XXX.—*The* cis-trans *Ethenoid Transformation.*

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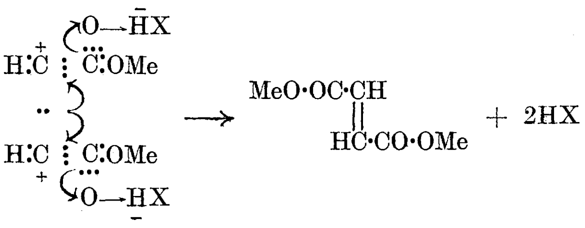
THE mechanism of the stereoisomeric transformation of ethylenic compounds has received considerable attention but remains far from clear. Several early workers noted that maleic acid and its esters were converted into the fumaric form by minerals acids, and Tanatar (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1742) and Pfeiffer (*Ber.*, 1914, **47**, 1592) describe the change of maleic to fumaric acid by means of ammonia and pyridine respectively. Recently, Meerwein and Weber (*Ber.*, 1925, **58**, 1266) have stated that potassium in ether converts methyl maleate into methyl fumarate.

As methyl fumarate is a highly crystalline solid with a solubility of about 1% in methyl maleate at the ordinary temperature, the conversion of the latter into the former furnishes a convenient method for studying this reaction.

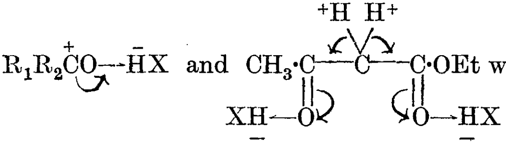
Apparently, the catalytic action of ammonia and organic bases has not been investigated in this connexion, but it has now been found that the former, and primary and secondary amines, effect the change. For instance, a trace of piperidine transforms methyl maleate in a few seconds into a crystalline mass of the fumarate, and since the former has much the greater energy content, the temperature rises very considerably. Dimethylamine, diethylamine, piperazine, methylamine, allylamine, benzylamine, *d*- and *l*-α-phenylethylamine, β-phenylethylamine, coniine, and aniline also effect the change, although some of them do not bring about a complete transformation. Tertiary amines such as triethylamine, dimethylaniline, diethylaniline, and pyridine, however, do not catalyse the inversion, although triethylamine is a much stronger base than many of the above primary and secondary ones. At first it seemed that triethylamine was an exception to the rule, as the base supplied by Kahlbaum effected some change; but after it had been freed from primary and secondary impurities by treatment with toluene-*p*-sulphonyl chloride (Clemo and Perkin, J., 1921, **119**, 648), it caused no conversion after a year at the ordinary temperature.

The mechanism usually favoured for the ethenoid inversion is that the catalyst adds itself in some way to the double bond, thus allowing free rotation with formation of the *trans*-form and regeneration of the catalyst. Even if it is assumed that a newly formed molecule may have enhanced activity, there still appears to be no adequate reason why some of the additive complexes should not reach a stable maturity.

Our experiments have shown that organic bases are only effective as catalysts when they contain amino- or imino-hydrogen, and this suggested the following mechanism for the inversion, in which the first stage is the formation of a co-ordinate link between the hydrogen atom of the base and the carbonyl oxygens of the ester. This would produce a mobility in the, at present, uncertain electronic system constituting the double bond, and lead to a very unstable complex in which both the ethylenic carbon atoms would become positive and surrounded by only seven electrons.



The well-known catalytic action of primary and secondary bases in the Knoevenagel reaction (*Annalen*, 1894, **281**, 25) may be explained as being due to the formation of two ionised systems such as



$\overset{+}{R_1R_2CO}\rightarrow\bar{H}X$ and $CH_3\cdot\underset{XH\leftarrow\bar{O}}{\overset{\|}{C}}-\overset{+H\ H^+}{C}-\underset{O\rightarrow\bar{H}X}{\overset{\|}{C}}\cdot OEt$ which would condense to give the reaction products.

Walden (*Z. physikal. Chem.*, 1896, **20**, 379) states that methyl maleate can be made from either maleic acid or anhydride, but no details are given, and recent workers have used the silver salt–methyl iodide method of preparation. It has now been found that methyl maleate can be easily prepared in good yield from maleic anhydride, methyl alcohol, and sulphuric acid.

EXPERIMENTAL.

Methyl Maleate.—Maleic anhydride (60 g.) was added to methyl alcohol (100 c.c.) and concentrated sulphuric acid (4 c.c.), and the mixture refluxed for 3½ hours on the water-bath. The bulk of the excess of alcohol was then distilled off and water added, followed by solid sodium carbonate to neutralise the sulphuric acid. The ester, when extracted with ether, dried over sodium sulphate, and fractionated, gave (a) 6 g., b. p. 200—204°, (b) 65 g., b. p. 204—206°, and (c) 1—2 g., b. p. above 206°. Fraction (a) alone contained traces of methyl fumarate, as shown by the silver nitrate test after hydrolysis with baryta [Found for (b): C, 49·7; H, 5·4. Calc. for $C_6H_8O_4$: C, 50·0; H, 5·55%].

The methyl fumarate formed by the inversion of the above was identified by the method of mixed m. p. with an authentic specimen.

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