CLXI.—*The Interaction of Alkali Sulphites with some Halogeno-compounds, and the Optical Resolution of α-Phenylpropanesulphonic Acid.*

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THE original object of this work was to determine whether the interaction of sodium sulphite and asymmetric halogen compounds of the type CHRR′X would afford a practicable method for the preparation of some optically resolvable sulphonic acids required for another investigation. We have, however, not been concerned with the sulpho-carboxylic acids, which have been simultaneously investigated by Backer and Burgers (see, for example, J., 1925, **127**, 233).

Cohen and Clutterbuck (J., 1923, **123**, 2507) stated that β-phenylethyl chloride was converted by boiling aqueous sodium sulphite into styrene, with evolution of sulphur dioxide. We find, however, that the chloride is converted under these conditions into a mixture of *sodium* β-*phenylethanesulphonate*, $CH_2Ph{\cdot}CH_2{\cdot}SO_3Na$ (65% yield), and β-phenylethyl alcohol, no appreciable evolution of sulphur dioxide occurring. Sodium or potassium sulphite converts β-phenylethyl bromide even more rapidly and completely into sulphonate.

β-*Phenylethanesulphonyl chloride* and the corresponding *amide* and *anilide* are readily obtainable from the sodium sulphonate. The isolation of the amide makes it possible to cite the series $Ph{\cdot}[CH_2]_x{\cdot}SO_2{\cdot}NH_2$ as another in which there is an alternation in melting point (compare Roberts, Turner, and Bury, J., 1926, 1443) : for $x = 0, 1, 2$, and 3, the m. p.'s are respectively 153°, 105°, 119°, and 35°.

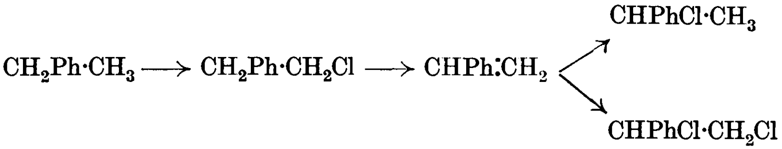
Similarly, α-phenylethyl chloride (bromide) reacts with boiling aqueous sodium sulphite to give *sodium* α-*phenylethanesulphonate*, $CHPhMe{\cdot}SO_3Na$ (yield, 43—45%). Considerable evolution of sulphur dioxide occurs and some styrene is formed.

Fittig and Kiesow (*Annalen*, 1870, **156**, 246) and, later, Anschütz (*ibid.*, 1886, **235**, 329) concluded that chlorination of boiling ethylbenzene afforded mainly β-phenylethyl chloride, whilst Schramm (*Monatsh.*, 1887, **8**, 102; *Ber.*, 1893, **26**, 1706) obtained a mixture of the α- and β-chlorides. We find that pure ethylbenzene, prepared from acetophenone (Clemmensen, *Ber.*, 1913, **46**, 1840), chlorinates readily in diffused daylight to give (corresponding to monochlorination) a mixture of α- and β-phenylethyl chlorides with higher-boiling material (αβ-dichlorophenylethane, etc.), increased illumination appearing to augment the proportion of α-chloride.

When the contained α- and β-chloride mixture is boiled with aqueous sodium sulphite, it gives rise to appreciable quantities of sulphur dioxide and styrene, but at the same time to a mixture of the corresponding sodium sulphonates.

Dimethylaniline is indifferent towards β-phenylethyl chloride, but combines with the α-chloride to give the crystalline *phenyl-α-phenylethyldimethylammonium chloride*, $CHPhMe{\cdot}NPhMe_2Cl$. When a mixture, with dimethylaniline, of the above purified chlorination mixture was kept for several months, it deposited no solid, a fact which shows that the mixture was predominatingly β-chloride.

The chlorination of ethylbenzene probably gives, as the first product, mainly β-phenylethyl chloride, but the decomposition of this substance, during the chlorination process, produces styrene, which combines either with hydrogen chloride or with chlorine :



$$\begin{tikzcd} & & & CHPhCl{\cdot}CH_3 \\ CH_2Ph{\cdot}CH_3 \arrow[r] & CH_2Ph{\cdot}CH_2Cl \arrow[r] & CHPh{:}CH_2 \arrow[ur] \arrow[dr] & \\ & & & CHPhCl{\cdot}CH_2Cl \end{tikzcd}$$

When *strychnine* dl-α-*phenylethanesulphonate* was crystallised from water, *strychnine* l-α-*phenylethanesulphonate* separated first.

As considerable quantities of phenylmethylcarbinol were required for this work, we re-examined the reduction of acetophenone, using sodium and moist ether–toluene. The main product was, however, αβ-diphenyl-αβ-dimethylethane-αβ-diol (acetophenone pinacol). This is therefore, apparently, the best way of obtaining this substance, since in 1917 (*J. Amer. Chem. Soc.*, **39**, 291) Johlin, who investigated various methods for its preparation, including the reduction of acetophenone by other processes, concluded that it was then most conveniently prepared from magnesium methyl iodide and benzil.

α-Phenylpropyl bromide also reacted with boiling aqueous sodium sulphite, but only about 10% was converted into *sodium* α-*phenylpropanesulphonate*, $CHPhEt{\cdot}SO_3Na$. Prolonged shaking of the reactants at the ordinary temperature, however, gave a 30% yield. When an aqueous solution of α-*phenylpropanesulphonic acid* was treated with half an equivalent of strychnine, it afforded the sparingly soluble *strychnine* d-α-*phenylpropanesulphonate* with $[\alpha]_D^{26°} - 23{\cdot}7°$; the mother-liquor gave, with cinchonine, the l-α-*phenylpropanesulphonate* of the latter base, having $[\alpha]_D^{25°} + 104{\cdot}9°$. From the two alkaloidal salts were obtained the two *sodium* salts, with $[\alpha]_D^{25°} + 5{\cdot}2°$ and $- 5{\cdot}2°$, respectively.

α-*Phenylbutyl bromide* reacted slowly with aqueous sodium sulphite at the ordinary temperature to give a little *sodium* α-*phenylbutane-*

sulphonate, $CHPhPr^{\alpha}\cdot SO_3Na$, the majority of the bromo-compound, however, being converted into α-phenyl-Δ^{α}-butene.

In other experiments designed to provide α-phenylbutanesulphonic acid, magnesium α-phenylbutyl bromide was found to react with sulphur dioxide to give, instead of the desired sulphinic acid, *di-α-phenylbutyl sulphide* $(PhPr^{\alpha}CH)_2S$ (compare Rosenheim and Singer, *Ber.*, 1904, **37**, 2152; Oddo, *Gazzetta*, 1911, **41**, 11).

The effect upon the conversion of α-phenylethyl halides into sodium sulphonates, of negative substituents in the benzene ring was also tested. 2 : 4-Dichloroiodobenzene (Ullmann, *Annalen*, 1904, **332**, 38) combined with magnesium to give magnesium 2 : 4-dichlorophenyl iodide, and this reacted with acetaldehyde to give 2 : 4-*dichlorophenylmethylcarbinol*. No difficulty was experienced in converting this substance into the corresponding *bromide*, but when the latter was treated with boiling aqueous sodium sulphite, it was almost quantitatively converted into the carbinol. This result is somewhat similar to that observed by Wedekind and Schenk (*Ber.*, 1911, **44**, 198) with diphenylhalogenomethanes, when the corresponding ether was formed as the only product. No 2 : 4-dichlorostyrene was produced in the above reaction, this fact and the above formation of carbinol being apparently due to the negative effect of the ortho-para chlorine atoms. Again, α-2 : 4-dichlorophenylethyl bromide is devoid of lachrymatory properties, unlike α-phenylethyl bromide itself.

β-Bromobutane, readily obtainable from methyl ethyl ketone (Bentley, J., 1895, **67**, 264; Norris, Green, and Johnson, *Amer. Chem. J.*, 1901, **26**, 293), reacted at a convenient rate with warm aqueous sodium sulphite to give over half the calculated quantity of *sodium α-methylpropanesulphonate*, $CHMeEt\cdot SO_3Na$. *Strychnine* d-*α-methylpropanesulphonate* is less soluble in water than its diastereoisomeride. No other alkaloidal salt could be obtained crystalline.

EXPERIMENTAL.

Sodium β-Phenylethanesulphonate.—(a) *From β-phenylethyl chloride.* A mixture of 20 g. of the chloride with a saturated aqueous solution of 40 g. of sodium sulphite heptahydrate was heated to boiling for 20 hours; 4 g. of oil, identified as β-phenylethyl alcohol, remained undissolved. No sulphur dioxide evolution was observed during the process. The cooled reaction mixture deposited a mass of crystals which, after crystallisation from water, gave white plates of *sodium β-phenylethanesulphonate* (yield, 65%) (Found : Na, 11·1. $C_8H_9O_3SNa$ requires Na, 11·1%). (b) *From β-phenylethyl bromide.* A mixture of 37 g. of the bromide and a saturated solution of 55 g. of sodium sulphite was boiled under reflux. Crystals began to form in the boiling solution after 2·5 hours, and in 3 hours the bromide had disappeared. On cooling, the liquid set to a crystalline mass, which was filtered off. The solid was crystallised from water, a 90% yield of the sodium sulphonate being obtained (Found : Na, 11·2%).

The *potassium* salt was obtained similarly, and separated from water in white plates (yield, 90%) (Found : K, 17·3. $C_8H_9O_3SK$ requires K, 17·4%). The *barium* salt was precipitated when concentrated solutions of barium chloride and of the above sodium salt were mixed. Recrystallised from water, it formed small leaflets (Found : Ba, 27·2. $C_{16}H_{18}O_6S_2Ba$ requires Ba, 27·0%).

β-*Phenylethanesulphonic acid*, obtained from the barium salt and an equivalent of sulphuric acid, crystallised from very concentrated solutions in small, deliquescent leaflets, m. p. 91°. After being left in contact with porous porcelain for a short time in a dry atmosphere, it was found to contain 5 mols. of water of crystallisation.

β-*Phenylethanesulphonyl Chloride*.—The sodium salt reacted normally with phosphorus pentachloride to give the *sulphonyl chloride*, which crystallised from light petroleum in white, silky needles, m. p. 34° (Found : Cl, 17·6. $C_8H_9O_2ClS$ requires Cl, 17·4%).

β-*Phenylethanesulphonamide* was obtained by passing dry ammonia into a well-cooled ethereal solution of the chloride. It separated from water in white plates, m. p. 119° (Found : N, 7·3. $C_8H_{11}O_2NS$ requires N, 7·6%). The chloride reacted readily in ethereal solution with aniline, giving the *anilide*, which crystallised from aqueous alcohol in white needles, m. p. 77° (Found : N, 5·2. $C_{14}H_{15}O_2NS$ requires N, 5·4%).

Sodium α-Phenylethanesulphonate.—A mixture of 40 g. of α-phenylethyl bromide and a saturated solution of 60 g. of sodium sulphite was boiled under reflux. A brisk evolution of sulphur dioxide occurred, and the layer of organic liquid, at first at the bottom, rose to the top. When, after 6 hours' boiling, no more sulphur dioxide was evolved, the liquid was cooled. The top layer consisted of styrene (10 g.), and the aqueous layer, after being evaporated to about two-thirds of its original bulk, deposited white plates on cooling. These were crystallised from water (yield, 45%) (Found : Na, 11·1. $C_8H_9O_3SNa$ requires Na, 11·1%).

When 100 g. of α-phenylethyl bromide was used for this preparation, only 10 g. of sulphonate were obtained; the use of small quantities is therefore to be recommended.

With α-phenylethyl chloride (30 g.) instead of the bromide, the reaction was complete in 9 hours, and a 43% yield of sodium salt was obtained.

Barium α-phenylethanesulphonate crystallised in long needles when a solution containing the sodium salt and the calculated quantity of barium chloride was cooled (Found: Ba, 27·3. $C_{16}H_{18}O_6S_2Ba$ requires Ba, 27·0%). The *potassium* salt, obtained from the barium salt and potassium sulphate, crystallised from water in plates (Found: K, 17·5. $C_8H_9O_3SK$ requires K, 17·4%).

α-Phenylethanesulphonyl chloride, formed from the sodium salt in the usual manner, separated from alcohol in small, white needles, m. p. 79° (Found: Cl, 17·5. $C_8H_9O_2ClS$ requires Cl, 17·4%).

Chlorination of Ethylbenzene.—When chlorine was passed into boiling ethylbenzene in bright sunlight (Sydney, N.S.W.), chlorination was very rapid and gave a mixture of polychloro-derivatives. Dry chlorine was passed for 4 hours into 30·7 g. of boiling ethylbenzene in bright sunlight (London) until an increase of 9 g. in weight occurred. The product separated when distilled into three fractions: (1) b. p. up to 82°/15 mm., 2 g.; (2) b. p. 82—100°/15 mm., 16 g.; and (3) b. p. 100—125°/15 mm., 12 g. Fraction (2) was boiled with sodium sulphite solution. Sulphur dioxide was evolved, and after 8 hours the solution was cooled; crystals of the sulphonate mixture then separated and 2 g. of styrene were isolated. Fraction (3) was rich in αβ-dichlorophenylethane.

A second chlorination of 43 g. of ethylbenzene, carried out on a very dull day, lasted 9 hours. The product was separated into 3 fractions: (1) b. p. up to 82°/15 mm., 3 g.; (2) b. p. 82—102°/15 mm., 20 g.; and (3) b. p. 102—120°/15 mm., 20 g. Fraction (2), the greater portion of which distilled at 90—100°/15 mm., was only slightly lachrymatory and was evidently mainly β-phenylethyl chloride; for, when it was heated with sodium sulphite, it gave rise to very little sulphur dioxide and styrene, and a good yield of sulphonate.

Equimolecular mixtures, with dimethylaniline, of α- and β-phenylethyl chlorides and fraction (2) of the last chlorination were allowed to remain at the ordinary temperature for 5 months. The mixture containing the α-chloride became almost solid. The product was left in contact with porous porcelain in a dry atmosphere, and then became a colourless, crystalline mass of *phenyl-α-phenylethyldimethylammonium chloride*, m. p. 95° (Found: Cl, 13·6. $C_{16}H_{20}NCl$ requires Cl, 13·6%). The other two mixtures deposited no solid.

Strychnine dl-*α-Phenylethanesulphonate.*—To a boiling aqueous solution of barium α-phenylethanesulphonate (21·99 g.) was added a boiling solution of 29 g. of strychnine in the equivalent quantity of *N*-sulphuric acid. The barium sulphate was collected, and the filtrate was evaporated almost to dryness. The solid so obtained was analysed (Found: N, 5·6. $C_{21}H_{22}O_2N_2,C_8H_{10}O_3S$ requires N, 5·4%).

Fractional crystallisation of this racemate gave *strychnine* l-α-*phenylethanesulphonate* as the less soluble salt. A 1·874% solution in 50% aqueous alcohol had $\alpha_{\mathrm{D}}^{18^\circ}$ − 0·81° (2-dcm. tube), whence $[\alpha]_{\mathrm{D}}^{18^\circ}$ − 20·5°.

Similarly, when a hot solution of 4·62 g. of sodium α-phenylethanesulphonate was treated with a hot solution of 3·71 g. of strychnine (dissolved in an equivalent of *N*-sulphuric acid), and the solution allowed to cool, pure strychnine *l*-sulphonate separated, having $[\alpha]_{\mathrm{D}}^{18^\circ}$ − 20·5°.

Potassium l-α-*phenylethanesulphonate* was obtained by treating the strychnine salt with potassium carbonate. A 1·90% solution in water had $\alpha_{\mathrm{D}}^{18^\circ}$ − 0·45° ($l = 2$ dcm.), whence $[\alpha]_{\mathrm{D}}^{18^\circ}$ − 11·8°.

Systematic treatment of the mother-liquors from the strychnine *l*-sulphonate did not afford a pure *d*-sulphonate.

Brucine dl-α-*phenylethanesulphonate* was obtained crystalline only after a great deal of preliminary treatment. It was very soluble in water, alcohol, ether, carbon tetrachloride, and acetone, though sparingly soluble in benzene, and could not be caused to crystallise systematically (Found : N, 5·1. $C_{23}H_{26}O_4N_2,C_8H_{10}O_3S$ requires N, 4·8%). *Cinchonidine* dl-α-*phenylethanesulphonate* was even more difficult to obtain crystalline, and could not be fractionally crystallised, being very soluble in most solvents (Found : N, 4·4. $C_{27}H_{32}O_4N_2,C_8H_{10}O_3S$ requires N, 4·2%).

Preparation of αβ-*Diphenyl*-αβ-*dimethylethane*-αβ-*diol*.—A solution of acetophenone (60 g.) in moist ether (150 c.c.) was slowly added to 46 g. of powdered sodium covered with 100 g. of toluene. Water was then added gradually. After a time, the whole became practically solid. Water was added until the solid redissolved, the ether–toluene layer then being removed, washed, dried and distilled, until the residue was at 150°. On cooling, it solidified, and after several crystallisations from alcohol and benzene melted at 121° (Found : *M*, cryoscopic in benzene, 232, 251. Calc. : *M*, 242).

Preparation of 2 : 4-*Dichlorophenylmethylcarbinol*.—2 : 4-Dichloroiodobenzene (68 g.; b. p. 255—257° [Ullmann, *Annalen*, 1904, **332**, 38, gives 262—263°]; obtained from 2 : 4-dichloroaniline), when dissolved in ether, combined readily with magnesium (6 g.) in presence of a little iodine. The solution was treated gradually with an ethereal solution of 16 g. of acetaldehyde. The mixture was left over-night and then treated with ice and dilute hydrochloric acid, and the ethereal solution was washed with aqueous sodium hydrogen carbonate, with aqueous sodium hydrogen sulphite, and with sodium hydrogen carbonate. It was then dried; the carbinol, by distillation under diminished pressure, was obtained as a pale yellow liquid, b. p. 145°/20 mm., or 154—155°/29 mm. (yield 67%) (Found : Cl, 38·5. $C_8H_8OCl_2$ requires Cl, 37·2%).

α-2 : 4-*Dichlorophenylethyl Bromide.*—Hydrogen bromide was passed into the carbinol for 4 hours, and the product was treated with dilute sodium carbonate solution, then with water, and finally distilled under diminished pressure. The bromide was obtained as a mobile, colourless liquid, b. p. 154°/37 mm., with hardly any odour or lachrymatory properties (Found : AgCl + AgBr, 0·3350. $C_8H_7Cl_2Br$ requires AgCl + AgBr, 0·3418).

Action of Sodium Sulphite on α-2 : 4-*Dichlorophenylethyl Bromide.*—The bromide (10 g.) was heated with a solution of sodium sulphite for 30 hours; 7 g. of the carbinol (calc., 7·5 g.) were then obtained, b. p. 154°/29 mm.

Preparation of 3 : 5-*Dichlorobromobenzene.*—When 2 : 4-dichloroacetanilide was brominated in glacial acetic acid solution, it was converted into slightly more than its own weight of 2 : 4-dichloro-6-bromoaniline, m. p. 81°, the acetyl group being eliminated in the process. Treatment of the base with sodium nitrite, alcohol, benzene and concentrated sulphuric acid in the usual manner gave a 38% yield of 3 : 5-dichlorobromobenzene. This substance, after several crystallisations from alcohol, melted at 74°, although Hartley (J., 1901, **79**, 1293) gives 77·5°, and Hantzsch (*Ber.*, 1897, **30**, 2351) gives 82—84°. It reacted with magnesium which had previously been activated with methyl iodide.

Sodium α-*Phenylpropanesulphonate.*—α-Phenylpropyl bromide (15 g.) was heated in the usual manner with sodium sulphite solution. Propenylbenzene was the main product, only 2 g. of impure sulphonate being obtained. Ammonium sulphite gave similar results.

The bromide (90 g.) was shaken vigorously for 120 hours with a solution of 120 g. of sodium sulphite heptahydrate in 240 c.c. of water. After several hours' shaking, crystals began to separate, and when no further change was apparent the solid was collected and the oily layer separated (35 g.). The solid was freed from bromide and sulphite by systematic crystallisation from water, and ultimately gave 30 g. (30% yield) of pure sodium α-phenylpropanesulphonate, very soluble in water, but almost insoluble in alcohol (Found : Na, 10·4. $C_9H_{11}O_3SNa$ requires Na, 10·4%).

In a second experiment, 60 g. of bromide gave 21 g. (32% yield) of sulphonate and 23 g. of oil. From the density of the latter it was estimated that it contained about 6 g. of unchanged bromide and 17 g. of propenylbenzene. This indicates that, in the above experiment, about 50% of the bromide underwent loss of hydrogen bromide.

α-*Phenylpropanesulphonic Acid.*—Addition of barium chloride solution to one of the sodium sulphonate caused the precipitation of a mixture of salts which could not be separated. The free acid was therefore prepared as follows : A hot concentrated solution of the sodium salt was treated with an excess of concentrated hydrochloric acid, and the sodium chloride removed. The liquid was evaporated, and the whole process repeated four times; on final evaporation, the sulphonic acid was obtained as a deliquescent, gummy solid which partly crystallised on desiccation for some weeks, but could not be recrystallised from a solvent.

α-Phenylpropanesulphonyl chloride was obtained from the sodium salt and phosphorus pentachloride as a colourless, heavy liquid, b. p. 175°/20 mm. (Found : Cl, 15·9. $C_9H_{11}O_2ClS$ requires Cl, 16·3%). The corresponding *amide* and *anilide* could not be caused to crystallise.

Resolution of dl-*α-Phenylpropanesulphonic Acid.*—Finely powdered strychnine (4·15 g.) was allowed to dissolve in a hot aqueous solution of 5 g. (2 equivs.) of the sulphonic acid. On cooling, the strychnine salt separated, and this, after being recrystallised three times from water, weighed 3 g. (0·1644 g. was equivalent to 3·00 c.c. of 0·1*N*-sodium hydroxide. $C_{21}H_{22}O_2N_2,C_9H_{12}O_3S$ requires 3·10 c.c.). The salt had $[\alpha]_D^{26^\circ}$ $-$ 23·7° in aqueous alcohol (water, 1 vol.; alcohol, 2 vols.), and was unaffected by further recrystallisation.

To the heated mother-liquor remaining after removal of the strychnine salt, 0·5 equivalent (3·7 g.) of cinchonine was added. When further dissolution ceased, a little cinchonine was filtered off, and the filtrate was cooled. The precipitated solid was recrystallised thrice from water; 2·6 g. of *cinchonine* salt were then obtained (0·1184 g. was equivalent to 2·20 c.c. of 0·1*N*-sodium hydroxide. $C_{20}H_{21}O_4N,C_9H_{12}O_3S$ requires 2·40 c.c.). The salt had $[\alpha]_D^{25^\circ}$ + 104·9° in aqueous alcohol, and was not affected by further crystallisation.

The alkaloidal salts were converted into the *sodium* salts by treatment with the calculated quantity of sodium hydrogen carbonate in aqueous solution. That from the strychnine salt had $[\alpha]_D^{25^\circ}$ + 5·2° ± 0·1° (Found : Na, 10·3%). That from the cinchonine salt had $[\alpha]_D^{25^\circ}$ $-$ 5·2° ± 0·2° (Found : Na, 10·4%).

α-Phenylbutyl bromide was obtained by passing hydrogen bromide through phenyl-*n*-propylcarbinol, prepared from benzaldehyde and magnesium *n*-propyl bromide (Grignard, *Ann. Chim. Phys.*, 1901, **24**, 466; Klages, *Ber.*, 1904, **37**, 2312). The bromide was thus obtained as a colourless, lachrymatory liquid, *d* about 1·24, b. p. 116°/28 mm., or 126°/47 mm. (Found : Br, 38·0. $C_{10}H_{13}Br$ requires Br, 37·6%).

Sodium α-Phenylbutanesulphonate.—The bromide (20 g.) was shaken with aqueous sodium sulphite at the ordinary temperature for 135 hours. From the density of the residual oily layer, it was estimated that 60% of the bromide had been converted into α-phenyl-Δ^{α}-butene, 30% had remained unchanged, and 10% had reacted in the desired manner. Only 1·2 g. of sodium salt (yield about 6%) were obtained (Found : Na, 9·6. $C_{10}H_{13}O_3SNa$ requires Na, 9·7%).

Action of Sulphur Dioxide on Magnesium α-Phenylbutyl Bromide.—The Grignard reagent obtained from α-phenylbutyl bromide (5·5 g.) was cooled in ice and salt, and saturated with sulphur dioxide. A white solid separated, but dissolved before the calculated quantity of sulphur dioxide had been used. The resulting yellow solution, when decomposed in the usual manner, gave an ethereal solution which, on evaporation, gave white crystals. These, when recrystallised from alcohol, melted at 96°, and consisted of the *sulphide*, $(PhPr^{\alpha}CH)_2S$ (Found : S, 10·5. $C_{20}H_{26}S$ requires S, 10·7%).

Sodium α-Methylpropanesulphonate.—α-Bromobutane (115 g.) was heated gently under reflux for 100 hours with aqueous sodium sulphite; it had then all disappeared. The solution obtained was evaporated in stages, the crude sulphonate being obtained as the most soluble fraction. Recrystallisation from water gave 65 g. (50% yield) of the *sodium* salt (Found : Na, 14·5. $C_4H_9O_3SNa$ requires Na, 14·4%). The salt forms colourless plates which are very soluble in cold water.

α-Methylpropanesulphonic acid was prepared by repeated evaporation of the sodium salt with hydrochloric acid. It forms colourless, hygroscopic, hexagonal plates. Half an equivalent of strychnine was dissolved in an aqueous-alcoholic solution of the acid. A *strychnine* salt separated on cooling, and this, after being recrystallised thrice from aqueous alcohol, formed white needles sparingly soluble in water, more soluble in aqueous alcohol (Found, by titration against 0·1*N*-NaOH : strychnine, 70·0. $C_{21}H_{22}O_2N_2,C_3H_{10}O_3S$ requires strychnine, 70·7%). A solution of 0·485 g. of the salt in 50 c.c. of 50% aqueous alcohol had $\alpha_D^{20°}$ — 0·57° in a 2-dcm. tube, whence $[\alpha]_D^{20°}$ — 29·3°.

The corresponding sodium salt was only obtained in a very small quantity, and a qualitative examination showed it to be dextrorotatory. The *cinchonine* salt of the acid could not be obtained crystalline.

Sodium sec.*-butyl sulphate* was obtained from methylethylcarbinol *via* the calcium salt, and crystallised from alcohol (Found : Na, 13·0. $C_4H_9O_4SNa$ requires Na, 13·1%).

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