but which could now be interpreted, in view of the analogous behavior of isovaleric ester in the Claisen condensation, as due in part, at least, to low acidity.[16]

We take pleasure in acknowledging the active interest of M. S. Kharasch throughout this work.

Summary

Sodium ethylate catalyzed hydrogen exchange reactions of various types of esters with deutero-alcohol are reported, and the influence of structure on acidity, as determined by the exchange reaction, is correlated with reactivity in condensation reactions.

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[16] The tacit assumption is made that decreased acid strength hinders the alkylation reaction through its effect in lowering the equilibrium anion concentration, and while this assumption appears to be valid in the malonic ester series, this will not be the dominant effect where the acidity is of such a high order that dissociation, under the conditions of alkylation, is practically complete. The introduction of alkyl groups in barbituric acid is known from ordinary acidometric measurements, to depress the acid strength, the isopropyl group being particularly effective [Preiswerk, *Helv. Chim. Acta*, **6**, 192 (1923)], but at the same time the ease of alkylation increases and the isopropyl derivative reacts with great ease. Less extreme illustrations are to be seen in the acetoacetic and cyanoacetic ester series, in which the isopropyl derivatives undergo alkylation readily [Fischer, Rohde and Brauns, *Ann.*, **402**, 364 (1913)] and which differ also from malonic ester in that a second alkyl group is introduced somewhat more readily than the first. In these instances the role of acidity is subordinate to the reactivity of the anions (or salts) toward alkyl halides which, as Conrad and Brückner pointed out [*Z. physik. Chem.*, **7**, 283 (1891)], varies inversely with the acid strength.

CHICAGO, ILLINOIS RECEIVED JULY 5, 1939

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

Mechanism of the Acid-catalyzed Dimerization of Anethole

BY WELDON G. BROWN AND ALEX H. WIDIGER

In connection with the possibility of obtaining evidence regarding the mechanism of the acid-catalyzed polymerization of olefins with the aid of deuterium, a study has been made of the dimerization of anethole catalyzed by deuterium chloride in methyl alcohol solution. This case was considered favorable for a test of the Whitmore[1] theory of acid catalyzed polymerizations because (1) the experimental conditions can be adjusted so as to yield almost exclusively the dimer, (2) the structure of the dimer is known and is in conformity with the Whitmore hypothesis, (3) the structure of the dimer is such that it contains no hydrogen atoms likely to be readily exchangeable under the influence of acids. It was recognized that the monomer contains at least one such hydrogen atom, namely, that attached to the β carbon atom, and that the exchange of this hydrogen with the deuterium of the medium, if fast in comparison with the polymerization process, would obscure the phenomenon we wished to observe.

The formation of isoanethole,[2] according to the mechanism of Whitmore, is shown in the equations

$$\mathrm{R{-}CH{=}CH{-}CH_3 + H^+ \longrightarrow R{-}CH^+{-}CH_2{-}CH_3} \quad (\mathrm{R} = \text{anisyl}) \qquad (1)$$

$$\mathrm{R{-}CH^+{-}CH_2{-}CH_3 + R{-}CH{=}CH{-}CH_3 \longrightarrow R{-}CH(C_2H_5){-}CH(CH_3){-}CH^+{-}R} \qquad (2)$$

$$\mathrm{R{-}CH(C_2H_5){-}CH(CH_3){-}CH^+{-}R \longrightarrow R{-}CH(C_2H_5){-}C(CH_3){=}CH{-}R + H^+} \qquad (3)$$

It will be noted that the proton added becomes incorporated in the ethyl side-chain of the dimer and that the proton eliminated is derived from the second molecule of anethole. A polymerization carried out with a deutero acid should therefore yield, if no exchange reactions occur, a product containing one atom of deuterium per molecule of dimer. In the more likely event that a hydrogen exchange reaction of the monomer accompanies the polymerization reaction, but is not too rapid in comparison, it is still possible to predict that the proportion of deuterium in the dimer formed in any small interval of time during the polymerization should be greater than that present in the monomer.

Experimental Part

The polymerization of anethole (Eastman Kodak Co. product, redistilled, b. p. 225° (750 mm.)) was carried out by refluxing with 5 *N* hydrochloric acid in methyl alcohol, according to the procedure of Goodall and Haworth, except that the methyl alcohol and the hydrochloric acid were partly deuterated. The deuteration was accomplished by treating methyl alcohol with pure heavy water, thus permitting an exchange of the hydroxyl hydrogen of the alcohol with the deuterium of the water, then removing water by repeated treatment with calcium oxide. Dry hydrogen chloride was passed into the anhydrous alcohol to yield a 5 *N* solution. Analysis for deuterium was carried out by combustion, after having first removed halogen by treatment with dry silver oxide, the water of combustion

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[1] Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

[2] The structure indicated for isoanethole is that established by Goodall and Haworth, *J. Chem. Soc.*, 2484 (1930).

being collected, purified, and analyzed for deuterium by the temperature-float method.

The dimer is of limited solubility in alcohol, and separates together with some unchanged anethole, making it possible to obtain samples by cooling and draining off the lower layer. The samples were taken up in ether, washed with aqueous alkali, then with water, and, after drying, the ether was allowed to evaporate. Fractional distillation at reduced pressure furnished samples of anethole and isoanethole which were analyzed for deuterium by combustion and density measurements on the water of combustion. The anethole fractions contained some chloride, evidently as a result of addition of hydrogen chloride but the extent of this addition was for our purposes negligible. During the period of heating a considerable part of the hydrogen chloride disappears by reacting with methyl alcohol.

In a typical experiment, a solution of 71 g. of anethole in 355 ml. (331 g.) of 5.30 *N* hydrogen chloride (HCl + DCl) in methyl alcohol was heated on a water-bath and samples were removed at intervals as described above. The deuterium present amounted to 8.90 mole per cent. of the total available hydrogen (hydroxyl hydrogen plus hydrogen chloride). The analytical results are given in Table I. The results are given in terms of mole per cent. of deuterium found in the water of combustion and in terms of the so-called exchange number.[3] In the present connection the exchange number may be considered simply as the number of deuterium atoms per anethole unit which would have been found had the available hydrogen of the medium been composed entirely of deuterium.

TABLE I

POLYMERIZATION OF ANETHOLE IN DEUTERO METHYL ALCOHOL–HYDROGEN CHLORIDE SOLUTION

Sample	Period[a] of heating, min.	Compn. of sample, g.	% D_2O in water of combustion	Exchange no.[b]
1	3	15 anethole	0.155	0.21
		7 isoanethole	.135	.18
2	6	7 anethole	.33	.45
		2 isoanethole	.18	.24
3	20	4 anethole	.61	.83
		7 isoanethole	.36	.48
4	120	4 isoanethole	.77	1.05

[a] Data in this column refer to time intervals. Thus the first sample was withdrawn three minutes after the start of the reaction, the second sample was withdrawn after a further period of six minutes, etc. [b] Atoms of deuterium per anethole unit.

Some information with regard to the position occupied by the deuterium in the dimer was obtained by oxidizing with alkaline permanganate, following the procedure of Goodall and Haworth, and analyzing the products for deuterium. The deuterium content of the isoanethole, expressed in terms of mole per cent. D_2O in the water of combustion (ordinary water being taken as zero), was 0.71%. The anisic acid contained 0.02%, and the ketone (3-anisylpentanone-2) contained 0.50%. Of the deuterium originally present 95% was found in the ketone. In view of the finding that deuterium is present only as a result of an exchange reaction of the monomer prior to polymerization, the conclusion was reached that virtually all of the deuterium present in the isoanethole is confined to the CH_2 group of the ethyl side chain.

Discussion

It is difficult to find any support in our results for the Whitmore mechanism of polymerization, or indeed for any mechanism involving an intermediate carbonium ion (or addition compound) in which the equivalence of the newly acquired hydrogen atom with hydrogen atoms previously present on the same carbon atom is to be assumed. The condition that there should not be a rapid interchange of hydrogen between the monomer and the medium is fulfilled, yet the predicted enrichment of the dimer with respect to deuterium is not observed. On the contrary, it is found that the dimer contains no more deuterium than can be accounted for as the result of a slow hydrogen exchange prior to its formation.

Summary

The dimerization of anethole in a partly deuterated medium of methyl alcohol and hydrogen chloride is accompanied by a slow hydrogen exchange reaction of the monomer and the dimer is found to contain no more deuterium than can be accounted for as a result of this exchange. The significance of this result for the mechanism of polymerization is pointed out.

CHICAGO, ILLINOIS RECEIVED NOVEMBER 6, 1939

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[3] For the definition of the exchange number, and the method of calculation, see Brown, Kharasch and Sprowls, *J. Org. Chem.*, **4**, 442 (1939); Brown, Widiger and Letang, THIS JOURNAL, **61**, 2597 (1939).