[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE]

2-Pyrones. VIII. Reaction of β-Methylglutaconic Anhydride with Aldehydes[1]

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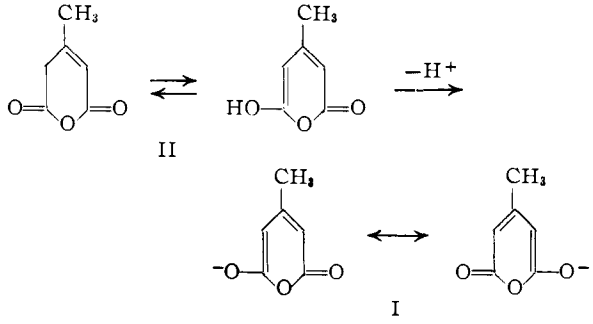
β-Methylglutaconic anhydride reacts with aldehydes to give two different types of characterizable products. With acetaldehyde an α-hydroxyethyl derivative VII is obtained. With aromatic aldehydes having effective electron donor groups, arylidene derivatives VIII are obtained. The arylidene derivatives vary in color from deep yellow to magenta and in stability. The most deeply colored, most stable products are obtained from dialkylaminobenzaldehydes. This is consistent with the possibility for increased resonance stabilization in such forms as are shown in IX.

Glutaconic anhydrides are of interest because their tendency to ionize indicates a resonance stabilization of the anion I formed on removal of a proton and because of the possibility for tautomerism with structures having an active methylene group II. These structural considerations suggest



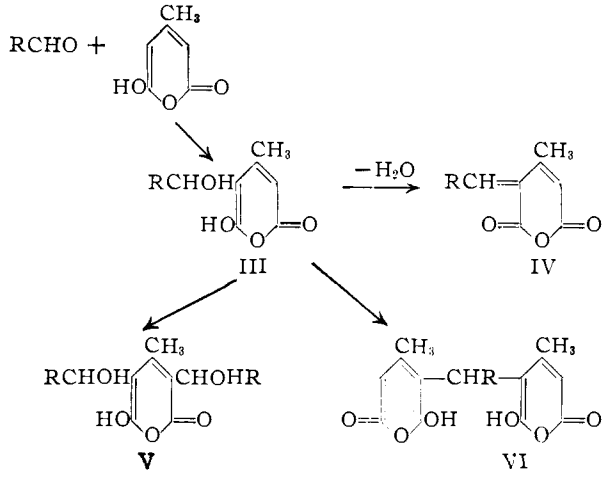
II

I

that aldol type condensations with aldehydes should be possible. Apparently only a few such condensation reactions are known. Alkylidene derivatives have been obtained from β-chloroglutaconic anhydride with cinnamaldehyde[3] and from β-methylglutaconic anhydride with cinnamaldehyde and with β-ionylideneacetaldehyde.[4] We wish to record some further observations on the reaction of a variety of aldehydes with β-methylglutaconic anhydride.

We have obtained characterizable solids from six aldehydes on reaction with β-methylglutaconic anhydride. The aldehydes and anhydride react readily at room temperature when dissolved in 95% ethanol. No catalyst is needed. This is unusual because previous workers[4] have apparently always used pyridine as a catalyst for such reactions. The products begin to precipitate from ethanol immediately or within a few minutes and the precipitation is complete within less than an hour. Some of the products redissolve if allowed to stand in contact with the reaction mixture and can thereafter be isolated only as polymers. For this reason the precipitate is collected after a reaction time of not over one hour.

The structure of these products presents some interesting features. The reactions of β-methylglutaconic anhydride with aldehydes can, by analogy, be anticipated to give products formed by combination of varying molecular ratios of reactants with or without the loss of water. The immediate possibilities are



III

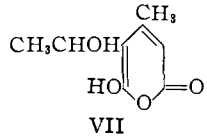
IV

V

VI

Compound III is a 1/1 product which is converted to IV, by loss of a molecule of water. Compound V is formed by condensation of the aldehyde in 2/1 and VI in 1/2 ratios. All of these compounds correspond to products obtained, for example, from phenol and aldehydes or malonic acid or ester and aldehydes.

The product obtained from acetaldehyde is a white solid, m.p. 96°. The analytical data for this product are in agreement with values required for β-methyl-γ-(α′-hydroxyethyl)-glutaconic anhydride (VII). It is the only compound isolated in



VII

these studies with this type of structure. Solid products obtained from *n*-butyraldehyde and from formaldehyde under similar conditions had, on the basis of the analytical data, undergone partial dehydration or further condensation or both.

The solid products obtained by condensation of the β-methylglutaconic anhydride with *p*-dimethylaminobenzaldehyde, *p*-diethylaminobenzaldehyde, 3,4-diethoxybenzaldehyde, 3,4-dimethoxybenzaldehyde and 1-naphthaldehyde were all well-defined, highly colored, crystalline solids. The analytical data for all of these products are in agreement with the arylidene structure VIII.

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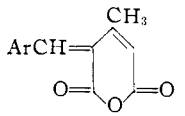
(2) Taken in part from a thesis submitted by E. L. DeYoung in partial fulfillment of the requirements for the M.S. degree.

(3) R. Malachowski and T. Kalinski, *Roczniki Chem.*, **6**, 768 (1926); *C. A.*, **21**, 3615 (1927).

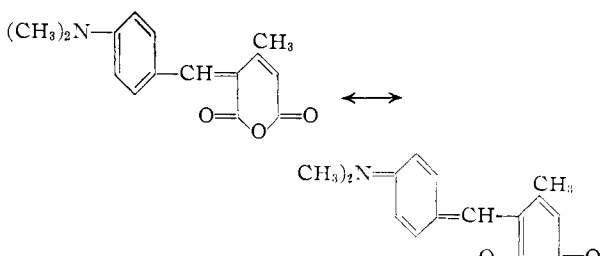
(4) V. Petrow and O. Stephenson, *J. Chem. Soc.*, 1310 (1950).



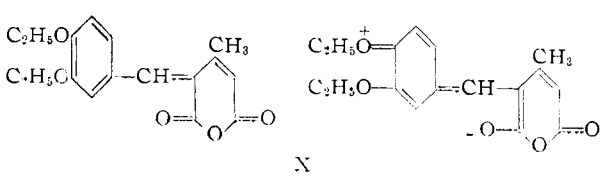
VIII

The dimethylamino and diethylamino derivatives are insoluble in all organic solvents tested and deep carmine in color. The products precipitated immediately on mixing the reactants in ethanol and were purified by washing with solvent. They undergo no change on prolonged contact with the reaction mixture. The same diethylamino compound, as judged by the absence of depression in the melting point of mixtures of the two, was obtained from the same reactants using benzene as a solvent and pyridine as a catalyst. The possibility for the existence of such resonance structures as IX probably accounts for the depth of color shown in these compounds and their increased stability as compared to other types.

The products obtained from the alkoxy aldehydes are yellow or orange solids which precipitate from the reaction mixture rapidly. If separated after a half-hour reaction period, the colored solids can readily, although not always in high yield, be recrystallized from ethyl acetate in analytically pure condition. The naphthaldehyde product precipitates as a recrystallizable solid after 15 or 20 minutes. In some instances it is obvious that these products undergo further reaction with the formation of resinous condensation products either during the reaction period, if extended, or during recrystallization. Furthermore, a number of other aromatic aldehydes readily precipitate solids under the reaction conditions described but no techniques have yet been developed for the isolation of characterizable individual compounds from these obviously less stable reaction products. This instability toward further condensation is entirely consistent with the known reactivity of this type of compound. The decreased stability of these types as compared to the dialkylamino types is probably related to a decreased resonance stabilization in the oxygen types as shown in X and to even less resonance stabilization in products derived from aldehydes with less effective donor groups.



IX



X

Experimental[5]

β-Methylglutaconic anhydride was prepared by the procedure described previously.[6] The aldehydes were obtained commercially and most of them were redistilled or recrystallized prior to use.

γ-(4′-Dimethylaminobenzylidene)-β-methylglutaconic Anhydride (IX).—One gram (0.008 mole) of β-methylglutaconic anhydride and 1.07 g. (0.007 mole) of *p*-dimethylaminobenzaldehyde were dissolved in 25.0 ml. of 95% ethanol. The deep-red precipitate which formed at once was collected, washed, and dried to give 1.2 g. (67% of the theoretical amount) of γ-(4′-dimethylaminobenzylidene)-β-methylglutaconic anhydride, m.p. 226–227°. The product is insoluble in all organic solvents tested.

Anal. Calcd. for $C_{15}H_{15}O_3N$: C, 70.02; H, 5.88; N, 5.44. Found: C, 70.02; H, 6.00; N, 5.33.

The same product, as evidenced by the absence of depression of melting points of mixtures, was obtained by refluxing 2.6 g. of the aldehyde with 1.7 g. of the anhydride in benzene with pyridine catalyst.

γ-(4-Diethylaminobenzylidene)-β-methylglutaconic Anhydride.—This compound was prepared by the procedure described for the dimethylamino derivative from 0.88 g. (0.005 mole) of diethylaminobenzaldehyde and 0.5 g. (0.004 mole) of the anhydride. The product is a deep carmine solid, m.p. 160–162°, yield 0.45 g. (40%).

Anal. Calcd. for $C_{17}H_{19}O_3N$: C, 71.56; H, 6.71; N, 4.90. Found: C, 71.22; H, 6.71; N, 5.11.

γ-(3′,4′-Diethoxybenzylidene)-β-methylglutaconic Anhydride.—One gram (0.008 mole) of β-methylglutaconic anhydride and 1.34 g. (0.007 mole) of 3,4-diethoxybenzaldehyde were dissolved in 25 ml. of 95% ethanol. The orange precipitate, which formed at once, was collected and dried to give 1.2 g. (57%) of γ-(3,4-diethoxybenzylidene)-β-methylglutaconic anhydride. The product was recrystallized from ethyl acetate as orange leaflets, m.p. 145°.

Anal. Calcd. for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.77; H, 5.88.

γ-(3,4-Dimethoxybenzylidene)-β-methylglutaconic Anhydride.—This compound was prepared by the procedure described for the diethoxy derivative from 0.83 g. (0.005 mole) of veratraldehyde and 0.5 g. (0.004 mole) of the anhydride. The yellow, crystalline product was recrystallized from ethyl acetate, m.p. 183–186°, yield 0.40 g. (37%).

Anal. Calcd. for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15. Found: C, 65.66; H, 5.48.

γ-(1-Naphthylidene)-β-methylglutaconic Anhydride.—This compound was prepared by the procedure described for the diethoxy derivative from 1.0 g. (0.008 mole) of the anhydride and 1.1 g. (0.007 mole) of 1-naphthaldehyde. The precipitation starts after about 20 minutes. The deep yellow, crystalline product was recrystallized from ethyl acetate, m.p. 205–208° dec.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 77.18; H, 4.70.

γ-(α-Hydroxyethyl)-β-methylglutaconic Anhydride (VII).—One gram (0.0079 mole) of 4-methylglutaconic anhydride and 0.32 g. (0.0073 mole) of acetaldehyde were dissolved in 25 ml. of 95% ethanol. The precipitated product was collected and dried as a white powder, m.p. 96°.

Anal. Calcd. for $C_8H_{10}O_4$: C, 56.46; H, 5.92. Found: C, 56.22; H, 5.84.

The following aldehydes gave solid products which precipitated from ethanol solutions containing β-methylglutaconic anhydride: benzaldehyde, 3,4-dichlorobenzaldehyde, piperonal, formaldehyde and butyraldehyde. None of these products were recrystallizable and none analyzed in accordance with any obvious structural possibilities.

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(5) Analyses by Micro-Tech Laboratories.

(6) R. H. Wiley and N. R. Smith, THIS JOURNAL, **75**, 3893 (1953).