This equation is based on our experimental results for $p = 5$ to 40% and $t = 10$ to 90°.

It is a remarkable and rather singular fact that any t^2-term is unnecessary to express with fair accuracy the wide variations due to temperature of the specific rotation of fructose from 10 to 90°.

The difference between the calculated and the found in the values of $[\alpha]_D$ lies in most cases under 0.1°. This empirical formula covers a wider range as compared with those previously proposed.[9] Moreover, it gives always higher values. That will be evident, if one compares, for instance, the following formulas (2) and (3) derived as special cases from our original equation (1) respectively with that of Ost–Vosburgh[9] and Vosburgh's second equation[9] (both giving highest values among the previously presented).

$$[\alpha]^{20}{}_D = -(91.80 + 0.140p) \qquad (2)$$

$$[\alpha]^{25}{}_D = -(88.85 + 0.1415p) \qquad (3)$$

As seen from the above statement these equations as well as the data obtained for the specific rotation of fructose may be available for estimating the purity of any sample of fructose with the accuracy of 0.1% by measuring polarimetrically at any temperature and concentration.

Summary

The specific rotation of fructose has been measured accurately and systematically at temperatures from 0 to 90°, and for concentrations from 5 to 40%. The values are without exception higher than those of previous investigators.

The specific rotation can be expressed by an equation

$$[\alpha]^t{}_D = -(103.6 + 0.134p) + (0.59 + 0.0003p)t$$

for $p = 5$ to 40% and for $t = 10$ to 90°.

TOKYO-HATAGAYA, JAPAN RECEIVED JULY 27, 1949

---

[9] Mention will be made of some important ones: the equation of Jungfleisch and Grimbert is valid for $t = 0$ to 40° and for c below 40%, that of Hönig and Jesser (*J. deut. Zuckerind.*, **38**, 1028 (1888)) for $p = 4$ to 40% and for $t = 12$ to 45°, that of Ost-Vosburgh: $[\alpha]^{20}{}_D = -(91.50 + 0.133\,p)$ for $p = 3$ to 30%, that of Vosburgh: $[\alpha]^t{}_D = [\alpha]^{25}{}_D + (0.566 + 0.0028\,c)(t - 25)$ for $c = 5$ to 10% and for $t = 15$ to 37°, and Vosburgh's second equation: $[\alpha]^{25}{}_D = -(88.50 + 0.145p)$ for $p = 2.6$ to 18.6%.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Preparation of Unsaturated Sulfones by Condensation Reactions[1]

BY SAUL CHODROFF[2] AND WILLETT F. WHITMORE

Tröger has found that aromatic aldehydes condense with phenylsulfonylacetic acids under conditions of the Perkin reaction,[3] and with sulfonylacetonitriles in the presence of alkali,[4] or pyridine[5] in alcoholic solution. It was felt that *p*-tolylsulfonylacetic acid could be substituted for malonic acid in the Doebner modification of the Knoevenagel reaction, to yield unsaturated sulfones of the type $p\text{-}CH_3C_6H_4SO_2CH{=}CHR$. The reaction was carried out by heating the acid with the carbonyl component in pyridine in the presence of piperidine for six hours, or until carbon dioxide evolution ceased. It was found that few carbonyl compounds reacted unequivocally to yield the unsaturated sulfone, the complicating feature of the reaction being the competitive decarboxylation of the acid to yield *p*-tolylmethyl sulfone.[6] Of the compounds studied, only cinnamaldehyde and benzaldehyde yielded isolable unsaturated sulfones. Aliphatic aldehydes, aliphatic and aromatic ketones yielded only the methyl sulfone and the unreacted carbonyl component under these conditions. The procedure of Schwenk and Papa,[7] employing triethylamine in acetic anhydride as a condensation medium, has not been found applicable for the preparation of unsaturated sulfones.

Using the procedure of Cope,[8] ethyl *n*-butylsulfonylacetate was condensed with both aliphatic and aromatic aldehydes, the theoretical amount of water being evolved in thirty minutes to two hours. Only in the case of chloral, which required the use of ammonium acetate instead of piperidine acetate, was the reaction time prolonged to twenty-three hours. Aliphatic and aromatic ketones failed to react with this ester under a variety of conditions, which included the use of such catalysts as piperidine acetate, ammonium acetate, triethylamine acetate and morpholine acetate. Other conditions used without success were prolonged refluxing with potassium acetate and acetic anhydride, and reaction in the presence of zinc chloride and acetic anhydride. In all cases, the original ester was recovered unchanged. The α-

---

[1] The material for this paper was abstracted in part from the thesis of S. Chodroff submitted to the Faculty of the Graduate School of the Polytechnic Institute in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1948.

[2] Present address: Rare-Galen Division, Nopco Chemical Company, Harrison, New Jersey.

[3] Tröger and Hille, *J. prakt. Chem.*, [2] **71**, 201 (1905).

[4] Tröger and Prochnow, *ibid.*, [2] **78**, 123 (1908).

[5] Tröger and Brenner, *Arch. Pharm.*, **247**, 613 (1910).

[6] Usually more vigorous conditions are required for the decarboxylation of the α-alkylsulfonylcarboxylic acids; for example, Otto and Otto (*Ber.*, **21**, 992 (1888)) found that α-ethylsulfonylpropionic acid yielded diethyl sulfone at 200°, and Tröger and Uhde (*J. prakt. Chem.*, [2] **59**, 334 (1899)) prepared phenylisopropyl sulfone by heating α-phenylsulfonylisobutyric acid with potassium hydroxide at 170°. It is only when these acids have one or more halogens attached to the α-carbon atoms, that the loss of carbon dioxide takes place at a lower temperature. Fouque and LaCroix, *Bull. soc. chim.*, **33**, 180 (1923), and Otto, *J. prakt. Chem.*, [2] **40**, 527 (1889).

[7] Schwenk and Papa, THIS JOURNAL, **67**, 1432 (1945).

[8] Cope and Hofman, *ibid.*, **63**, 3456 (1941); Cope, Hofman, Wycoff and Hardenbergh, *ibid.*, **63**, 3452 (1941).

TABLE I

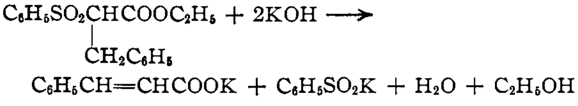
α-*n*-BUTYLSULFONYL-α-CARBETHOXY β-ALKYLETHYLENES $n\text{-}C_4H_9SO_2\overset{COOC_2H_5}{\overset{|}{C}}=CHR$

Aldehyde used	R	B. p. °C.	B. p. Mm.	Yield, %	$n^{27}D$	d^{27}_{27}	Sulfur, % Calcd.	Sulfur, % Found
Cinnamaldehyde	Styryl	195–200	0.09	84	1.5940	1.1002	9.94	9.67
o-Cl-benzaldehyde	*o*-Cl-phenyl	173–176	0.2	71	1.5409	1.1756	9.69	9.59
Benzaldehyde	Phenyl	190–195	5.0	83	1.5349	1.1082	10.82	10.89
n-Butyraldehyde	*n*-Propyl	182–185	13.0	77	1.4652	1.0402	12.22	12.44
Isobutyraldehyde	Isopropyl	147–149	5.0	88	1.4639	1.0024	12.22	11.87
Furfuraldehyde	Furyl	175–177	1.0	62	1.5349	1.1384	11.20	11.02
Chloral	Trichloromethyl	165–167	1.0	61	1.4885	1.2717	9.50	9.72

n-butylsulfonyl-α-carbethoxy-β-alkylethylenes obtained from this condensation, were viscous, non-crystallizable liquids, colorless to yellow in appearance. The yields ranged from 60 to 90%. These unsaturated sulfones do not absorb bromine and are attacked by permanganate in acetone. Action by hydrolytic agents such as concentrated hydrochloric acid and aqueous or alcoholic alkali cause a reversal of the original condensation.

α-*n*-Butylsulfonyl-α-carbethoxy-β-phenylethylene was reduced with hydrogen in the presence of Raney nickel to ethyl α-*n*-butylsulfonyl β-phenylpropionate, which did not depress the melting point of an authentic sample, prepared unequivocally. Adams catalyst was ineffective in promoting this reduction.

A series of phenylsulfonyl-alkyl-substituted-acetic acids was submitted to the Mannich reaction with formaldehyde and diethylamine, resulting in the formation of unsaturated sulfones of the type, $C_6H_5SO_2\overset{R}{C}=CH_2$. The phenylsulfonylacetic acids (Table III) were prepared by saponification of the corresponding esters (Table II), which in turn were prepared by alkylation of ethyl phenylsulfonylacetate according to the procedure commonly used in the malonic ester syntheses. Although Michael and Comey[9] reported that the benzyl derivative was cleaved with alcoholic alkali, in the following manner

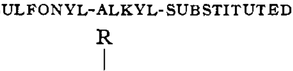


$$C_6H_5SO_2\underset{CH_2C_6H_5}{\underset{|}{C}H}COOC_2H_5 + 2KOH \longrightarrow$$
$$C_6H_5CH=CHCOOK + C_6H_5SO_2K + H_2O + C_2H_5OH$$

the saponification of these esters was accomplished without difficulty, in good yields with alcoholic potassium hydroxide.[10] The reaction of the phenylsulfonyl-alkyl-substituted-acetic acids with diethylamine and formaldehyde was carried out under a modification of the conditions of Mannich and Ritsert.[11]

TABLE II

ETHYL PHENYLSULFONYL-ALKYL-SUBSTITUTED-ACETATES,



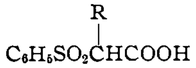
$$C_6H_5SO_2\overset{R}{\overset{|}{C}H}COOC_2H_5$$

R	Yield, %	M. p., °C.	Sulfur, % Calcd.	Sulfur, % Found
Ethyl	75	61–62	12.51	12.19
n-Butyl	55	156–162[a]	11.27	11.10
Isopropyl	45	59.5–60.5	11.86	12.05
Benzyl	92	91–92	9.94	10.15

[a] B. p. at 2 mm.

TABLE III

PHENYLSULFONYL-ALKYL-SUBSTITUTED-ACETIC ACIDS



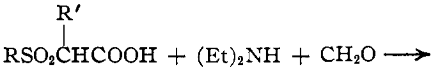
$$C_6H_5SO_2\overset{R}{\overset{|}{C}H}COOH$$

R	Yield, %	Recrystallization solvent	M. p., °C.	Sulfur, % Calcd.	Sulfur, % Found
Ethyl	86	Aqueous acetone	122–123	14.17	14.07
n-Butyl	92	Benzene–hexane	66.5–67	12.51	12.27
Isopropyl	68	Ethylene dichloride	110.5–111.5	13.18	12.85
Benzyl	73	Ethyl acetate–benzene	162–163	11.04	11.36

This reaction required five to seven days at room temperature for a reasonable degree of completion. The neutral fraction yielded the unsaturated sulfones (Table IV), as colorless to yellow high boiling liquids, in about 50% yields. In the case of the isopropyl derivative, the yield was 9% with a conversion of the acid of 33%, indicating the pronounced effect on the yield shown by the sulfonylacetic acids containing a secondary alkyl substituent.

α-*p*-Tolylsulfonyl-α-methylethylene, $p\text{-}CH_3C_6H_4SO_2\overset{CH_3}{\overset{|}{C}}=CH_2$, prepared in 42% yield from diethylamine, formaldehyde and α-*p*-tolylsulfonylpropionic acid was a solid melting at 56–57°, in contradistinction to the liquid phenylsulfonylethylenes. Proof of structure was established by reduction with hydrogen in the presence of Raney nickel to isopropyltolyl sulfone, m. p. 79–80°, which did not depress the melting point of an authentic sample. This ethylenic sulfone adds bromine very slowly in acetic acid, the reaction being about 70% complete in ninety-six hours.

A mechanism is proposed for the formation of these unsaturated sulfones. The components combine to form the intermediate Mannich condensation product.



$$RSO_2\overset{R'}{\overset{|}{C}H}COOH + (Et)_2NH + CH_2O \longrightarrow$$

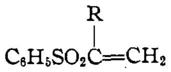
---

[9] Michael and Comey, *Am. Chem. J.*, **5**, 116 (1883).

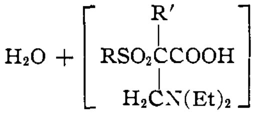
[10] Ashley and Shriner, THIS JOURNAL, **54**, 4410 (1932).

[11] Mannich and Ritsert, *Ber.*, **57**, 1116 (1924).

TABLE IV

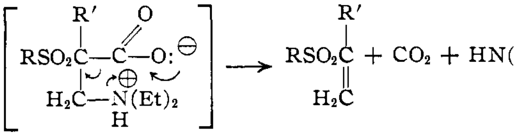
α-PHENYLSULFONYL-α-ALKYLETHYLENES 
$C_6H_5SO_2\overset{R}{C}{=}CH_2$

R	Yield, %	Conversion from acid, %	B. p. °C.	Mm.	$n^{27}D$	d^{27}_{27}	Sulfur, % Calcd.	Sulfur, % Found
Ethyl	43	60	143–146	2.0	1.5380	1.1624	16.34	16.20
n-Butyl	44	75	158–159	1.0	1.5270	1.1035	14.29	14.07
Isopropyl	9	33	144–146	0.6	1.5278	1.1425	15.25	14.96
Benzyl	65	..	172–175	0.2	1.5809	1.1511	12.41	12.18


(1)

$$H_2O + \left[\begin{array}{c} R' \\ | \\ RSO_2CCOOH \\ | \\ H_2CN(Et)_2 \end{array}\right] \quad (1)$$

The zwitterion can than eliminate carbon dioxide and diethylamine.


(2)

$$\left[\begin{array}{c} R' \quad O \\ RSO_2C-C-O:^{\ominus} \\ H_2C-\overset{\oplus}{N}(Et)_2 \\ H \end{array}\right] \longrightarrow RSO_2\underset{\underset{H_2C}{\|}}{\overset{R'}{C}} + CO_2 + HN(Et)_2 \quad (2)$$

This is similar in some respects to the mechanism of decarboxylation of β-keto acids proposed by Westheimer and Jones,[12] and that of King,[13] for the decarboxylation of malonic acid.

The ethyl esters of the phenylsulfonyl-alkyl-substituted-acetic acids failed to participate in the Mannich reaction under a variety of conditions, for, in all cases, the original ester was recovered unchanged in high yield. These conditions included refluxing the ester with diethylamine hydrochloride and paraformaldehyde in isopropyl alcohol or isoamyl alcohol for fifteen hours. Allowing the reactants to stand at room temperature in these solvents for several weeks was equally unsuccessful. Since the Mannich reaction is known to be reversible, the equilibrium may not favor the condensation product.

Experimental

Materials.—*p*-Tolylsulfinic acid was prepared in 90% yield according to the method of Oxley,[14] by reduction of *p*-tolylsulfonyl chloride with sodium sulfite. The sulfinic acid was condensed with chloroacetic acid according to Gabriel,[15] to yield *p*-tolylsulfonylacetic acid in 68% yield.

α-*p*-Tolylsulfonyl-β-styrylethylene.—A solution of 9.1 g. of *p*-tolylsulfonylacetic acid in 25 ml. of anhydrous pyridine was heated on the steam-bath with 6.6 g. of cinnamaldehyde and 0.5 ml. of piperidine for five hours, until the evolution of carbon dioxide had ceased. The dark red liquid was cooled and poured on 30 ml. of concentrated hydrochloric acid and 100 g. of ice. The brown solid which precipitated was filtered, and crystallized from 150 ml. of methanol with decolorization. The unsaturated sulfone was obtained as long yellow needles in a yield of 6.0 g. (50%), m. p. 134.5–135.5°.

Anal. Calcd. for $C_{17}H_{17}O_2S$: S, 11.23. Found: S, 11.26.

α-*p*-Tolylsulfonyl-β-phenylethylene.—A mixture of 6.85 g. of *p*-tolylsulfonylacetic acid, 3.4 g. of benzaldehyde, 20 ml. of pyridine and 0.5 ml. of piperidine was worked up as described above, and yielded after two recrystallizations from ethanol and one from methanol, 1.52 g. (18%) of the unsaturated sulfone, m. p. 119.5–120°.

Anal. Calcd. for $C_{15}H_{14}O_2S$: S, 12.44. Found: S, 12.63.

***n*-Butylthioacetic Acid.**—A solution of 76 g. of thiourea in 500 ml. of 95% ethanol was refluxed four hours with 137 g. of *n*-butyl bromide and 400 ml. of alcohol was removed by distillation. To the hot solution were added 60 g. of sodium hydroxide in 300 ml. of water, and refluxing was continued for an additional two hours. The pink oily mercaptan which separated was dissolved by the addition of 40 g. of sodium hydroxide in 200 ml. of water. The reaction mixture was cooled to 0.5°, and to this was added a neutral solution made up of 94.5 g. of chloroacetic acid, 40 g. of sodium hydroxide and 300 ml. of water. The solution was permitted to warm to room temperature and then refluxed for one hour. The cooled solution was acidified to congo red with 180 ml. of concentrated hydrochloric acid, and the *n*-butylthioacetic acid was extracted with three 75-ml. portions of ether. The ether extracts were washed to neutrality with 10% sodium chloride solution, dried over sodium sulfate, the solvent removed on the steam-bath and the residue vacuum distilled, yielding 133 g. (90%) of the thioacid, b. p. 112–115° at 1 mm.

Ethyl *n*-Butylsulfonylacetate.—The oxidation of 260 g. of *n*-butylthioacetic acid was carried out according to the procedure of Pomerantz and Connor[16] to yield *n*-butylsulfonylacetic acid. The crude sirupy acid was esterified with 700 ml. of ethanol and 20 ml. of concentrated sulfuric acid to yield 264 g. of the ethyl ester (72% from the thioacid), b. p. 170–175° at 15 mm., $n^{27}D$ 1.4543, d^{27}_{27} 1.1184.

Anal. Calcd. for $C_8H_{16}O_4S$: S, 15.39. Found: S, 15.35.

Preparation of Unsaturated Sulfones (Table I) from Ethyl *n*-Butylsulfonylacetate and Aldehydes.—The following aldehydes, obtained commercially, were purified by distillation: benzaldehyde, *o*-chlorobenzaldehyde, cinnamaldehyde, isobutyraldehyde, *n*-butyraldehyde and furfural. Chloral was obtained by shaking chloral hydrate with concentrated sulfuric acid and distilling over calcium carbonate. The procedure of Cope[8] was used for the condensations and is illustrated below for the preparation of α-*n*-butylsulfonyl-α-carbethoxy-β-phenylethylene.

A mixture of 20.8 g. of ethyl *n*-butylsulfonylacetate, 10.6 g. of benzaldehyde, 60 ml. of benzene, 0.34 ml. of piperidine and 1.22 ml. of acetic acid was refluxed, collecting the theoretical amount of water evolved in a Dean-Stark[17] trap in two hours. The solution was cooled, washed with dilute hydrochloric acid and with water until neutral and the solvent removed *in vacuo* on the steam-bath. The residue was vacuum distilled through a 15-cm. Vigreux column, collecting 24.5 g. (83%) of the unsaturated sulfone, b. p. 190–195° at 5 mm.

Ethyl α-*n*-Butylsulfonyl-β-phenylpropionate.—A solution of 5.92 g. (0.02 mole) of α-*n*-butylsulfonyl-α-carbethoxy-β-phenylethylene in 150 ml. of isopropyl alcohol was reduced at atmospheric pressure in the presence of 10 g. of prereduced Raney nickel. The hydrogen uptake was

---

[12] Westheimer and Jones, THIS JOURNAL, **63**, 3283 (1941).

[13] King, *ibid.*, **69**, 2739 (1947).

[14] Oxley, Partridge, Robson and Short, *J. Chem. Soc.*, 767 (1946).

[15] Gabriel, *Ber.*, **14**, 834 (1881).

[16] Pomerantz and Connor, THIS JOURNAL, **61**, 3144 (1939).

[17] Dean and Stark, *Ind. Eng. Chem.*, **12**, 486 (1920).

101% and required twelve minutes. The catalyst was filtered, washed with three 20-ml. portions of isopropyl alcohol, and the combined filtrates concentrated to 15 ml. This was diluted with 6 ml. of water and chilled, yielding 3.10 g. of ethyl α-*n*-butylsulfonyl-β-phenylpropionate, m. p. 42–43°, which did not depress the melting point of a sample prepared unequivocally below.

Anal. Calcd. for $C_{15}H_{22}O_4S$: S, 10.75. Found: S, 10.79.

α-**Bromo-β-phenylpropionic acid** was prepared according to "Organic Syntheses,"[18] by benzylation of malonic ester, saponification, and acidification to the substituted acid. Bromination of the benzylmalonic acid and decarboxylation gave α-bromo-β-phenylpropionic acid. This acid was condensed with *n*-butyl mercaptan prepared *in situ* from *n*-butyl bromide and thiourea, to yield α-*n*-butylthio-β-phenylpropionic acid, which, after esterification and oxidation with hydrogen peroxide in glacial acetic acid, yielded ethyl α-*n*-butylsulfonyl-β-phenylpropionate.

Ethyl Phenylsulfonylacetate.[10]—This compound was prepared in 70% yield by condensing equimolar amounts of sodium phenylsulfinate and ethyl chloroacetate in absolute alcohol.

Alkylation of Ethyl Phenylsulfonylacetate (Table II).—The procedure was that employed for the preparation of the ethyl[10] and benzyl[9] substituted derivatives.

Saponification of Ethyl Phenylsulfonyl-alkyl-substituted-acetates (Table III).—The procedure of Ashley and Shriner[10] was used.

α-Phenylsulfonyl-α-alkyl-ethylenes (Table IV).—The procedure is illustrated for the preparation of the *n*-butyl derivative. To 13.9 g. of phenylsulfonyl-*n*-butylacetic acid, cooled to 0°, was added with swirling, 10 g. of diethylamine, followed by 10 g. of 34% formaldehyde. The solution was permitted to warm to room temperature, and to stand three days with occasional swirling to permit the escape of carbon dioxide. The two layers were then shaken with 100 ml. of ether and 100 ml. of 10% potassium carbonate. The ether extract was washed successively with water, dilute acid and water. The solution was dried and the solvent evaporated to leave a residue which was distilled under vacuum to yield 5.34 g. of the unsaturated sulfone, b. p. 158–159° at 1 mm. The carbonate solution on acidification yielded 5.72 g. of the original acid.

α-*p*-Tolylsulfonyl-α-methylethylene.—α-*p*-Tolylsulfonylpropionic acid was prepared in 90% yield, by heating equimolar amounts of sodium *p*-tolylsulfinate and sodium α-bromopropionate in aqueous solution on the steam-bath for fifteen hours, and acidifying with mineral acid. To 53 g. of α-*p*-tolylsulfonylpropionic acid cooled to 0°, was added 43.5 g. of diethylamine at this temperature, followed by 43.5 g. of 34% formaldehyde. The clear solution remained at room temperature for five days without the appearance of a second phase. The reaction mixture was then warmed on the steam-bath for ten minutes without any visible effect. After cooling to 25°, 20 ml. of 50% sulfuric acid was added, resulting in the vigorous evolution of carbon dioxide and the appearance of an oil. This was extracted with three 30-ml. portions of chloroform, and the extracts washed with 10% sodium hydroxide, 10% sulfuric acid and with water until neutral. After drying and removal of the solvent by evaporation, the residue was vacuum distilled to yield 20.85 g. of the unsaturated sulfone, b. p. 134–137° at 1 mm. The crude product melting at 48–50°, was recrystallized from 50 ml. of benzene and 100 ml. of hexane, yielding 17.7 g. (42%), m. p. 56–57°.

Anal. Calcd. for $C_{10}H_{12}O_2S$: S, 16.34. Found: S, 15.98.

Isopropyl *p*-Tolyl Sulfone.—Two-hundredths of a mole (3.92 g.) of α-*p*-tolylsulfonyl-α-methylethylene was reduced at atmospheric pressure in 100 ml. of isopropyl alcohol, in the presence of 12 g. of prereduced Raney nickel. The theoretical amount of hydrogen was absorbed in seven minutes. The catalyst was filtered and washed with 20 ml. of isopropyl alcohol, and the combined filtrates concentrated to 10 ml. The solution was diluted with an equal volume of water, and deposited 3.4 g. of isopropyl *p*-tolyl sulfone, m. p. 76–78°. After recrystallization from aqueous alcohol, the sulfone melted at 79.5–80.5°, reported,[19] 80°. A mixture with an authentic sample, prepared from isopropyl bromide and sodium *p*-toluenesulfinate, melted at 80°.

1,2-Dibromoisopropyl-*p*-tolyl Sulfone.—Two grams of α-*p*-tolylsulfonyl-α-methylethylene in 20 ml. of acetic acid and 2 ml. of bromine was permitted to stand two weeks at room temperature. The excess bromine and acetic acid were removed *in vacuo* at 40°, and the oily residue triturated with 15 ml. of ethanol, yielding 2.4 g. (66%), m. p. 94–95°. The melting point remained unchanged after recrystallization from ethanol.

Anal. Calcd. for $C_{10}H_{12}O_2Br_2S$: S, 9.00. Found: S, 8.92.

Summary

The condensation of *p*-tolylsulfonylacetic acid with benzaldehyde and cinnamaldehyde to yield unsaturated sulfones has been described.

Unsaturated sulfones have been prepared by condensing aldehydes and ethyl *n*-butylsulfonylacetate.

A series of phenylsulfonyl alkyl substituted acetic acids have been subjected to a Mannich reaction to yield unsaturated sulfones of the type, $C_6H_5SO_2CR{=}CH_2$. α-*p*-Tolylsulfonyl-α-methylethylene and its dibromide have been prepared.

Proof of structure of the unsaturated sulfones has been established by reduction.

BROOKLYN 2, N. Y. RECEIVED[20] SEPTEMBER 29, 1949

---

[18] Marvel, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1941, Vol. 21, p. 99.

[19] Tröger and Uhde, *J. prakt. Chem.*, **59**, 334 (1899).

[20] Original manuscript received March 8, 1949.