XCIX.—*Some Properties and Reactions of β-Chloroethyl, β-Cyanoethyl, and β-Carbethoxyethyl Toluene-*p*-sulphonates, including an Extension of the Friedel–Crafts Reaction.*

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THE introduction of the β-chloroethyl group into phenols has been effected by treating the phenol with β-chloroethyl toluene-*p*-sulphonate, $C_7H_7{\cdot}SO_2{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl$ (subsequently called ester A) in the presence of caustic soda, 80% yields of phenyl β-chloroethyl ethers being obtained (Clemo and Perkin, J., 1922, **121**, 642).

It was thought that the halogen atom in these ethers, on treatment with potassium cyanide, would be replaced to give the β-cyanoethyl ethers, and, on hydrolysis, the β-phenoxypropionic acids. These compounds are troublesome to prepare in quantity by present methods,* and on ring closure give the chromanones, which are valuable for synthetic work on certain natural products. Attempts to effect the replacement of the chlorine atom in the β-chloroethyl ethers by the cyano-group, however, have been unsuccessful.

Attention was then turned to the preparation of β-*cyanoethyl toluene*-p-*sulphonate*, $C_7H_7{\cdot}SO_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CN$, itself, with a view to the direct introduction of the β-cyanoethyl group into phenols. Although this ester can be easily prepared from toluene-*p*-sulphonyl chloride and ethylene cyanohydrin, it has been found to be readily hydrolysed by cold dilute alkalis, and hence it is unsuitable for use as an alkylating agent. When β-cyanoethyl toluene-*p*-sulphonate

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* β-Phenoxypropionic acid itself was obtained in a yield of 20% from phenol and β-iodopropionic acid (Bischoff, *Ber.*, 1900, **33**, 924); Arndt and Kallner (*Ber.*, 1924, **57**, 202), using β-chloropropionic acid, obtained a 36% yield.

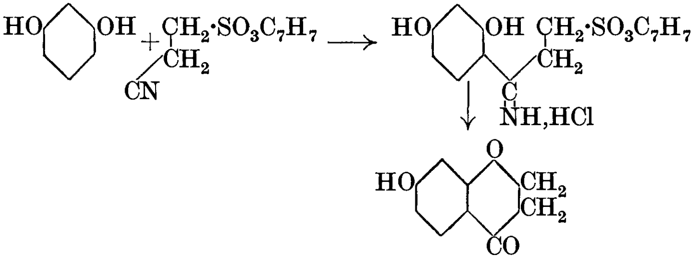
(subsequently called ester B) is treated with anhydrous alcoholic hydrogen chloride, it is easily converted into the *hydrochloride* of *γ-imino-γ-ethoxypropyl toluene*-p-*sulphonate*, which is hydrolysed by water to give *β-carbethoxyethyl toluene*-p-*sulphonate* :

$$C_7H_7\cdot SO_2\cdot O\cdot CH_2\cdot CH_2\cdot C(OEt){:}NH,HCl \xrightarrow{H_2O} C_7H_7\cdot SO_2\cdot O\cdot CH_2\cdot CH_2\cdot CO_2Et.$$

This carbethoxy-ester (subsequently termed ester C), although more stable to alkalis than ester B, is, nevertheless, hydrolysed too easily for it to be of use as an alkylating agent for the direct introduction of the β-carbethoxyethyl group into phenols.

(It has been found that various other nitriles, such as β-phenylpropionitrile, react smoothly with cold alcoholic hydrogen chloride, giving good yields of highly crystalline iminoethyl ether hydrochlorides, which are especially useful for the identification of liquid nitriles, and their treatment with water furnishes a very convenient method for the direct conversion of the cyano- into the carbethoxy-group.)

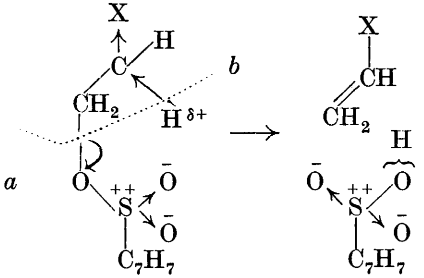
There remained, however, the possibility that the ester B could be applied for the synthesis of the desired chromanones in the well-known Hoesch reaction (*Ber.*, 1915, **48**, 1122) thus :



The reaction, however, does not occur in this manner, but the isomeric compound, 7-hydroxy-3 : 4-dihydrocoumarin, is formed in fairly good yield (compare Langley and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 2320). This constitutes, therefore, a further anomaly of the Hoesch reaction (see Chapman and Stephen, J., 1925, **127**, 885). Neither ester A nor C reacts with resorcinol under similar conditions.

As none of the esters A, B, and C appeared to be suitable for the preparation of the chromanones, attention was directed to a comparison of their reactions. Ester A was relatively very stable to alkalis, being hydrolysed to the extent of only 25% after boiling for 2 hours with 2 equivalents of 2*N*-sodium hydroxide; on being shaken with the same proportion of alkali at the ordinary temperature, ester B was hydrolysed completely in 4 minutes to acrylonitrile and toluene-*p*-sulphonic acid, and ester C in 40 minutes to acrylic ester and the sulphonic acid. This ease of hydrolysis was also well shown when ester B was warmed at 80° with anhydrous potassium carbonate, acrylonitrile distilling in 75% yield. This method for preparing acrylonitrile is therefore much superior to those described by Moureu (*Bull. Soc. chim.*, 1893, **9**, 424; 1920, **27**, 903 : yields, 30% and 47% respectively). In a similar manner, when the ester C was heated with anhydrous potassium carbonate at about 100°, a quantitative yield of ethyl acrylate was given off. The same behaviour was shown when the three esters A, B, and C were treated with potassium phthalimide. In the first case phthal-β-chloroethylimide was produced, and with B and C, acrylonitrile and acrylic ester, respectively, distilled.

The marked difference in the ease of the alkaline hydrolysis of the esters A, B, and C can be explained in the following manner :



When X represents either the cyano- or the carbethoxy-group, both of which commonly act as electron-sinks, electron displacements occur which produce slight intramolecular ionisation, with the result that the hydrogen atoms of the CH_2X group acquire a small positive charge. Further, as two of the oxygen atoms of the sulphonic group are joined to the sulphur atom by semi-polar double bonds, *i.e.*, have, according to Lowry, a negative charge, there is an urge for the molecule to split, as shown, along *ab*. In ester A, however, the chlorine atom is not an electron-sink, but behaves much as it does in alkyl chlorides, so that the hydrogen atoms do not become positively charged, and hence the molecule is relatively stable. This explanation, rather than one involving a co-ordinated hydrogen atom, would appear to be borne out by the boiling points of the esters, which rise in the order A, C, B; whereas if it be supposed that the split along *ab* is facilitated by a co-ordinate link between one of the oxygen atoms and a hydrogen atom, then the expected order of ascending boiling points would be, according to Sidgwick's work, B, C, A.

The fact that, in the alkaline hydrolysis of the esters B and C, the cyano- and the carbethoxy-group remained intact caused attention to be directed to the action of the Grignard reagent on these esters. Gilman and Beaber (*J. Amer. Chem. Soc.*, 1923, **45**, 839; 1925, **47**, 518) have described the action of organic magnesium halides on alkyl sulphonates, and in particular that of magnesium phenyl bromide on the ester A, in which case β-chloroethylbenzene resulted. When esters B and C are substituted for A in this reaction, violent action occurs and no definite compounds have been isolated from the resulting complex mixtures.

In contrast with this result, however, it has now been found that when the ester A is treated with benzene in the presence of aluminium chloride a good yield of dibenzyl results, whereas, under similar conditions, the esters B and C undergo reaction very smoothly at the sulphonic ester linking alone, with the direct production of good yields of β-phenylpropionitrile and ethyl β-phenylpropionate respectively :

$$2C_6H_6 + C_7H_7{\cdot}SO_3CH_2{\cdot}CH_2Cl \xrightarrow{AlCl_3} C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$$

$$C_6H_6 + C_7H_7{\cdot}SO_3CH_2{\cdot}CH_2{\cdot}CN \text{ (or } CO_2Et) \xrightarrow{AlCl_3} C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CN \text{ (or } CO_2Et).$$

This modification of the Friedel–Crafts reaction along apparently new lines furnishes a very convenient method for the production of alkylated aromatic hydrocarbons, and the action, which is being further investigated, appears capable of considerable extension, as a great variety of sulphonic esters of the type A are obtainable. For instance, in the simple case, from ethyl toluene-*p*-sulphonate, benzene, and aluminium chloride, a 65% yield (approximately\) of ethylbenzene, calculated on the ester used, has been obtained.

EXPERIMENTAL.

β-*Cyanoethyl Toluene*-p-*sulphonate* (ester B).—This compound is readily prepared by boiling a mixture of pure toluene-*p*-sulphonyl chloride (190 g.), ethylene cyanohydrin (100 g.), and xylene (150 c.c.) under reflux for about 3½ hours. Hydrogen chloride is rapidly evolved at first, and later the mixture darkens with the separation of *ammonium toluene*-p-*sulphonate* (25 g.) in colourless prisms, m. p. 325—330° (Found : N, 7·4; S, 17·0. $C_7H_{11}O_3NS$ requires N, 7·4; S, 16·9%). The mixture is steam-distilled to expel the xylene, and the residue poured into cold water (2000 c.c.). Ester B, which separates as an oil and quickly solidifies, is dried on a porous plate and recrystallised from methyl alcohol (yield, 146 g. or 65%) (Found : C, 53·0; H, 5·2; N, 5·8; S, 14·5. $C_{10}H_{11}O_3NS$ requires C, 53·3; H, 4·9; N, 6·2; S, 14·2%). It crystallises from benzene and alcohol in colourless prisms, and from water, in which it is only slightly soluble, in needles, the melting point of both varieties being 64°; it boils at 187—189°/0·5 mm. without decomposition.

*γ-Imino-γ-ethoxypropyl Toluene-*p*-sulphonate Hydrochloride.*—A mixture of ester B (10 g.) and a saturated solution of hydrogen chloride in absolute alcohol (50 c.c.) is shaken at room temperature until all the solid has dissolved, and then, after 1—1½ hours, slowly diluted with anhydrous ether (200 c.c.). The *hydrochloride* of the iminoethoxypropyl ester, which crystallises, is washed with dry ether until free from hydrogen chloride, and recrystallised from absolute alcohol, containing a trace of hydrogen chloride, by slow addition of dry ether (yield, about 11 g. or 81%) (Found: S, 10·4; Cl, 12·1. $C_{12}H_{17}O_4NS,HCl$ requires S, 10·4; Cl, 11·5%). It crystallises in colourless leaflets, m. p. 101°, is fairly stable in air, but dissolves easily in, and is readily hydrolysed by, water.

*β-Carbethoxyethyl Toluene-*p*-sulphonate* (ester C).—This ester quickly separates as an oil when a solution of the above imino-salt (10 g.) from ester B in water (50 c.c.) is warmed to 70°. It is isolated by means of ether, dried, and fractionated, the portion distilling at 167—169°/0·2 mm. being collected (yield, 7·5 g. or about 85%) (Found: C, 52·8; H, 5·9; S, 11·7. $C_{12}H_{16}O_5S$ requires C, 52·9; H, 5·9; S, 11·8%). The ester C is a colourless syrup, insoluble in water. It distils with slight decomposition into acrylic ester and the sulphonic acid, even in a very good vacuum, and is readily hydrolysed into the same two compounds by cold aqueous alkalis.

7-Hydroxy-3 : 4-dihydrocoumarin.—A mixture of ester B (9 g.), resorcinol (6·1 g.), and zinc chloride (1 g.) in anhydrous ether (80 c.c.) is saturated with dry hydrogen chloride. The crystals obtained after 4 hours, when washed free from traces of oil and acid with ether and dissolved in water (50 c.c.), decompose with separation of the dihydrocoumarin as an oil, which soon solidifies to a crystalline compound (m. p. 133°), similar in all respects to that obtained by Langley and Adams (*loc. cit.*) from β-chloropropionitrile and resorcinol. The yield is 3·2 g. (49%) (Found: C, 66·1; H, 5·2. Calc.: C, 65·8; H, 4·9%).

Acrylonitrile.—An intimate mixture of ester B (9 g.) and anhydrous potassium carbonate (4·5 g.) is heated carefully with occasional stirring. At about 80° acrylonitrile begins to distil, and at 120°, when some water follows, the heating is stopped, and the distillate dried over calcium chloride and fractionated; the greater portion passes over at 77—79° (yield, 1·6 g. or 75%) (Found: C, 68·1; H, 6·0; N, 26·9. Calc.: C, 67·9; H, 5·7; N, 26·4%).

Ethyl Acrylate.—Similarly this ester may be prepared by carefully heating a mixture of ester C (10·8 g.) and anhydrous potassium carbonate (4 g.). It passes over at a little above 100°, is dried over calcium chloride and fractionated, almost the whole distilling at 100—101°; the yield (3·9 g.) is approximately theoretical (Found: C, 59·3; H, 7·8. Calc.: C, 60·0; H, 8·0%).

Phthal-β-chloroethylimide.—A mixture of potassium phthalimide (9·5 g.) and ester A (11·7 g.) is heated for about 3 hours at 200° with occasional stirring. The cooled mass is extracted with boiling water, and the residual oil, which solidifies, is crystallised two or three times from alcohol; it then melts at 79—81° (compare Seitz, *Ber.*, 1891, **24**, 2626). The yield of crude product is 9 g. or 86% (Found: Cl, 17·4. Calc.: Cl, 17·0%).

Dibenzyl.—A mixture of ester A (11·7 g.), benzene (100 c.c.), and aluminium chloride (20 g.) is heated under reflux for 2 hours, and the product, when cool, is poured into dilute hydrochloric acid (600 c.c.) and steam-distilled; 7 g. of dibenzyl (b. p. 284°; m. p. 51°) are obtained from the distillate by fractionation.

β-*Phenylpropionitrile.*—When ester B (11·2 g.) is submitted to the treatment described in the preceding paragraph (benzene, 80 c.c.; aluminium chloride, 10 g.), β-phenylpropionitrile is obtained as an oil, b. p. 254° (yield, 4·7 g. or 72%) (Found: C, 82·3; H, 6·9. Calc.: C, 82·5; H, 6·9%).

Ethyl β-*Phenylpropionate.*—This also is obtained in a similar manner from ester C (13·6 g.), benzene (80 c.c.), and aluminium chloride (10 g.) (yield, 6·6 g. or 74%); b. p. 245° (Found: C, 74·3; H, 7·8. Calc.: C, 74·2; H, 7·9%).

Ethylbenzene.—Ethyl toluene-*p*-sulphonate (30 g.) is dissolved in benzene (150 c.c.), and aluminium chloride (30 g.) added. After the evolution of hydrogen chloride, which is at first spontaneous, has somewhat abated, the mixture is refluxed for 2 hours and then worked up as in the above cases. The portion of the distillate passing over at 133—137° (10·2 g. or 64%), on refractionation, distils almost wholly at 135°, the b. p. of ethylbenzene (Found: C, 90·6; H, 9·35. Calc.: C, 90·6; H, 9·4%).

γ-Imino-γ-ethoxy-α-phenylpropane Hydrochloride.—β-Phenylpropionitrile (2·5 g.) is dissolved in a concentrated ethyl-alcoholic solution of hydrogen chloride (15 c.c.). The solution, which becomes warm, is kept for about 2 hours and is then slowly diluted with anhydrous ether (150 c.c.). The *hydrochloride* of the corresponding iminoethoxy-compound, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C(OEt){:}NH,HCl$, which crystallises, is recrystallised from a solution in absolute alcohol, containing a trace of hydrogen chloride, by the gradual addition of ether, and then forms needles, m. p. 130° (yield, 3·1 g. or about

76%) (Found: Cl, 16·6. $C_{11}H_{15}ON,HCl$ requires Cl, 16·6%). It dissolves very readily in water, quickly hydrolysing to ethyl β-phenylpropionate (yield, more than 95%).

α-Chloro-γ-imino-γ-ethoxypropane Hydrochloride.—To a solution of acrylonitrile (1 g.) in dry ethyl-alcoholic hydrogen chloride (15 c.c.), which has been kept for about 2 hours, anhydrous ether (150 c.c.) is slowly added; the *hydrochloride*, $CH_2Cl{\cdot}CH_2{\cdot}C(OEt){:}NH,HCl$, formed by the addition of a further molecule of hydrogen chloride to the carbon–carbon double bond, then crystallises. The compound can be recrystallised as described above for the imino-ethoxy-salt from β-phenylpropionitrile (yield, 2·1 g. or about 65%) [Found: Cl (total), 41·8; Cl (ionic), 20·4. $C_5H_{10}ONCl,HCl$ requires Cl (total), 41·3; Cl (ionic), 20·6%]. It forms colourless plates, m. p. 109°, and dissolves very readily in water with hydrolysis into ethyl β-chloropropionate.

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