504. *Alkylation of the Aromatic Nucleus. Part V.* The Course of the Alkylation by Thermal Decomposition of Alkyl Sulphonates.*

By M. S. Grant and W. J. Hickinbottom.

Optically active s-butyl and s-octyl esters of methanesulphonic acid, when heated with mesitylene, give s-butyl- and s-octyl-mesitylenes having no optical activity. The significance of these results is discussed in relation to the observation that a mixture of n-butyl- and s-butyl-mesitylenes is formed when the n-butyl ester of methanesulphonic acid decomposes in mesitylene.

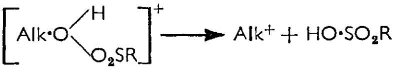
It is concluded that the alkylation can occur without the intermediate formation of an olefin and that it has the characteristics of an electrophilic substitution involving a carbonium ion.

In the alkylation of mesitylene, using n-butyl methanesulphonate, isodurene and mesityl methyl sulphone are formed as well as the expected butyl-mesitylenes. It is established that these arise from the action of methanesulphonic acid on mesitylene at its boiling point.

Földi [1] observed that the thermal decomposition of benzyl benzenesulphonate in aromatic hydrocarbons resulted in liberation of benzenesulphonic acid and introduction of the benzyl group into the solvent's nucleus. This reaction has since been extended to many alkyl and cycloalkyl sulphonates and has been applied to alkylation of some benzenoid and polycyclic hydrocarbons, phenols, and ethers.[2–5] It is a useful new method of introducing alkyl groups into aromatic systems.

Földi suggested that the reaction, in so far as benzylation was concerned, could be explained by assuming a decomposition into free sulphonic acid and a benzylidene radical, but it is now certain that the alkylation is more complex. Kinetic measurements by Ogata *et al.*[3] and by Nenitzescu *et al.*[4] of the decomposition of benzyl esters permit of no other interpretation than that the reaction is catalysed by protons; the acid necessary for this comes from the thermal decomposition of the sulphonic ester. These conclusions are borne out by our qualitative observations.

From the established regularities of substitution in alkylbenzenes and phenols, it is concluded that the alkylation has the general characteristics of an electrophilic substitution.[2] A substituting agent to fit this requirement can be derived from a sulphonic ester by (*a*) thermal fission to sulphonic acid and olefin with subsequent reaction of the olefin and the aromatic nucleus under the influence of the free sulphonic acid, (*b*) proton-catalysed fission of the sulphonic ester to give a carbonium ion and free sulphonic acid



$$\left[\mathrm{Alk{\cdot}O}\begin{matrix}\diagup\mathrm{H}\\ \diagdown\mathrm{O_2SR}\end{matrix}\right]^{+}\longrightarrow \mathrm{Alk^{+}} + \mathrm{HO{\cdot}SO_2R}$$

or (*c*) bimolecular displacement between the ester and the aromatic system.

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* Part IV, preceding paper.

[1] Földi, *Chem. Ber.*, 1928, **61**, 1609.

[2] (*a*) Hickinbottom and Rogers, *J.*, 1957, 4124; (*b*) Part II; (*c*) Part III; (*d*) Part IV; (*e*) Hickinbottom and Rogers, *J.*, 1957, 4131.

[3] Ogata, Yonetani, and Oda, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1943, **22**, 583.

[4] Nenitzescu, Auram, and Sliam, *Bull. Soc. chim. France*, 1955, 1266.

[5] Nenitzescu, Joan, and Teodorescu, *Chem. Ber.*, 1957, **90**, 585.

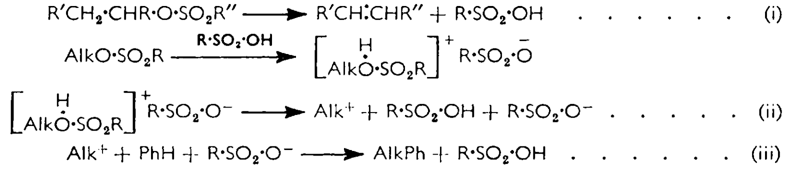
It is known that alkyl sulphonates decompose thermally to olefin and free sulphonic acid [2d,6] and that the process is reversible.[5] This is undoubtedly the initial phase of the alkylation in the absence of free acid: it accounts for the induction period in these alkylations and provides the free sulphonic acid for the subsequent phases of the reaction. Unless the olefin is removed by virtue of its volatility, it can react with the nucleus under the influence of the free sulphonic acid. This simple explanation is insufficient to cover the observed facts: it cannot account for the benzylation of aromatic systems by benzyl esters, and this benzylation has all the characteristics of alkylation by use of alkyl and cycloalkyl sulphonates.

Furthermore, the introduction of a n-butyl group into mesitylene, by using n-butyl methanesulphonate, is impossible if alkylation were wholly dependent on the formation of olefin. Yet the product of this reaction contains a high proportion of n-butylmesitylene. Also, Nenitzescu [5] found that reaction between n-propyl benzenesulphonate and benzene yields isopropylbenzene almost entirely. It was necessary to use 2 mol. of benzenesulphonic acid to initiate alkylation by 0·5 mol. of the n-propyl ester: consequently it is not possible to compare Nenitzescu's results with those now recorded.

Since the alkylation is not entirely dependent on formation of olefin the alternative courses are bimolecular displacement or proton-catalysed fission to a carbonium ion which can then attack the nucleus in the presence of some ionic group, such as sulphonate, as proton acceptor. Decision was sought by using sulphonic esters of optically active alcohols; with bimolecular displacement, the optical activity of the alkyl groups should be retained; the optical activity would be largely lost if a carbonium ion were the active substituting agent. It is necessary to allow for any of the alkyl group converted into olefin. For this reason the observations on the optically active s-butyl ester are the more reliable since the olefin then formed is largely volatilised away. Mesitylene was used as aromatic hydrocarbon on account of its relatively high reactivity towards alkylation. The s-butylmesitylene formed was almost completely inactive. A similar result was obtained by using optically active 1-methylheptyl methanesulphonate. It was also established that the loss of activity is not due to racemisation of the ester, but that it is coincident with its decomposition into olefin and sulphonic acid.

Nenitzescu *et al.*[5] have recorded almost complete loss of optical activity in the alkylation of benzene by optically active s-butyl benzenesulphonate. However, Nenitzescu added a considerable amount of free sulphonic acid to initiate the reaction, and this makes the deductions from his observations less certain.

On the basis of these observations and those of Nenitzescu it is possible to present a picture of the course of thermal alkylation. The initial phase in the absence of added acid is thermal decomposition to olefin and free sulphonic acid, followed by proton-catalysed decomposition of the ester to sulphonic acid and carbonium ion.



$$R'CH_2{\cdot}CHR{\cdot}O{\cdot}SO_2R'' \longrightarrow R'CH{:}CHR'' + R{\cdot}SO_2{\cdot}OH \quad \text{. . . . . . . (i)}$$

$$AlkO{\cdot}SO_2R \xrightarrow{R\cdot SO_2\cdot OH} \left[Alk\overset{H}{\dot{O}}{\cdot}SO_2R\right]^{+} R{\cdot}SO_2{\cdot}\bar{O}$$

$$\left[Alk\overset{H}{\dot{O}}{\cdot}SO_2R\right]^{+} R{\cdot}SO_2{\cdot}O^{-} \longrightarrow Alk^{+} + R{\cdot}SO_2{\cdot}OH + R{\cdot}SO_2{\cdot}O^{-} \quad \text{. . . . . (ii)}$$

$$Alk^{+} + PhH + R{\cdot}SO_2{\cdot}O^{-} \longrightarrow AlkPh + R{\cdot}SO_2{\cdot}OH \quad \text{. . . . . . . (iii)}$$

At stage (ii) the carbonium ion Alk^+ may, by loss of a proton to $R{\cdot}SO_3^-$, give more olefin or polymerise if stage (iii) is slow because of deactivation of the aromatic nucleus.

EXPERIMENTAL

Preparation of s-Butylmesitylene.—Boron trifluoride was passed into a mixture of mesitylene (25 g.) and butan-2-ol (15 g.) for about 1 hr. Two layers formed: after about another ½ hr. the upper one was removed, washed, dried, and fractionated. The *product* (10 g.) had b. p. 117°/19 mm., n_D^{20} 1·5065 (Found: C, 88·6; H, 11·3. $C_{13}H_{20}$ requires C, 88·5; H, 11·5%).

[6] Drahowzal and Klamann, *Monatsh.*, 1951, **82**, 467.

Preparation of n-*Butylmesitylene*.—Hydrogenation of n-butenylmesitylene (10 g.) in alcohol (Pd–C, 3 atm.) gave n-butylmesitylene (8 g.), b. p. 116—118°/25 mm., n_D^{20} 1·5029 (Found: C, 88·4; H, 11·7%).

n-Butenylmesitylene, b. p. 120—125°/19 mm., n_D^{20} 1·5191 (Found: C, 89·5; H, 10·6. Calc. for $C_{13}H_{18}$: C, 89·5; H, 80·5%), was obtained by dehydrogenation of 1-mesitylbutanol, m. p. 44°, by toluene-*p*-sulphonic acid.

The mesitylene used throughout was either "synthetic mesitylene" (Kodak) or a good commercial grade purified through its sulphonic acid.

Preparation of Mesityl Methyl Sulphone.—A mixture of mesitylenesulphinic acid (2 g.) and methyl iodide (1·5 g.) in alcohol (20 c.c.) containing sodium carbonate (1·5 g.) was refluxed for 2 hr. Evaporation of the filtered solution and crystallisation of the residue after washing it with water, gave *mesityl methyl sulphone*, m. p. 129—131° (from alcohol) (Found: C, 60·4; H, 7·1; S, 16·0. $C_{10}H_{14}O_2S$ requires C, 60·5; H, 7·1; S, 16·2%).

Reaction of n-*Butyl Methanesulphonate with Mesitylene*.—(i) Mesitylene (95·5 g.) and n-butyl methanesulphonate (30 g.) were stirred and heated at 171° for 24 hr. But-2-ene (5·6 g.) was collected in cold traps. The reaction mixture was washed with aqueous alkali, dried, and distilled, yielding a fraction (A), b. p. 70—90°/10 mm., n_D^{20} 1·5070, and mesityl methyl sulphone (1·5 g.).

Redistillation of fraction (A) gave isodurene, b. p. 79°/15 mm., n_D^{20} 1·5085 (Found: C, 89·4; H, 10·4. Calc. for $C_{10}H_{14}$: C, 89·5; H, 10·5%), identified by its infrared spectrum; the higher-boiling material was concentrated into a fraction, b. p. 95—96°/15 mm., n_D^{20} 1·5005, estimated by infrared spectroscopy to contain isodurene (50%), n-butylmesitylene (20%), and s-butylmesitylene (20%) (Found: C, 88·9; H, 11·4. Calc. for $C_{13}H_{20}$: C, 88·5; H, 11·5%).

(ii) Reaction between mesitylene (120 g.) and n-butyl methanesulphonate (38 g.) at 160° for 63 hr. gave but-2-ene (5·3 g.), mesityl methyl sulphone, and butylmesitylenes (6 g.). Further distillation of the last fraction gave one of b. p. 128—132°/32 mm., n_D^{20} 1·5022, consisting of n-butyl- (70%) and s-butyl-mesitylene (20%), and isodurene (5%).

(iii) The same amounts being used but at 168° for 24 hr., gave but-2-ene (6·3 g.), mesityl methyl sulphone, and a mixture, b. p. 128°/24 mm., n_D^{20} 1·5055, of n-butyl- (40%) and s-butylmesitylene (45%) and isodurene.

Reaction of (+)-s-*Butyl Methanesulphonate with Mesitylene*.—(+)-s-Butyl methanesulphonate was prepared from (+)-butan-2-ol ($[\alpha]_D^{18}$ +17·3°; *c* 3·2 in pyridine) as already described for the n-butyl ester. Purified by distillation it had b. p. 56—58°/10^{-4} mm., n_D^{20} 1·4290, $[\alpha]_D^{18}$ +19·1° (*c* 4·4 in mesitylene).

The optically active ester (6·3 g.) and mesitylene (24 g.) when heated at 120° for 6 hr. gave s-butylmesitylene, b. p. 107—110°/13 mm., n_D^{20} 1·5072. It was optically inactive in mesitylene (*c* 4, *l* 1).

Reaction of (—)-1-*Methylheptyl Methanesulphonate with Mesitylene*.—The optically active ester, b. p. 86—90°/5 × 10^{-3} mm., n_D^{21} 1·4360, $[\alpha]_D^{21}$ —11·5°, was prepared from (—)-octan-2-ol, $[\alpha]_D^{18}$ —11·6°. When it (7 g.) was heated with mesitylene (20 g.) for 9 hr. at 120° 2-1′-methylheptylmesitylene was formed, b. p. 143°/14 mm., n_D^{20} 1·4995 (Found: C, 87·7; H, 11·9. $C_{17}H_{20}$ requires C, 87·9; H, 12·1%). It was optically inactive.

Racemisation of (—)-1-*Methylheptyl Methanesulphonate*.—Aliquot parts of a solution of (—)-1-methylheptyl methanesulphonate in sodium-dried toluene (9·08 g. in 100 c.c.) were kept in sealed ampoules in a thermostat at 100°. The ampoules were withdrawn at intervals and the specific rotation of the solution measured. The amount of free acid was also determined by titration after addition of an excess of alkali. There was no appreciable fall in rotation during the first 2 hr.: after 5 hr. the rotation had fallen from $[\alpha]_{5461}^{20}$ —11° to —9·3°, with about 2·5% decomposition of the ester. After 6 hr. the solution was too dark for polarimetric readings and thereafter decomposition of the ester was rapid; 73·5% had decomposed after 7 hr.: 84% after 8 hr.

Reaction of Methanesulphonic Acid with Mesitylene.—Methanesulphonic acid (5·3 g.) and mesitylene (25 g.) were refluxed for 48 hr. The solution became dark brown but sulphur dioxide was not evolved.

The product was cooled, diluted with an equal volume of ether, and washed with sodium hydrogen carbonate solution. Distillation of the washed and dried solution through a spinning-band column, after removal of ether, gave the following fractions: (*a*) b. p. 149—162°/760 mm., n_D^{20} 1·4950 (1 g.), consisting of mesitylene with some *m*-xylene—as shown by its infrared spectrum; (*b*) b. p. 162—164°, n_D^{20} 1·4992 (19 g.), mesitylene; (*c*) b. p. 59—64°/8 mm., n_D^{20} 1·5124 (5 g.), which is almost entirely isodurene (infrared spectrum); (*d*) a residue which solidified and was crystallised from aqueous alcohol; it was mesityl methyl sulphone, m. p. and mixed m. p. 128—129°.

It was established that mesityl methyl sulphone is unchanged in boiling mesitylene during 6 days.

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