

A STUDY OF THE PREPARATION AND REARRANGEMENT OF THE DIALKYL ESTERS OF MALEIC ACID¹

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Maleic acid and maleic anhydride are two products appearing now on the market in commercial quantities manufactured by application of a process of catalytic oxidation of benzene with oxygen in the presence of vanadium pentoxide under the patents and processes devised by Weiss and Downs. Prior to this process maleic acid along with its isomer, fumaric acid, were only compounds of importance as classical examples of geometric isomorphism. Today a large portion of the tartaric acid used in this country is made by an oxidizing saturation of maleic acid. It is interesting however that the possibilities for the use of the maleic esters in this solvent field are almost unexplored. This problem therefore was initiated to extend the commercial application of this acid and to throw some light upon the rearrangement of the maleic esters into their corresponding fumarates.

Anschutz in 1878 and 1879 first prepared only the methyl and ethyl maleate esters by reaction of the normal silver maleate with an alkyl halide with excellent yields due to the precipitation of the silver halide. He found, however, that great care was necessary to avoid excess of the alkyl halide as that compound converts the maleate ester quantitatively into its corresponding fumarate. Very few data have been published on the physical constants of these esters. In fact nothing is given on any of the higher alkyl alcohol esters of either maleic or fumaric acids. It is true Lyman and Reid have studied the solid p-nitro benzyl ester of these acids but only as a means for preparing a sharp melting point compound to be used in the identification of these acids.

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The methods of B. B. Corson and H. T. Clarke for the preparation of esters were tested out, the first using a slow addition of large amounts of the alcohol with removal of the excess alcohol and the water in order to obtain a high ester yield. This method did not produce anything like the published ester yields claimed for it. Clarke's method was next tried which employs a lower boiling non-miscible solvent to remove the water. This method showed possibilities and an all glass and glass jointed apparatus was devised of simple construction which brought about complete elimination of rubber joints. The latter were shown definitely to accelerate the rearrangement to the corresponding fumarate. Molal proportions of 1:3 of the acid and alcohol respectively were added to the reaction flask with eight grams of concentrated sulphuric acid per gram mole of the acid or maleic anhydride along with 200 c.c. of the suitable solvent. The reaction mixture was refluxed from four to twenty-four hours depending on the ester being prepared, the simpler the alcohol used the longer the time necessary for the completion of the esterification. The excess solvent was distilled off from the impure ester, and the alcohol if miscible with water was removed by distillation. Otherwise it was allowed to remain while the crude ester was washed free from sulphuric and maleic acid with 10 percent sodium carbonate. If the water ester layers showed a tendency to emulsify, the aqueous layer was made denser by the addition of salt.

The crude ester was extracted with ether, was dried with anhydrous magnesium sulphate, and the alcohol then being distilled off, the ester was finally purified by distillation with an oil seal vacuum pump at four mm. pressure.

In choosing a non-miscible solvent for water removal a solvent boiling approximately at the temperature of water, and yet below that of the alcohol used, made such a procedure impossible as far as the methyl and ethyl maleates were concerned. In this case the esterification was much slower and less complete although an attempt was made to remove the water from the circulating alcohol with a dehydrating agent. Further efforts will be made to raise the yields of these two esters. The other esters studied ranged in yield from 70 per

cent to 90 per cent of the theoretical. The majority however gave an 80 per cent yield.

These esters were first identified as esters of unsaturated acids by alkaline permanganate which showed them to be true esters and not simply addition compounds. They were then saponified and the melting point of the phenyl aspartic anilide made was compared with the literature value which showed the ester studied to have been a maleate without any traces of fumaric acid, showing no rearrangement during esterification. For further proof of the maleate, the p-nitro benzyl ester was taken from the acid of the saponified alkyl ester and it gave a melting point identical with the literature value. These esters so compared were thus shown to be pure maleate esters without contamination or rearrangement and the various physical constants of these newly prepared compounds were then determined and recorded.

Preliminary runs in the production of the esters using rubber stoppers showed a rearrangement with the fumaric esters with a considerable amount of decomposition products. To push this further, small pieces of rubber were refluxed four hours with the various esters on a steam bath. The methyl maleate was 87 percent rearranged and the ethyl maleate 63 percent rearranged although none of the other esters was affected. The same procedure was carried out with concentrated sulphuric acid, giving negative results. When both rubber and the same amounts of sulphuric acid were used less rearrangement of the methyl ester occurred while the ethyl ester was quantitatively changed. This fragmentary information suggests a more detailed study of this rearrangement. Attempts will also be made to obtain higher methyl and ethyl ester yields.