

LXXXII.—*On the Decomposition of Aromatic Ethereal Salts of Fumaric Acid.*

By RICHARD ANSCHÜTZ and QUIRIN WIRTZ.

WE have for some time been occupied with the study of the action of phosphorus pentachloride on maleïc anhydride. W. H. Perkin (*Ber.*, **14**, 2548), who has examined this reaction, states that on distilling maleïc anhydride with phosphorus pentachloride, as might have been expected, fumaric chloride is produced. The reaction, however, is not a complete one, and a great part of the unaltered anhydride passes over towards the end of the operation. We have

worked in such a manner that after the reaction was completed, we distilled the products under diminished pressure, and after repeated fractional distillation, we succeeded in isolating a liquid boiling at 70—71° under about 11 mm. pressure; this on analysis gave numbers which are in accordance with the formula of maleïc chloride. We observed that fumaric chloride boils under 14 mm. pressure at 60°.

Circumstances compelled us to discontinue the experiments for three months, and during this time the product of the action of phosphorus pentachloride on maleïc acid anhydride remained untouched, sealed in a glass tube. On continuing the research we subjected the liquid which previously boiled at 70—71° under 14 mm. pressure again to rectification under diminished pressure. The chloride now began to boil at 60° under 14 mm. pressure, the temperature rising to 75° towards the conclusion of the distillation, so that the chloride had evidently changed its nature.

As one of us had formerly (*Ber.*, 12, 2281) observed that maleïc acid is completely changed by acetyl chloride into its anhydride, and that maleïc acid is not converted to fumaric acid by dry hydrogen chloride, it seemed possible that two different ethereal salts would be produced if fumaric chloride and the product of the reaction of phosphorus pentachloride on maleïc acid were treated with a dry alcohol.

By the hydrolysis of the ethereal salts prepared from the product of the reaction of phosphorus pentachloride on maleïc acid anhydride we might obtain the desired information as to the nature of the chloride produced. This consideration induced us, in the first place, to prepare phenylic fumarate from fumaric chloride and phenol, because—of the more easily obtainable alcohols—phenol is the most readily secured free from water.

$\text{CH}\cdot\text{COOC}_6\text{H}_5$
Phenylic fumarate, \parallel , crystallises from alcohol in white
 $\text{CH}\cdot\text{COOC}_6\text{H}_5$

needles melting at 161—162°, very sparingly soluble even in hot alcohol. If rapidly distilled, it passes over partly unchanged, but is partly decomposed into carbon dioxide and *stilbene*. If phenylic fumarate is heated very slowly, it is almost wholly decomposed in this manner, an oil of aromatic odour, which we have not yet studied, accompanying the stilbene.

The explanation of this reaction, which is given in the preceding communication, involves the intermediate formation of phenylic cinnamate; the correctness of our explanation would be placed beyond doubt if we could succeed in finding this compound among the products of the decomposition. We therefore tried to conduct the reaction step by step, and ceased heating the phenylic fumarate as

soon as half the quantity of carbon dioxide formerly observed had been expelled. The residue in the fractionating flask was distilled under diminished pressure, and the solid distillate recrystallised from alcohol. The greater part of it consisted of stilbene, but we succeeded without difficulty in isolating *phenylic cinnamate* from the alcoholic mother-liquor; this on treatment with an alcoholic solution of potash, gave pure cinnamic acid.

Paracresylic fumarate, $\begin{array}{c} \text{CH}\cdot\text{COOC}_6\text{H}_5 \\ \parallel \\ \text{CH}\cdot\text{COOC}_6\text{H}_5 \end{array}$, is very sparingly soluble in alcohol, and melts at 162° ; it is decomposed when heated, losing carbon dioxide and yielding two crystalline substances, one of which is sparingly, the other easily soluble in alcohol. The former is *dimethylstilbene* melting at 179° . It gives a bromide, easily soluble in chloroform and very sparingly soluble in alcohol, melting with decomposition at $203\text{--}204^\circ$. The soluble substance melts at 79° and crystallises in glistening scales; it is perhaps phenylic methylcinnamate.

From these results it follows that hydrocarbons belonging to the stilbene group may be prepared from the fumaric and cinnamic acid ethers of the monohydric phenols, and of course the ethers of cinnamic acid, with the exception of the phenyl ether, give hydrocarbons with different aromatic radicles—that is, “mixed stilbenes;” whilst the fumaric acid ethers give hydrocarbons with the same aromatic radicles, that is, “symmetric stilbenes.” Moreover, the fumaric ethers of the phenols give phenyl ethers of acids belonging to the cinnamic acid group.

The formation of stilbene from phenyl fumarate is of special interest also, from the hydrobenzoïns being brought into near relation with fumaric acid by this transition, although in an indirect manner. We shall endeavour to prepare the acetyl ethers of the hydrobenzoïns from the phenyl ethers of the acetyltartaric acids by elimination of carbon dioxide.