756. *Alkylation of the Aromatic Nucleus. Part XIII.*[1] p-*Xylene*

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Alkylation of *p*-xylene by the thermal decomposition of sulphonic esters of the three n-pentanols and n-hexanols has been studied. The distribution of isomers in each of the products is compared with that brought about by alkylation of the alcohol with boron trifluoride, sulphuric acid, or phosphoric acid as condensing agent.

Pentan-2-ol and pentan-3-ol give the same ratio of isomers whatever method of alkylation is used. Similarly, hexan-2-ol and hexan-3-ol give the same products with the same isomer ratio.

With primary alcohols, a notable proportion of the alkyl group retains its configuration when alkylation is brought about by boron trifluoride or by decomposition of the sulphonic ester.

The significance of these results is discussed.

IN earlier Papers of this Series, evidence was adduced to support the view that alkylation of aromatic systems by thermal decomposition of alkyl esters of sulphonic acids in an excess of aromatic compound is an electrophilic substitution involving a carbonium ion.[2,3] There was also evidence of bimolecular displacement as an alternative in some alkylations. Thus, phenethyl toluene-*p*-sulphonate reacts with mesitylene or phenol to give products in which the phenethyl group retains its configuration.[3] In mesitylene, also, decomposition of the methanesulphonic ester of butan-1-ol give a high proportion of n-butylmesitylene.[2]

TABLE 1

Percentage distribution of isomers in the products of alkylation of *p*-xylene

Alcohol	Position of the *p*-xylyl group	Method *					
		(*a*)	(*b*) (i)	(*b*) (ii)	(*b*) (iii)	(*c*)	(*d*)
Hexan-1-ol ...	1	18	5	3	8	1	1
	2	57	66	58	59	57	59
	3	25	29	39	33	42	40
Hexan-2-ol ...	2	58	58			54	55
	3	42	42			46	45
Hexan-3-ol ...	2	58	57			47	49
	3	42	43			53	51
Pentan-1-ol ...	1	21	10			3	1
	2	58	54			57	62
	3	21	36			40	37
Pentan-2-ol ...	2	65	66			59	61
	3	35	34			41	39
Pentan-3-ol ...	2	64	61			60	55
	3	36	39			40	45
Butan-1-ol ...	1	16	14	8	13	2	1
	2	84	86	92	87	98	99
Propan-1-ol ...	1	17	16	9	14	3	2
	2	83	84	91	86	97	98

* See Experimental section.

In this Paper, the alkylation of *p*-xylene by sulphonic esters of the three n-pentanols is compared with alkylation brought about by the same alcohols with boron trifluoride, sulphuric acid, or phosphoric acid as the condensing agent. Alkylation by the three n-hexanols under the same conditions is also studied. The results are summarised in Table 1.

A striking feature is that pentan-2-ol and pentan-3-ol both gives a mixture of 2- and

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[1] Part XII, K. M. Davies and W. J. Hickinbottom, *J.*, 1965, 2295.

[2] M. S. Grant and W. J. Hickinbottom, *J.*, 1957, 2520.

[3] J. Blackwell and W. J. Hickinbottom, *J.*, 1963, 518.

3-*p*-xylylpentanes in which the ratio of the two isomers is the same, whichever method of alkylation is used. Hexan-2-ol and hexan-3-ol also give products having approximately the same composition whichever method is used.

Pentylation of benzene by the three n-pentanols and boron trifluoride has been studied by Streitwieser *et al.*[4] They found that each of the pentanols gave a mixture of 2- and 3-phenylpentanes having the same isomer ratio. The product also contained significant amounts of t-pentylbenzene and some polymerised olefins, evidence of secondary reactions brought about by too-drastic conditions [5] or by the low reactivity of benzene towards the alkylating complex. They also found no 1-phenylpentane in the product from pentan-1-ol.

In this Paper, the product from the sulphonic ester of pentan-1-ol contains about 20% of 1-*p*-xylylpentane: a lower but quite unmistakable amount is also formed by alkylation with the primary alcohol and boron trifluoride. Other primary alcohols, propan-1-ol, butan-1-ol, and hexan-1-ol, also give notable amounts of the 1-arylalkane under similar conditions.

In previous Papers, evidence has been presented to show that alkylations involving a sulphonic ester, or an alcohol and a Lewis acid, are best represented as an electrophilic substitution by a carbonium ion. In alkylations by primary alcohols, isomerisation of the primary alkyl group, in part, to secondary suggests that the reaction course is similar to that of the secondary alcohols. That some of the primary alkyl group survives unchanged suggests that the primary alkyl carbonium ion is sufficiently active to react before it isomerises, or that there is a concurrent bimolecular reaction when boron trifluoride is used for alkylation, or when the reaction is brought about by use of the sulphonic ester.

A decision on this is possible from observations of the behaviour of sulphonic esters of neopentyl alcohol, which are relatively stable: the toluene-*p*-sulphonic ester is unchanged after being heated in boiling *p*-xylene for 18 hr. In boiling mesitylene, decomposition occurs to give a high-boiling polymer. With the 2,5-dibromobenzenesulphonate in phenol at 100—110° the product consists of *o*- and *p*-t-pentylphenols, with no detectable amount of neopentylphenol. It is concluded that, in phenol, the neopentyl group reacts as a carbonium ion which rearranges to t-pentyl before alkylation. Presumably this is the pattern of nearly all the alkylations, except that some primary alkyl groups can alkylate, in part at least, without change of configuration.

EXPERIMENTAL

Alkylation of p-*Xylene*.—(a) *By alkyl esters of sulphonic acids.* For all secondary alcohols, the methanesulphonic ester (0·2 mole) was heated in xylene (1 mole) at 125° for 5 hr. Olefin evolved during the reaction was collected in cold traps. For primary alcohols, the ester of 2,5-dibromobenzenesulphonic acid was heated in an excess of *p*-xylene under reflux for 48 hr. The product of each alkylation was isolated by the procedure used in earlier work. The yields and constants are given in Table 2.

(b) *Boron trifluoride.* (i) For secondary alcohols, it was sufficient to pass boron trifluoride into a mixture of the alcohol and an excess of *p*-xylene for about 1 hr. at 25°. After a further hour, the upper layer was removed and treated for the isolation of the alkyl-*p*-xylene. It was necessary with primary alcohols, to pass boron trifluoride into a mixture of the alcohol and *p*-xylene at 100° for 1 hr.

(ii) Alkylation was also brought about by saturating a mixture of the primary alcohol and *p*-xylene at room temperature with boron trifluoride and then adding sulphuric acid (96%) and heating at 120° until the mixture had separated into two layers.

(iii) Alternatively, the sulphuric acid was replaced by phosphorus pentoxide.

(c) *Sulphuric acid.* Aqueous sulphuric acid (80%; 100 c.c.) was added dropwise to a stirred solution of the alcohol (0·2 mole) in *p*-xylene (1 mole) at below 10°. The product was isolated after stirring at room temperature for 15 hr. For primary alcohols, the reaction was completed by heating.

[4] A. Streitwieser, D. P. Stevenson, and W. D. Schaeffer, *J. Amer. Chem. Soc.*, 1959, **81**, 1110.

[5] B. S. Friedman and F. L. Morritz, *J. Amer. Chem. Soc.*, 1956, **78**, 3430.

TABLE 2

Alkylation of *p*-xylene by alkyl esters of sulphuric acids

Alcohol	Yield (%) *	B. p./mm.	n_D^{20}	Found (%) C	Found (%) H	Calc. (%) C	Calc. (%) H
Hexan-1-ol	50	120—123°/15	1·4942	88·7	11·4	88·3	11·7
Hexan-2-ol	60	112—116/12	1·4949	88·5	11·5	88·3	11·7
Hexan-3-ol	58	115—118/12	1·4950	88·5	11·5	88·3	11·7
Pentan-1-ol	41	110—112/15	1·4970	88·4	11·5	88·6	11·4
Penten-2-ol †	42	103—106/15	1·4971	88·3	11·7	88·6	11·4
Pentan-3-ol †	40	104—107/15	1·4974	88·4	11·2	88·6	11·4
Butan-1-ol ‡	64	90—93/14	1·4991	88·8	11·1	88·8	11·2
Propan-1-ol §	40	80—83/13	1·5017	89·0	10·6	89·1	10·9

* Total yield of mixed isomers. † Also formed was pent-2-ene (~1 c.c.), b. p. 30—33°; dibromide, b. p. 44—46°/15 mm., n_D^{20} 1·5105 (Found: Br, 68·6. Calc. for $C_5H_{10}Br_2$: Br, 69·3%). ‡ Also formed was but-2-ene (~1 c.c.) at −35°; 2,4-dinitrobenzenesulphenyl adduct, m. p. 128°. § Also formed was propene (~1 c.c.) at −35°; 2,4-dinitrobenzenesulphenyl adduct, m. p. 76°.

(d) *Phosphoric acid.* The alcohol (0·2 mole) was added dropwise to a stirred mixture of *p*-xylene (1·0 mole) and phosphoric acid (100%; 150 c.c.) at 110° over 4—6 hr. Thereafter, the stirring was continued at room temperature for 15—20 hr.

The product from each alkylation had constants comparable with those from the sulphonic esters, and also gave satisfactory analyses. The yields are given in Table 3.

TABLE 3

Percentage yields from reactions using different condensing agents

	BF_3	H_2SO_4	H_3PO_4		BF_3	H_2SO_4	H_3PO_4
Hexan-1-ol	50	45 *	24	Pentan-2-ol	59	65	32
Hexan-2-ol	54	56	24	Pentan-3-ol	64	60	30
Hexan-3-ol	50	61	27	Butan-1-ol	62	68	36
Pentan-1-ol	62	55 †	34	Propan-1-ol	68	71	25

* Heated at 70° after all the acid had been added. † Treated with sulphuric acid (80%) at 50—70° for 3 hr.

Neopentylation of Phenol.—The 2,5-dibromobenzenesulphonate of neopentyl alcohol, heated in an excess of phenol at 100—110° for 5 hr., gave a mixture of 15% *o*- and 85% *p*-t-pentylphenols, with no recognisable amount of neopentylphenol. On treatment with 10% aqueous sodium hydroxide, the sodium salt of the *para*-isomer separated, and from it the free phenol, m. p. 93° was obtained (Found: C, 80·4; H, 9·8. Calc. for $C_{11}H_{16}O$: C, 80·4; H, 9·8%); *dinitro-derivative*, m. p. 65° (Found: C, 52·0; H, 5·4; N, 11·2. $C_{11}H_{14}N_2O_5$, requires C, 52·0; H, 5·6; H, 11·0%).

TABLE 4

p-Xylylalkanes

Product	B. p./mm. (lit.)	n_D^{20} (lit.)	Found (%) C	Found (%) H	Calc. (%) C	Calc. (%) H	Ref.
1-*p*-Xylylpropane	80—81°/12 (73°/6·5)	1·5025 (1·4996)					*a*
2-*p*-Xylylpropane *	77—79/12	1·4947					—
1-*p*-Xylylbutane	90—91/12 (93/8)	1·4993 (1·4996)					*b*
2-*p*-Xylylbutane †	90—91/12	1·4991					—
1-*p*-Xylylpentane	110—111/17 (96/4·5)	1·4955 (1·4914) ‡					*a*
2-*p*-Xylylpentane	102—103/12	1·4969	88·5	11·4	88·6	11·4	—
3-*p*-Xylylpentane	103/12	1·4975	88·4	11·5	88·6	11·4	—
1-*p*-Xylylhexane	130—132/17 (110/5)	1·4931 (1·4903)					
2-*p*-Xylylhexane	118—119/15	1·4934	88·2	11·5	88·3	11·7	—
3-*p*-Xylylhexane	115—117/12	1·4947	88·2	11·8	88·3	11·7	—

* From propan-2-ol, *p*-xylene, and sulphuric acid (80%) at 0° (yield 75%). † From s-butyl alcohol, *p*-xylene, and boron trifluoride (yield 70%). ‡ At 30°. (*a*) C. T. Lester and E. C. Suratt, *J. Amer. Chem. Soc.*, 1949, **71**, 2262. (*b*) D. V. Nightingale and H. D. Radford, *J. Org. Chem.*, 1949, **14**, 1089.

The *ortho*-isomer was obtained reasonably pure; dinitro-compound, m. p. 68° unchanged by admixture with an authentic specimen; depressed by the dinitro-derivative of the *para*-isomer (Found: C, 52·5; H, 5·5; N, 11·3%).

A pure sample of *p*-t-pentylphenol was obtained by crystallisation of the phenolic products of the reaction of t-pentyl alcohol with phenol and zinc chloride at 100—110° for 3 hr., m. p. 93°; dinitro-compound, m. p. 64—65°.

o-t-Pentylphenol, from 2-*o*-nitrophenyl-2-methylbutane, was characterised as its dinitro-derivative, m. p. 68°.

Analysis of Products.—The alkylation products were analysed by vapour-phase chromatography, for which a Pye Argon unit with an ionisation detector was used; the stationary phase was 10% Apiezon L on Celite (100—120 mesh) at 125° for hexyl- and pentyl-*p*-xylenes; at 100° for butyl- and propyl-*p*-xylenes.

The reproducibility with any one mixture was about 1% and the experimental error, estimated from comparative determinations was about ±2%.

For the chromatographic identification of the products of alkylation, reference compounds were made, most of them by reaction of the Grignard compound from 2-bromo-*p*-xylene and the appropriate carbonyl compound, dehydration of the alcohol and hydrogenation of the resulting olefin (Pd–C; ethanol; 50 p.s.i.).

No isomerisation of 2-*p*-xylylhexane, 2-*p*-xylylpentane, 1-*p*-xylylbutane, or 1-*p*-xylylpropane could be detected when each was heated in *p*-xylene with methanesulphonic acid for 5 hr. at 120°. They were also unchanged by treatment with boron trifluoride or by heating with phosphoric acid at 120° for 5 hr., or by stirring with sulphuric acid (80%) for several hours.

Preparation of Sulphonic Esters.—The sulphonic esters were made by adding the alcohol (0·3 mole) in small amounts to a stirred mixture of methanesulphonyl chloride (0·3 mole) in dry pyridine (30 c.c.) at 0—10°. The methanesulphonic esters of the secondary alcohols have been described by Williams and Mosher.[6] There are differences between their boiling points and those observed in this work. The properties of the esters are shown in Table 5.

TABLE 5

Methenesulphoric esters

				Found (%)			Calc. (%)		
Methanesulphonate	B. p./mm.	n_D^{20}	Yield (%)	C	H	S	C	H	S
3-Hexyl *	85°/0·2	1·4387	70	47·0	9·0	17·8	46·7	8·9	17·8
2-Hexyl †	86—88/0·2	1·4320	74	46·6	8·8	17·8	46·7	8·9	17·8
3-Pentyl ‡	74—76/0·1	1·4317	68	42·9	8·4	19·4	43·4	8·4	19·3
2-Pentyl §	75—77/0·1	1·4295	70	43·3	8·5	19·2	43·4	8·4	19·3

* Lit.,[6] b. p. 54—55°/0·5 mm., n_D^{20} 1·4388. † Lit.,[6] b. p. 60—61°/0·5 mm., n_D^{20} 1·4322. ‡ Lit.,[6] n_D^{20} 1·4315. § Lit.,[6] n_D^{20} 1·4304.

Also prepared were the following 2,5-dibromobenzenesulphonates: 1-hexyl, n_D^{20} 1·4227, unstable; 1-pentyl, n_D^{20} 1·4388, unstable; ***neopentyl***, m. p. 138° (Found: C, 34·5; H, 3·9; Br, 40·9; S, 8·0. $C_{11}H_{14}Br_2O_3S$ requires C, 34·7; H, 3·7; Br, 41·1; S, 8·3%); 1-butyl, m. p. 57—58°; 1-propyl, m. p. 74—75°.

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[6] H. R. Williams and H. S. Mosher, *J. Amer. Chem. Soc.*, 1954, **76**, 2984.