Synthesis of Methanesulphonyl- and of Certain Arylsulphonyl-Esters of Hydroxyalkyl-substituted Primary Aromatic Amines

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Methanesulphonyl, *p*-toluenesulphonyl, and similar esters can be obtained in good yields under carefully controlled conditions from aromatic nitro-compounds bearing hydroxyalkyl substituents joined to the ring, either directly, or through various linking atoms or groups. Reduction of the products to primary amines, without loss of the labile ester groups, is frequently accompanied by serious practical difficulties, and in some cases, it was not possible to obtain the amines in a pure state.

DURING a comparative investigation of dyes containing various fibre-reactive systems,[1] we wished to prepare primary aromatic amines containing hydroxyalkyl substituents joined to the aromatic ring either by a carbon-carbon bond, or through various links such as O, S, SO_2, CH_2S, CH_2O, CH_2SO_2, CH_2NH, CONH, or CH_2NMe, and certain of their esters, especially the methanesulphonyl and *p*-toluenesulphonyl derivatives. Labile amino-esters of these types had not been described previously, and apart from their possible technological application as diazo components for azo dyes, it was of interest to ascertain the limitations of general synthetic methods in relation to this particular problem and to attempt the preparation of sulphonated derivatives of a similar type.

Several aromatic hydroxyalkyl nitro-compounds required as starting materials had been described in the literature,[2-10] and no serious difficulties were encountered in converting most of them into their methanesulphonyl derivatives in good yields, provided that conditions were controlled carefully. The ease with which such esters were formed varied considerably from one compound to another, and also with the medium used; in a few instances, the reaction between the hydroxyalkyl compound and methanesulphonyl chloride was still incomplete after several days. Pyridine was the most suitable medium, but limitations of solubility, especially of sulphonated compounds, led to other solvents being tried. Moderate yields of esters were sometimes obtained in triethylamine, but mixtures of dimethylformamide and *NN*-diethylaniline, in which sulphonated compounds were more soluble, gave no useful results.

As no suitable conditions were discovered for converting sulphonated hydroxyalkyl nitro-compounds into their methanesulphonyl esters, attempts were made to prepare the latter by direct sulphonation and nitration of suitable unsulphonated methanesulphonyl esters. All such efforts were unsuccessful, however, because no conditions were found for effecting sulphonation and nitration which were sufficiently mild to obviate hydrolysis of the methanesulphonyl group.

Pyridine was also the preferred medium for preparing the *p*-toluenesulphonyl and *m*-methylsulphonyl benzenesulphonyl esters listed in Table 1, but in these cases, conditions were rather less critical, and the products were easier to isolate than the corresponding methanesulphonyl derivatives.

The progress of these reactions was conveniently followed by i.r. spectroscopy, unesterified aromatic hydroxyalkyl nitro-compounds showing strong absorption in the region of 3330 $cm.^{-1}$ which disappeared completely in the pure methanesulphonyl and *p*-toluenesulphonyl esters. Methanesulphonyl esters showed fresh absorption bands around 1180, 970, and 800 $cm.^{-1}$, and *p*-toluenesulphonyl esters around 1180, 970, 770, and 665 $cm.^{-1}$.

The major difficulty in preparing the required amino-esters lay in the final stage of reducing the corresponding nitro-compounds. Owing to the extreme lability of the methanesulphonyl and *p*-toluenesulphonyl groups, only mild conditions of reduction were permissible, and it was essential to avoid the use of reagents or solvents capable of decomposing the esters. Hydrogenation in

[1] For Reviews see: H. Zollinger, *Angew. Chem.*, 1961, **73**, 125; O. A. Stamm, *J. Soc. Dyers and Colourists*, 1964, **80**, 416.
[2] E. Ferber, *Ber.*, 1929, **62**, 189.
[3] D.R.P. 887,505/1953.
[4] A. H. Ford-Moore, R. A. Peters, and R. W. Wakelin, *J. Chem. Soc.*, 1949, 1754.
[5] B.P. 735,511/1955.
[6] M. Izumi, I. Aiko, M. Yokoo, and H. Kimoto, *J Pharm. Soc. Japan*, 1952, **72**, 21 (*Chem. Abs.*, 1952, **46**, 11183b).
[7] S. B. Binkley and C. S. Hamilton, *J. Amer. Chem. Soc.*, 1937, **59**, 1716.
[8] U.S.P. 3,006,963/1961.
[9] H. Brintzinger and H. Koddebusch, *Chem. Ber.*, 1949, **82**, 201.
[10] R. Hill and G. Powell, *J. Amer. Chem. Soc.*, 1945, **67**, 1462.

the presence of Raney nickel under mild conditions proved to be the only useful method, but even this was of rather restricted application because of a marked tendency for some of the compounds to poison the catalyst, and because of limitations in the choice of suitable solvents. Isolation of the amino-esters also presented difficulties on account of their ease of decomposition, even in the form of hydrochlorides, and whilst those included in Table 2 were obtained pure, several others gave high chlorine and low sulphur analyses, suggesting that even in an ethereal medium, hydrogen chloride causes some decomposition of the ester with formation of the corresponding chloro-compound.

EXPERIMENTAL

Many of the hydroxyalkyl nitro-compounds listed as starting materials in Table 1 were prepared by literature methods.[2-10] The non-nitrated derivatives shown were used either as spectroscopic reference compounds or in sulphonation–nitration experiments.

3-(p-*Nitrophenylthio*)*propane*-1,2-*diol*, previously described [6] as an oil, was prepared by boiling *p*-nitrothiophenol (62 g.) with 3-chloropropane-1,2-diol (48·4 g.) in ethanol (600 ml.) containing dissolved sodium (10·4 g.) for 3 hr., filtering and evaporating the solution to a syrup which slowly crystallised. Recrystallised from aqueous ethanol, the *compound* had m.p. 92—93°; on reduction, it gave the corresponding *amine* (see Table 2).

m-*Nitrotoluene*-ω-*thiol* [11] and 2-*Methyl*-5-*nitrotoluene*-ω-*thiol* (prepared similarly from 2-chloromethyl-4-nitrotoluene [12]) gave 2-(*m*-nitrobenzylthio)ethanol and 2-(2-methyl-5-nitrobenzylthio)ethanol [8] (m.p. 56—57°) respectively when condensed with 2-chloro-ethanol in aqueous sodium hydroxide. Oxidation of these compounds with hydrogen peroxide in acetic acid [5] gave 2-*m*-nitrobenzylsulphonylethanol and 2-(2-methyl-5-nitrobenzylsulphonyl)-ethanol respectively. The latter, after recrystallisation from acetic acid, had m.p. 114°. On reduction, both compounds gave the corresponding *amines* (see Table 1).

N-β-*Hydroxyethyl*-2-*methyl*-5-*nitrobenzylamine*.—2-Amino-ethanol (92 g.) in ethanol (200 ml.) was added to a stirred solution of 2-chloromethyl-4-nitrotoluene [12] (93 g.) in ethanol (40 ml.) at 15—20°, and the mixture was boiled under reflux for 2 hr. The solvent was distilled and the residue (85—90 g.) was ground with water. Recrystallised from water, the *compound* had m.p. 93° (Found: C, 57·1; H, 6·65; N, 13·6. $C_{10}H_{14}N_2O_3$ requires C, 57·15; H, 6·65; N, 13·35%).

2-(2-*Methyl*-5-*nitrobenzyloxy*)*ethanol*.—Sodium (6·9 g.) in ethylene glycol (300 ml.) was added to a stirred solution of 2-chloromethyl-4-nitrotoluene [12] (55·8 g.) in ethylene glycol (300 ml.) at 45—50°. After 1 hr. at 70—75°, the solution was concentrated under reduced pressure to one-half of its original volume and diluted with water (200 ml.). The oily product (56 g.) which was extracted with ether and recovered from the dried ($MgSO_4$) extract, became crystalline when rubbed with light petroleum (b.p. 40—60°) at −70°. Recrystallised from aqueous ethanol, the *compound* had m.p. 51—52° (Found: C, 56·8; H, 6·2; N, 6·6. $C_{10}H_{13}NO_4$ requires C, 56·85; H, 6·15; N, 6·65%).

N-(2,3-*Dihydroxypropyl*)-m-*nitrobenzenesulphonamide*.—*m*-Nitrobenzenesulphonyl chloride (66·5 g.) was added portionwise to stirred 2,3-dihydroxypropylamine (27·3 g.) in water (210 ml.) and ethanol (30 ml.) at 40—50°, whilst maintaining a pH of 9—10 by simultaneous addition of sodium hydroxide (12 g.) in water (75 ml.). Finally, 10N-sodium hydroxide (5 ml.) was added and the mixture was stirred at 45 ± 3° for 3 hr. The solution was acidified with hydrochloric acid, evaporated to dryness and the residue was extracted with boiling ethanol (250 ml.). The filtered extract was evaporated and the solid residue (92 g.) was ground with ether. Recrystallised from water, the *compound* had m.p. 60° (Found: C, 39·0; H, 4·8; N, 9·9; S, 11·6. $C_9H_{12}N_2O_6S$ requires C, 39·15; H, 4·35; N, 10·1; S, 11·6%).

N-β-*Hydroxyethyl*-N-*methyl*-p-*nitrobenzylamine*.—*p*-Nitrobenzyl bromide (27 g.) was boiled under reflux for 17 hr. with 2-methylaminoethanol (9·4 g.) and sodium carbonate (13·3 g.; anhydrous) in acetone (250 ml.). After filtration, the solution was evaporated and the residual oil was stirred with hydrochloric acid (25 ml.; *d*. 1·18) and water (150 ml.). The resulting solution was filtered and basified with potassium carbonate. The oil was extracted with ether and the dried ($MgSO_4$) extract was distilled, affording the nitro-compound as an oil.

Hydrogenation of this nitro-compound in methanolic solution in the presence of Raney nickel and subsequent fractional distillation gave two major products. The first (b.p. 40°/0·1 mm.) was identified as *p*-toluidine, whilst the second consisted of the required amine (see Table 2).

2-p-*Sulphophenoxyethanol* was obtained as the *sodium salt hemihydrate* by condensation of phenol-*p*-sulphonic acid with 2-chloro-ethanol in hot aqueous sodium hydroxide (Found: C, 38·8; H, 4·2; Na, 9·55; S, 12·9. $C_8H_9NaO_5S.\frac{1}{2}H_2O$ requires C, 38·55; H, 4·0; Na, 9·25; S, 12·85%).

Methanesulphonyl Derivatives of Hydroxyalkyl Nitro-compounds.—The methanesulphonyl derivatives listed in Table 1 (except the di-methanesulphonyl derivative of *p*-nitrophenylsulphonylpropane-2,3-diol) were prepared by stirring solutions of the hydroxyalkyl nitro-compounds in pyridine (*ca.* 750 ml. per g. mol.; dried by distillation over solid potassium hydroxide) with methanesulphonyl chloride (1·1—1·25 mol. per mol. of hydroxy compound; twice this quantity was used with compounds capable of forming di-methanesulphonyl derivatives) at 0—5°. Progress of the reaction was followed by isolating portions of the product at intervals and observing the gradual disappearance of absorption in the region of 3330 $cm.^{-1}$ of the i.r. spectrum. For the compounds included in Table 1, the reaction was virtually complete in 45—90 minutes.

To isolate the products, the pyridine solution was stirred with ice-water until any excess of methanesulphonyl chloride had been hydrolysed. Most of the derivatives then solidified, and were collected and dried *in vacuo* at room temperature. Those which did not solidify were isolated by extraction with an immiscible solvent, *e.g.*, chloroform. Yields of methanesulphonyl derivatives obtained by the foregoing method were usually high (>80%) and the crude products were only slightly impure. Many esters additional to those included in Table 1 were made for technological purposes, but were characterised spectroscopically and not further purified and analysed before reduction.

In a few instances, the desired products were not obtained. For example, 2,3-dihydroxypropyl-3-nitrobenzene-

[11] T. S. Price and D. F. Twiss, *J. Chem. Soc.*, 1909, **95**, 1726.
[12] V. M. Berezovskii, V. A. Kurdyukova, and N. A. Preobrazhenskii, *Zhur. obshchei Khim.*, 1951, **21**, 1163 (*Chem. Abs.*, 1952, **46**, 5006d).

sulphonamide (27·6 g.) in pyridine (75 ml.) treated for 1½ hr. with methanesulphonyl chloride (16·4 ml.) gave only a treacle-like product showing increased absorption near 1180 cm.$^{-1}$ and decreased absorption near 3330 cm.$^{-1}$, indicating that the reaction was incomplete. Prolongation of the reaction time to 45 hr. had little effect upon the spectrum of the product.

β-Hydroxyethyl-*N*-methyl-*p*-nitrobenzylamine gave a reflux for ½ hr. with hydrogen peroxide (8 ml.; 30%) and acetic acid (40 ml.). The product separated during subsequent distillation of the solvent, and was purified by recrystallisation (see Table 1).

p-*Toluenesulphonyl-* and m-*methylsulphonyl benzenesulphonyl derivatives* were prepared in a similar manner to the methanesulphonyl derivatives, using *p*-toluenesulphonyl chloride or *m*-methylsulphonyl benzenesulphonyl-chloride [13]

TABLE 1

Esters of hydroxyalkyl aromatic compounds and nitro-derivatives

Hydroxyalkyl compound	Derivative	M.p.	Recryst. from	Found (%) C	H	N	S	Formula	Required (%) C	H	N	S
$PhCH_2{\cdot}CH_2{\cdot}OH$	Ms	†		53·6	5·8		16·2	$C_9H_{12}O_3S$	54·0	6·0		16·0
p-$O_2N{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ [2]	Ms	66—67°	E	43·8	4·3	5·9	12·8	$C_9H_{11}NO_5S$	44·1	4·5	5·7	13·05
	Ts	130—131	E			4·4	9·9	$C_{15}H_{15}NO_5S$			4·35	9·95
	Mb	113	E	46·6	4·1	3·9	16·3	$C_{15}H_{15}NO_5S_2$	46·75	3·9	3·65	16·6
p-$O_2N{\cdot}C_6H_4{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ [3]	Ms	57—58	E	39·5	4·2	5·05	22·6	$C_9H_{11}NO_5S_2$	39·0	3·95	5·05	23·1
	Ts	96—97	E	51·2	4·4	4·0	18·1	$C_{15}H_{15}NO_5S_2$	51·0	4·25	3·95	18·15
$PhSO_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ [4]	Ac	‡		53·1	5·1		14·2	$C_{10}H_{12}O_4S$	52·65	5·25		14·05
	Ms	76—77	M	41·4	4·7		24·1	$C_9H_{12}O_5S_2$	40·9	4·55		24·25
	Sp		W	31·6	3·4		21·4	$C_8H_9KO_6S_2$ *	31·55	2·95		21·05
m-$O_2N{\cdot}C_6H_4{\cdot}SO_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ [5]	Ms	96—97	B	35·3	3·6	4·2	20·7	$C_9H_{11}NO_7S_2$	34·95	3·55	4·55	20·7
	Ts	123—124	E	47·2	3·8	3·8	16·2	$C_{15}H_{15}NO_7S_2$	46·75	3·9	3·65	16·6
p-$O_2N{\cdot}C_6H_4{\cdot}SO_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ [3]	Ms	151—152	A	35·4	3·8	4·4	20·4	$C_9H_{11}NO_7S_2$	34·95	3·55	4·55	20·7
p-$O_2N{\cdot}C_6H_4{\cdot}S{\cdot}CH_2{\cdot}CH(OH)CH_2{\cdot}OH$ [6]	Di-Ms	106	C	34·8	4·4	3·4	24·8	$C_{11}H_{15}NO_8S_3$	34·3	3·9	3·65	24·95
p-$O_2N{\cdot}C_6H_4{\cdot}SO_2{\cdot}CH_2{\cdot}CH(OH)CH_2{\cdot}OH$ [6]	Di-Ms	130—131	X	32·1	3·9	3·2	23·5	$C_{11}H_{15}NO_{10}S_3$	31·65	3·6	3·35	23·0
m-$O_2N{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ [7]	Ms	71—72	M	41·4	4·2	5·5	12·7	$C_9H_{11}NO_6S$	41·4	4·2	5·35	12·25
2-Me-5-$O_2N{\cdot}C_6H_3{\cdot}CH_2{\cdot}SO_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ [8]	Sp		W	31·9	3·6	3·9	16·9	$C_{10}H_{12}KNO_8S_2$	31·75	3·2	3·7	16·9
2-Me-5-$O_2N{\cdot}C_6H_3{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	Di-Ms	154	Y	39·6	4·9	7·8	18·0	$C_{12}H_{18}N_2O_7S_2$	39·35	4·9	7·65	17·5
2-Me-5-$O_2N{\cdot}C_6H_3{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	Ms	55—56	Z			4·85	10·6	$C_{11}H_{15}NO_6S$			4·85	11·1
m-$O_2N{\cdot}C_6H_4{\cdot}CO(NH)CH_2{\cdot}CH_2{\cdot}OH$ [9]	Ms	91	M	41·9	4·2	9·7	10·6	$C_{10}H_{12}N_2O_6S$	41·65	4·15	9·7	11·1
p-$O_2N{\cdot}C_6H_4{\cdot}CO(NH)CH_2{\cdot}CH_2{\cdot}OH$ [10]	Ms	100	M	41·4	4·2	9·4	11·3	$C_{10}H_{12}N_2O_6S$	41·65	4·15	9·7	11·1

Ms = Methanesulphonyl derivative; Di-Ms = dimethanesulphonyl derivative; Ts = *p*-toluenesulphonyl derivative; Ac = acetate; Sp = sulphate; Mb = *m*-methylsulphonyl benzenesulphonyl derivative.

A = Acetone; B = benzene; C = β-ethoxyethanol; E = ethanol; M = methanol; W = water; X = ethylacetate (10 pt.) + ethanol (1 pt.); Y = acetic acid; Z = aqueous ethanol.

* Found: K, 13·1; required, 12·85%. † B.p. 118—120°/0·1 mm. ‡ B.p. 142°/0·15 mm.

TABLE 2

Primary aromatic hydroxyalkyl amines and esters

Amine	Derivative	M.p.	Recryst. from	Found (%) C	H	Cl	N	S	Formula *	Required (%) C	H	Cl	N	S
p-$H_2N{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	Ms	136° (decomp.)	P	42·5	5·8	14·6	5·7	12·2	$C_9H_{14}ClNO_3S$	42·95	5·55	14·1	5·55	12·7
	Ts	122	P			11·4		9·25	$C_{15}H_{16}ClNO_3S$			10·85		9·75
	Mb	123—125 (decomp.)	P	46·5	4·8	8·5	3·6	16·0	$C_{15}H_{16}ClNO_3S_2$	46·0	4·6	9·05	3·6	16·35
m-$H_2N{\cdot}C_6H_4SO_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	Ms	(decomp.)	P					20·0	$C_9H_{14}ClNO_5S_2$					20·3
	Ts	142—144 (decomp.)	P			8·7		15·8	$C_{15}H_{16}ClNO_5S_2$			9·05		16·35
p-$H_2N{\cdot}C_6H_4{\cdot}SO_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	Ms	170—171	P	33·9	4·4	11·8	4·4	19·8	$C_9H_{14}ClNO_5S_2$	34·25	4·45	11·25	4·45	20·3
	Ms †	135	W	39·0	4·9		5·0	22·9	$C_9H_{13}NO_5S_2$	38·7	4·65		5·0	22·95
p-$H_2N{\cdot}C_6H_4{\cdot}S{\cdot}CH_2{\cdot}CH(OH)CH_2{\cdot}OH$		174	E	45·8	5·9	15·0	5·6	13·3	$C_9H_{14}ClNO_4S$	45·85	5·95	15·1	5·95	13·6
p-$H_2N{\cdot}C_6H_4{\cdot}SO_2{\cdot}CH_2{\cdot}CH(OH)CH_2{\cdot}OH$			P	40·1	5·5	13·8	5·5	11·9	$C_9H_{14}ClNO_6S$	40·35	5·25	13·3	5·25	11·95
	Di-Ms	60 (decomp.)	P			7·8		22·1	$C_{11}H_{18}ClNO_8S_3$			8·4		22·7
m-$H_2N{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	Ms	138—139 (decomp.)	P				5·5	11·45	$C_9H_{14}ClNO_5S$				5·25	11·95
m-$H_2N{\cdot}C_6H_4{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}OH$		129	P	48·8	6·6	16·7	6·3	14·1	$C_9H_{14}ClNOS$	49·2	6·4	16·15	6·4	14·6
2-Me-5-$H_2N{\cdot}C_6H_3{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}OH$			P	51·3	6·8		5·9		$C_{10}H_{16}ClNOS$	51·4	6·85		6·0	
m-$H_2N{\cdot}C_6H_4{\cdot}CH_2{\cdot}SO_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$		164 (decomp.)	E	42·8	5·6		5·5		$C_9H_{14}ClNO_5S$	42·95	5·55		5·55	
2-Me-5-$H_2N{\cdot}C_6H_3{\cdot}CH_2{\cdot}SO_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$		120—121	E	52·3	6·4		5·8	13·6	$C_{10}H_{15}NO_3S$	52·4	6·55		6·1	13·95
	Sp		Z				3·7	18·7	$C_{10}H_{14}KNO_6S_2$				4·0	18·45
p-$H_2N{\cdot}C_6H_4{\cdot}CH_2{\cdot}NMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$		‡		66·2	9·2		15·0		$C_{10}H_{16}N_2O$	66·65	8·9		15·5	

Ms = Methanesulphonyl derivative; Di-Ms = di-methanesulphonyl derivative; Ts = *p*-toluenesulphonyl derivative; Sp = sulphate; Mb = *m*-methylsulphonyl benzenesulphonyl derivative.

E = Ethanol; P = reprecipitated from cold ethanol with ethereal hydrogen chloride; W = water; Z = aqueous ethanol.

* Where chlorine is present, the compound analysed was the amine hydrochloride. † Free base, obtained by crystallisation of the hydrochloride from water. ‡ B.p. 130°/0·1 mm.

product of m.p. 79—80° which analysed approximately for a 1 : 1 complex of the methanesulphonyl derivative and pyridine.

All attempts to convert sulphonated aromatic hydroxyalkyl compounds (*e.g.*, 2-*p*-sulphophenoxyethanol) into their methanesulphonyl esters, using pyridine, triethylamine, water, or mixtures of *NN*-diethylaniline and dimethylformamide as media, were unsuccessful.

Methanesulphonyl esters of hydroxyalkylsulphones were sometimes conveniently obtained by oxidation of the corresponding sulphides. The *di-methanesulphonyl* derivative of *p*-nitrophenylsulphonylpropane-2,3-diol, for example, was prepared in good yield by boiling the di-methanesulphonyl derivative of the corresponding sulphide (15·4 g.) under in place of methanesulphonyl chloride. Conditions were generally less critical than with the latter.

Sulphate esters were prepared by treating hydroxyalkyl nitro-compounds with sulphuric acid (*d* 1·84) at 25—30° for 2—3 hr., diluting the solution with ice and isolating the product by addition of potassium chloride.

Reduction of Nitro-compounds to Amines.—Unesterified hydroxyalkyl nitro-compounds were reduced with powdered iron (300 g. per g. mol. of nitro-compound) in boiling ethanol containing some concentrated aqueous hydrochloric acid (2 ml. per 100 ml. of ethanol). The mixture was subsequently basified, and the ethanolic extract was evaporated. The resulting amine was either purified by

[13] R. F. Twist and S. Smiles, *J. Chem. Soc.*, 1925, **127**, 1251.

solvent crystallisation, or converted into its hydrochloride by treatment with ethereal hydrogen chloride.

Methanesulphonyl and other esters of hydroxyalkyl nitro-compounds were reduced by shaking their solutions with hydrogen at *ca.* 1 atm. pressure and room temperature, in the presence of Raney nickel until no further absorption occurred. Except for sulphate esters, which were reduced in aqueous medium, choice of solvents was practically limited to ethyl acetate, dioxan, or dimethylformamide. In most instances, a greater or lesser degree of catalyst poisoning was evident, and fresh catalyst was added from time to time. Certain of the nitro-compounds appeared to be so toxic towards the catalyst that the corresponding amines were not obtained.

The amines were isolated by filtration from catalyst and evaporation of the solutions under reduced pressure at temperatures below 40°. Treatment of the residue with ether, saturated with hydrogen chloride, gave the amine hydrochlorides. The latter usually decomposed on attemped purification by crystallisation from hot solvents, and were purified by fractional precipitation from cold ethanolic solution with ethereal hydrogen chloride.

Attempted Sulphonation and Nitration of Methanesulphonyl Esters.—Under all conditions examined, direct sulphonation and nitration of the methanesulphonates of 2-phenylethanol, 2-phenoxyethanol, and similar compounds, gave products in which the ester group had been wholly or partly hydrolysed.

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