XXXII.—*On Ethylbenzoic Acid.*

By A. KEKULÉ and T. E. THORPE.

ETHYLBENZOIC acid, $C_6H_4\left\{\begin{matrix}CO_2H\\C_2H_5\end{matrix}\right.$, was first synthetically obtained by one of us about four years ago, from ethylbenzol, according to the method by which he then prepared benzoic, toluylic, and xylylic acids;[*] this acid, however, was not at the time more accurately investigated. Subsequently Fittig and König[†] have also obtained ethylbenzoic acid by the oxidation of diethylbenzol by means of nitric acid. The two acids must necessarily be identical, since the monobromethylbenzol served as the starting point in each case. Indeed Fittig and König were disposed to regard the two acids as identical, although it appears that they entertained some degree of doubt concerning the success of the synthetical experiments.

We considered it necessary, however, to submit this question of identity to experimental proof, and accordingly we have more closely investigated a quantity of the acid obtained from the former preparation, and at the same time we have prepared a fresh amount, according to the method above referred to, that is, by allowing carbonic acid and sodium to act simultaneously upon monobromethylbenzol.

A quantity (about 20 grms.) of the bromide, $C_6H_4BrC_2H_5$, is placed in a comparatively large flask, and diluted with six or seven times its volume of perfectly anhydrous ether, so that the mixture covers the bottom of the flask to a depth of about half an inch; the theoretical quantity of sodium cut into slices as thin as possible is next added, and a slow continuous current of carbonic acid is then sent through the liquid; the apparatus is attached to a condenser in such a manner that the condensed portion may return to the flask, and if necessary the action is regulated by immersing the flask from time to time in cold water. In about 24 hours the process is completely finished. The dark green slimy mass is next repeatedly treated with ether, the excess of sodium carefully removed, the salt dis-

[*] Kekulé, Ann. Chem. u. Pharm., 137, 178.

[†] Fittig u. König, Ann. Chem. u. Pharm, 143, 288.

solved in a small quantity of water, and the solution filtered. The acid is then precipitated by the addition of a slight excess of hydrochloric acid, separated by filtration, and washed slightly with a small quantity of cold water. In order to purify it, the mass is next dissolved in warm baryta-water, the excess of baryta removed by a current of carbonic acid gas, the solution filtered, and the acid again precipitated from the warm solution by hydrochloric acid. The acid is once more dissolved in baryta-water, and the above process repeated; on the third precipitation by hydrochloric acid, the substance is obtained perfectly pure.

The reaction which occurs in the synthesis of ethylbenzoic acid may be represented as follows:—

$$C_6H_4Br.C_2H_5 + Na_2 + CO_2 = C_6H_4.C_2H_5CO_2Na + NaBr.$$

Practically, however, the reaction appears to be far more complicated than is represented by the above equation. Although in all cases the same amounts of the bromide of sodium and of ether were employed, still the quantity of acid obtained in successive operations varied very considerably. We have not studied the conditions under which the acid is formed, with the accuracy necessary to enable us to state the causes of these differences; it would appear, however, that the presence of a small quantity of moisture favours in some unknown manner the production of the sodium salt.

The acid thus prepared is identical in every particular with the ethylbenzoic acid described by Fittig and König. It crystallises from boiling water in small leaflets, which possess a considerable degree of resemblance to benzoic acid. Its solubility in cold water is considerably less, however, than that of the latter acid. The pure acid melts at 110°—111° (Fittig and König, 110°—111°), and on cooling solidifies to a confused crystalline mass. It begins to sublime a few degrees below its melting point, and when heated with a quantity of water insufficient for its complete solution, melts to a heavy, colourless oil. The acid is easily soluble in alcohol and ether. The acid prepared by repeated crystallisation from alcohol invariably melted 3°—4° lower than that purified by recrystallisation from water.

The barium salt $Ba(C_9H_9O_2)_2 + 2H_2O$, prepared by neutralzing the acid with barium carbonate, crystallises with difficulty in plates. It dissolves in about 45 parts of cold water, but far more easily in hot water. It loses its water of crystallisation when placed over sulphuric acid.

0·5637 grm. of the air-dried salt, lost on drying at 120°, 0·0430 grm. water, and gave 0·2633 grm. barium sulphate.

	Calculated.		Found.
$2(C_9H_9O_2)$	298	63·28	—
Ba................	137	29·10	29·4
$2H_2O$	36	7·62	7·63

The copper salt $Cu(C_9H_9O_2)_2$ is a bluish green amorphous powder, nearly insoluble in water, obtained by adding copper sulphate to a dilute solution of sodium ethylbenzoate.

0·2218 grm. of the salt, dried at 130°, gave—

0·4827 grm. carbonic acid,
0·1004 grm. water, and
0·0489 grm. copper oxide.

	Calculated.		Found.
C_{18}	216	59·75	59·34
H_{18}	18	5·00	5·02
Cu..............	63·5	17·57	17·61
O_4..............	64	17·68	—

The above experiments conclusively prove that the acid obtained synthetically from ethylbenzol is identical with that obtained by Fittig and König by the oxidation of diethylbenzol.