethene-1-sulfonyl chloride is readily cyclized by aluminum chloride in nitrobenzene.[10] Moreover, 2-*o*-nitrophenylethene-1-sulfonyl chloride, a by-product in the nitration of 2-phenyl-

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[1] A grant from the University of Michigan Faculty Research Fund supported part of this work.

[2] Abbott Laboratories Fellow, 1950–1951.

[3] E. P. Kohler and H. Potter, THIS JOURNAL, **57**, 1316 (1935).

[4] E. P. Kohler, *Am. Chem. J.*, **20**, 680 (1898).

[5] H. P. Koch, *J. Chem. Soc.*, 2892 (1950), and previous papers.

[6] H. L. Holmes in "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 141.

[7] A. Lambert and J. D. Rose, *J. Chem. Soc.*, 46 (1949).

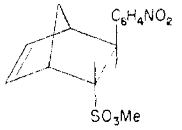
[8] These rules, which predict the steric nature of the adduct, are discussed briefly by M. C. Kloetzel in "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 10.

[9] C. S. Rondestvedt, Jr., Ph.D. Thesis, Northwestern University, 1948.

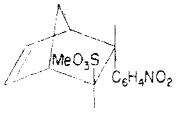
[10] F. G. Bordwell and Marvin Peterson, private communication.

ethene-1-sulfonyl chloride, appears to possess the *trans* configuration.[11] Thus, unless *cis–trans* isomerization has occurred during one of the steps in the preparation of our dienophile from 2-phenylethene-1-sulfonyl chloride,[12] its *trans* configuration seems assured.

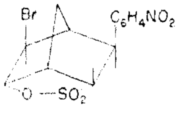
Since a nitrophenyl and a sulfomethoxy group are probably about equally negative, it is not surprising that a mixture of stereoisomers A and B is obtained.



A



B



C

The adduct obtained initially melted in the range 90–100°; it analyzed correctly but, upon hydrolysis and bromination, only 60–65% formed a bromosultone (C). After fourteen crystallizations, from several solvents, the adduct melted at 112–116°, analyzed correctly, but then gave 93% of bromosultone.[13] We may conclude that the crude adduct contains approximately 65% of A, in which the position of the sulfo group is favorable for sultone formation, and 35% of B (or possibly *exo-cis* isomer). These results further support the conclusion that 2-phenylethene-1-sulfonic acid and derived compounds possess the *trans* configuration.

It has not been possible to separate A from its stereoisomer completely by fractional crystallization nor by chromatography. It is surprising, however, that the mixed adduct. melting low and over a range, can be converted to a benzylthiuronium salt or a *p*-toluidine salt in high yield, and that these crude derivatives melt very close to the purified analytical samples. Possibly the mixture of A and B with which we are dealing forms mixed derivatives of nearly eutectic composition.

In line with our objective, various related compounds were studied for dienophilic reactivity. Methyl 2-phenylethene-1-sulfonate and cyclopentadiene under similar reaction conditions formed only 9% of adduct, isolated as its bromosultone. Attempts to isolate the adduct itself were unsuccessful. Variations in experimental conditions were even less propitious. Since methyl ethenesulfonate reacts readily,[7] it appears to us that the ability of a phenyl group to act as an electron source reduces the electrophilic reactivity of the double bond so much that side reactions become dominant.[14] This electromeric shift is decreased, or even reversed, by a nitro group in the para position, and normal adduct formation proceeds.

Neither methyl 2-*p*-nitrophenylethene-1-sulfonate nor methyl 2-phenylethene-1-sulfonate formed adducts with butadiene. The contrast is striking, but it is in line with the known relative reactivities of butadiene and cyclopentadiene in the Diels–Alder reaction.[6,8] Nor would the sodium salt, the sulfonyl chloride, nor the N-substituted or unsubstituted amide nor either acid react with butadiene, cyclopentadiene, or (in one case) furan. This result likewise was unexpected, since acid chlorides and N-alkylimides are known to react with dienes.[6,8] At present, we have no satisfactory explanation of this anomaly, but we hope that experiments now in progress will clarify the results.

Experimental[15]

Sodium 2-phenylethene-1-sulfonate,[16] its chloride[16] and amide,[16] and 2-*p*-nitrophenylethene-1-sulfonyl chloride[11] were prepared as described previously. The methyl esters were prepared from the corresponding chlorides by the procedure of Boyle[17] in about 75% yields, using acetone as solvent; the product was isolated by pouring into ice-water and filtering.

Methyl 2-Phenylethene-1-sulfonate.—M.p. 68.0–68.7° (CCl_4). *Anal.* Calcd. for $C_9H_{10}O_3S$: C, 54.55; H, 5.08; sapn. equiv., 198.2. Found: C, 54.64; H, 4.99; sapn. equiv., 198.8. An attempt to determine a bromine number as has been done with the sodium salt[18] was unsuccessful; the reaction was very slow, reminiscent of the slow bromination of the chloride and amide.[18]

Methyl 2-*p*-Nitrophenylethene-1-sulfonate.—M.p. 157–159° (acetone–methanol). *Anal.* Calcd. for $C_9H_9O_5NS$: C, 44.48; H, 3.73. Found: C, 44.43; H, 3.56.

N,N-Diethyl-2-*p*-nitrophenylethene-1-sulfonamide.—2-*p*-Nitrophenylethene-1-sulfonyl chloride (3.0 g.) was dissolved in 50 ml. of acetone, and 3.0 g. of diethylamine and 5 ml. of pyridine were added. After 1.5 hours, the mixture was drowned in water. The amide separated as an oil which soon solidified. The amide was recrystallized from alcohol, using Norite; 2.2 g., 63% yield, m.p. 116.5–119°. The analytical sample melted at 117.5–119°.

Anal. Calcd. for $C_{12}H_{16}O_4N_2S$: C, 50.70; H, 5.67. Found: C, 50.99; H, 5.38.

Benzylthiuronium 2-*p*-Nitrophenylethene-1-sulfonate.—The nitrosulfonyl chloride was hydrolyzed with alcoholic alkali. After making the hydrolysate faintly acidic, benzylthiuronium chloride was added. The product was crystallized from dilute ethanol, m.p. 214–215°.

Anal. Calcd. for $C_{16}H_{17}O_5N_3S_2$: C, 48.67; H, 4.32. Found: C, 48.54; H, 4.21.

The *p*-toluidine salt was prepared from a portion of the above hydrolysate by the previously described procedure,[16] for comparison with the salt derived from the adduct; m.p. 260–263° (dec.).

Anal. Calcd. for $C_{15}H_{16}N_2O_5S$: C, 53.58; H, 4.80. Found: C, 53.68; H, 4.55.

Methyl 6-*p*-Nitrophenyl-2,5-endomethano-1,2,5,6-tetrahydrobenzenesulfonate.—A mixture of 5 g. of methyl 2-*p*-nitrophenylethene-1-sulfonate and 15 g. of recently distilled cyclopentadiene in 150 ml. of bromobenzene was refluxed for one hour. Two such runs were combined, the solvent and excess of cyclopentadiene were removed at the water pump, and three crops of crystals were taken. Each was crystallized once from methanol; 5.4 g., m.p. 95–102°; 2.2 g., m.p. 91–98°; 1.0 g., m.p. 78–86°, yield 68%. A sample from another run, m.p. 92–100°, was analyzed.

Anal. Calcd. for $C_{14}H_{15}O_5NS$: C, 54.32; H, 4.89; N, 4.53. Found: C, 54.56; H, 4.85; N, 4.47. The saponification equivalent of another sample, m.p. 102–108°, was determined: calcd., 309; found, 303.

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(11) F. G. Bordwell, A. B. Colbert and B. Alau, THIS JOURNAL, 68, 1778 (1946).

(12) *Cf.* ref. 11, footnote 7.

(13) F. G. Bordwell, C. M. Suter and A. J. Webber, THIS JOURNAL, 67, 827 (1945), found that 2-methyl-3-phenyl-2-propene-1-sulfonic acid was converted by bromine water almost quantitatively to an insoluble compound to which they assigned the structure 2-bromo-2-methyl-3-phenylpropane-1,3-sultone. Their results and our experience indicate that this reaction may be used to estimate certain β,γ- or γ,δ-unsaturated sulfonic acids in mixtures. The reaction is not completely general for these classes of unsaturated acids, since β,γ-unsaturated acids form bromosultones only if a phenyl group is in the γ-position (F. G. Bordwell, private communication).

(14) Compare the reactivities of acrylic acid and cinnamic acid, ref. 6, pp. 102, 108.

(15) Melting points are uncorrected. Microanalyses by Clark Microanalytical Laboratory, Urbana, Illinois.

(16) F. G. Bordwell, C. M. Suter, J. M. Holbert and C. S. Rondestvedt, Jr., THIS JOURNAL, 68, 139 (1946).

(17) M. Boyle, *J. Chem. Soc.*, 97, 216 (1910).

(18) F. G. Bordwell and C. S. Rondestvedt, Jr., THIS JOURNAL, 70, 2429 (1948).

The benzylthiuronium salt was prepared in 98% yield by hydrolyzing the adduct, acidifying, and adding benzylthiuronium chloride; m.p. 235° (dec.).

Anal. Calcd. for $C_{21}H_{23}O_5N_3S_2$: C, 54.73; H, 5.03; N, 9.12; S, 13.90. Found: C, 54.81; H, 5.20; N, 8.93; S, 12.99.

The *p*-toluidine salt was prepared in 97% yield from the hydrolysate; m.p. 217.5–219°.

Anal. Calcd. for $C_{20}H_{22}O_5N_2S$: C, 59.73; H, 5.51; N, 6.96; S, 7.97. Found: C, 60.03; H, 5.52; N, 6.83; S, 7.68.

2-*p*-Nitrophenyl-6-bromo[2,2,1]bicycloheptane-3,5-sultone.—When a once-recrystallized sample of adduct was hydrolyzed with dilute methanolic sodium hydroxide, followed by acid and potassium tribromide solution, the compound precipitated in 60–65% yield (crude). This was recrystallized several times from methanol–acetone; m.p. 206–208°.

Anal. Calcd. for $C_{13}H_{12}O_5NBrS$: C, 41.74; H, 3.23. Found: C, 42.11; H, 3.46.

It was also observed that the adduct, after hydrolysis, could be titrated quantitatively by bromate–bromide[18]; the yield of sultone remained 60–65%.

A sample of low-melting adduct was recrystallized fourteen times from methanol, petroleum ether, acetonitrile, nitromethane and acetone; it finally melted at 112–116°. This purer material gave a 93% yield of bromosultone.

2-Phenyl-6-bromo[2,2,1]bicycloheptane-3,5-sultone.—A mixture of 1.5 g. of methyl 2-phenylethene-1-sulfonate, 5 g. of cyclopentadiene, and 50 ml. of bromobenzene was refluxed for two hours. Volatile material was removed completely on the water-pump; the residue was taken up in methanolic sodium hydroxide and boiled for one hour. After adding water and extracting with ether, treatment with bromate–bromide and acid precipitated 0.223 g. (9%) of crude sultone, m.p. 103–113°. It was recrystallized from methanol for analysis; m.p. 114.5–116.5°.

Anal. Calcd. for $C_{13}H_{13}O_3BrS$: C, 47.43; H, 3.98. Found: C, 47.10; H, 4.00.

Unsuccessful Attempts to Form Adducts.—Combinations of reagents and conditions which did not yield an isolable adduct are tabulated.

Dienophile[a,d,e]	Diene[b]	Temp., °C.	Time, hr.
R_1Cl	B	150	10
R_1Cl	B	100	5
R_1NH_2	B	150	9
R_1ONa	B	150	10
R_1OMe	B	100	18
R_1OMe	B[c]	[c]	[c]
R_1Cl	F	100	20
R_1OMe	C	100	36
R_2Cl	B	150	10
R_2Cl	C	100	11.5
R_2OMe	B	100	25
R_2NEt_2	C	150	1.0

[a] $R_1 = C_6H_5CH = CHSO_2$; $R_2 = p\text{-}NO_2C_6H_4CH = CHSO_2$. [b] B = butadiene; C = cyclopentadiene; F = furan. [c] A large excess of butadiene was used; the mixture was heated for 20 hours at 100°; then 34 hours at 80°. A large amount of polybutadiene was formed. [d] Solvents employed were benzene, toluene or bromobenzene; alcohol was used with the sodium salt. [e] Recovery of starting material usually exceeded 65% except with the sulfonyl chlorides.

Acknowledgment.—The assistance of Mr. Duane Sunderman in preparing some starting materials is greatly appreciated.

ANN ARBOR, MICHIGAN RECEIVED APRIL 27, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MAINE]

Methylsulfur Trichloride[1]

BY KAY ROBERT BROWER AND IRWIN B. DOUGLASS

Methyl disulfide reacts with chlorine at −10 to −20° to form crystalline methylsulfur trichloride, CH_3SCl_3, in nearly quantitative yield. The new compound is unstable and decomposes on standing at room temperature into chloromethanesulfenyl chloride, $ClCH_2SCl$, as a principal product. It is hydrolyzed by water and weakly alkaline solutions into methanesulfinic acid. Phenyl disulfide is chlorinated to the corresponding sulfenyl chloride by methylsulfur trichloride and the latter compound is reduced to methanesulfenyl chloride. The compound also reacts slowly with ethylene by a mechanism not yet fully established to yield a product believed to be methyl chlorovinyl sulfide.

In continuing the study of the α-chloroalkanesulfenyl chlorides[2] the preparation of chloromethanesulfenyl chloride was attempted by the method of Brintzinger and others.[3] Methyl disulfide, diluted with methylene chloride, smoothly absorbed one mole of chlorine at −20° but when additional chlorine was passed in at this temperature a crystalline white solid began to separate. This solid was isolated and in elementary analysis corresponded to methylsulfur trichloride, CH_3SCl_3.

The diarylsulfur dichlorides, dibromides and diiodides are well known as are also certain dialkylsulfur dibromides and diiodides. The only dialkylsulfur dichloride to which reference has been found was prepared by Lawson and Dawson[4] who treated mustard gas in carbon tetrachloride with chlorine at −5 to 0°, and obtained bis-(2-chloroethyl)-sulfur dichloride, $(ClCH_2CH_2)_2SCl_2$. Methylsulfur trichloride is apparently the first monosubstituted organic derivative of sulfur tetrachloride to be reported.

Methylsulfur trichloride is unstable and decomposes spontaneously on standing at room temperature. The decomposition takes place chiefly according to the reaction

$$CH_3SCl_3 \longrightarrow ClCH_2SCl + HCl \qquad (1)$$

A 10-g. sample on decomposition gave the purest specimen of chloromethane-sulfenyl chloride, $ClCH_2SCl$ II, yet obtained but when larger quantities were allowed to decompose products boiling lower and higher than II were also formed.

Methylsulfur trichloride is insoluble in non-polar solvents such as isopentane, and the chlorinated hydrocarbons. No evidence other than its solubility characteristics has been found for an ionic structure for the compound.

In cold water methylsulfur trichloride reacts instantly with the formation of water soluble color-

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[1] This work was done on Project NR-055-165 under contract N8onr77000 with the Office of Naval Research, United States Navy.

[2] Douglass and Martin, *J. Org. Chem.*, **15**, 795 (1950).

[3] Brintzinger, Pfannstiel, Koddebusch and Kling, *Chem. Ber.*, **83**, 87 (1950).

[4] Lawson and Dawson, THIS JOURNAL, **49**, 3119 (1927).