

XXXIII.—*Tertiary Butylphenol.*

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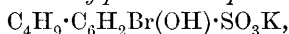
IN studying the action of bromine on the alkyl derivatives of phenol-*p*-sulphonic acid, in order to determine the degree in which the inhibiting influence of the alkyl is dependent on the character of the radicle (Armstrong and Lewis, Proc., 1900, 16, 157), experiments were made with what at the time was supposed to be *ter*.-butylphenyl ether sulphonate; but as the effect produced by the tertiary radicle seemed to be altogether different, not only from that of methyl and ethyl, but also from that of normal and *isobutyl*, the experiments were continued. The object of this note is to point out that the interpretation to be put upon the results is entirely different from that which at the time seemed to be the natural one.

Finding that the phenol-*p*-sulphonate could not be alkylated by the method successfully adopted in all other cases by digesting the salt with *ter*.-butyl chloride in presence of alkali, in order to prepare the ether, a mixture of phenol with the chloride and excess of alkali, together with sufficient alcohol to make a clear solution, was digested until interaction was complete; much gas (butylene) was given off during the operation. To isolate the product, the oil which separated on pouring the strongly alkaline alcoholic solution into water was distilled in a current of steam; the oil thus obtained was assumed to be the required ether and therefore a portion was at once sulphonated. The potassium salt of the acid so produced—which gave correct values on analysis—rapidly absorbed a molecular proportion of bromine, but the sulphonic group was not displaced, a monobromosulphonate being apparently the only product. This result was confirmed by a repetition of the experiments and by a determination of the acidity of the solution after bromination.

Suspicion was first aroused when a small quantity of the oil which escaped sulphonation was identified with *ter.*-butylphenol; it then appeared probable either that the supposed ether was in reality butylphenol or that the ether or a part of it underwent isomeric change under the action of the sulphonating agent (monochlorhydrin). On further brominating the monobromosulphonate, a product was obtained possessing the properties of a phenol, not those of an ether, so that there could be no doubt that butylphenolsulphonic acid and not *ter.*-butylphenyl ethersulphonic acid had been formed. In order to decide between the two alternatives, a considerable quantity of phenol (150 grams) was butylated as before. On subjecting the steam distillate to a rigorous washing with caustic soda solution of moderate strength, the greater part of the oil dissolved in the alkali; the insoluble portion amounted to only about 5 grams, boiling between 190° and 210°. This latter, however, as well as the soluble part, gave only butylphenolsulphonic acid on sulphonation; so that if the oil insoluble in alkali were indeed the ether, it had undergone isomeric change during sulphonation. Experiments made subsequently showed that no such change occurs in the case of *isobutylphenyl* ether, for on sulphonating this substance the sulphonic acid of *isobutylphenyl* ether was alone obtained.

The following new derivatives of *ter.*-butylphenol have been obtained in the course of the experiments.

Potassium-2-bromo-4-ter.-butylphenol-6-sulphonate,



obtained by the action of a molecular proportion of bromine on an aqueous solution of potassium *ter.*-butylphenolsulphonate, crystallises from water in anhydrous, glistening, flattened needles or thin flakes:

0.0981 gave 0.0247 K_2SO_4 . $\text{K} = 11.29$.

0.0978 „ 0.0532 AgBr . $\text{Br} = 23.15$.

$\text{C}_{10}\text{H}_{12}\text{OBr} \cdot \text{SO}_3\text{K}$ requires $\text{K} = 11.24$; $\text{Br} = 23.05$.

2:6-Dibromo-ter.-butylphenol, obtained by the further action of bromine on an aqueous solution of the bromosulphonate just described, crystallises in colourless, glistening flakes which melt at 70—71°; it has a faint but rather pleasant odour recalling that of artificial musk:

0.1179 gave 0.1438 AgBr . $\text{Br} = 51.70$.

$\text{C}_{10}\text{H}_{12}\text{OBr}_2$ requires $\text{Br} = 51.95$.

It is evident from the above observations that the principal product of the action of *ter.*-butyl chloride on phenol in presence of alkali is *p-ter.*-butylphenol. No satisfactory evidence of the production of an isomeric butylphenol has been obtained. If any ether is produced, it is formed in very small quantity and is converted into

the isomeric phenol on sulphonating. The ease with which *p-ter.*-butylphenol is volatilised by steam from a strongly alkaline liquid and the comparative difficulty with which it dissolves in caustic alkali point to its being an extremely weak acid.

The difficulty of obtaining mixed ethers of phenols containing a tertiary alkyl group has been brought under notice since the above experiments were carried out by Spiegel and Sabbath (*Ber.*, 1901, 34, 1946). They found that on heating potassium *p*-nitrophenate with *ter.*-butyl chloride and alcohol under pressure at 140° no trace of ether was obtained; even after adding an alcoholic solution of the chloride to the silver salt of *p*-nitrophenol and allowing the two substances to interact at ordinary temperatures, the *p*-nitrophenol was recovered unchanged. Similar results were obtained when *ter.*-amyl chloride was used.

Observations recorded by Mackenzie (*Trans.*, 1901, 79, 1209, 1216) seem to bear on the same point. He was unable to prepare an ether by the action of benzophenone chloride on sodium phenate (or phenol), the isomeric-4:4'-dihydroxytetraphenylmethane being formed instead; in a similar manner benzal chloride and phenol give dihydroxytriphenylmethane and not the corresponding ether.

The ease with which the tertiary butyl group attaches itself to a carbon atom of the benzene nucleus is brought out very clearly by the production of *ter.*-butylphenol in fair quantity, under such mild conditions, and under circumstances under which the formation of an ether might have been expected. The well-known fact that attempts to prepare homologues of benzene containing the *isobutyl* group attached to a nuclear carbon atom invariably involve the formation of their *tertiary* isomers (*cf.* Baur, *Ber.*, 1891, 24, 2832—2835; Schramm, *Monatsh.*, 1888, 9, 613—625) is apparently of the same order.

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