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Alkylation of Maleic Acid and Related Compounds with Alkyldiimine and Azoalkanes

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During the early attempts to synthesize roccellic acid, (+)-2*S*:3*R*)-2-methyl-3-dodecylsuccinic acid,¹ various methods for the stereoselective synthesis of alkylsuccinic acids were investigated. Since diimine reduction is stereospecific² it seemed possible that alkyldiimines and azoalkanes would react stereoselectively with maleic acid and related compounds to give alkyl and dialkylsuccinic acids. Some preliminary experiments along these lines are reported in this communication.

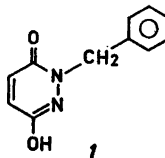
Methyldiimine and phenyldiimine, generated by oxidation of the hydrazines, were found to add to maleic acid to give low yields of methyl- and phenylsuccinic acid, respectively. Similar experiments have recently been carried out by Cohen and Nicholson who also describe an efficient method for generating phenyldiimine.³

To investigate the stereospecificity of the addition, methyldiimine was generated in the presence of acetylenedicarboxylic acid by oxidation of methylhydrazine. A very low yield of methylmaleic and methylfumaric acid was obtained. The high ratio of maleic to fumaric acid (4:1) indicates that the reaction is relatively stereospecific. The low yield makes the reaction unattractive for preparative work. It is possible that the yield is improved if other methods

are used for the generation of methyldiimine (*cf.* Ref. 3). In the early experiments to dialkylate maleic acid derivatives, azo(2-propane) was photolysed in the presence of dimethylmaleate or dimethylfumarate. Under the most favorable conditions a trace of dimethyl diisopropylsuccinate was obtained. Approximately the same ratio of *erythro* and *threo* esters (3:1) was obtained from maleate and fumarate, presumably due to photo isomerisation of fumarate to maleate. When maleic anhydride or maleimide derivatives were used, no dialkylsuccinic acid derivatives could be isolated.

The crude product from the reaction of dimethylmaleate and azo(2-propane) contained nitrogen and rapidly turned brown on contact with air. It therefore seemed possible that some diazetidine was formed, but the attempts to isolate a defined nitrogen containing product were unsuccessful.

Diimine reduction is highly sensitive to steric hindrance.⁴ The failure of azo(2-propane) to give appreciable amounts of dialkylation products in the reaction with dimethyl maleate might be due to steric hindrance. The reaction between azophenylmethane and dimethyl maleate was therefore investigated. Azophenylmethane is an attractive model compound since it may be thermally decomposed at moderate temperature.⁵ In the photochemical reaction of azophenylmethane and dimethylmaleate no dimethyl dibenzylsuccinate was formed (GLC). Dibenzyl, stilbene, and polymers were the main products.



When azophenylmethane was decomposed in the presence of dimethyl maleate, a trace of dimethyl dibenzylsuccinate was formed and also some dibenzyl and stilbene. In addition, 2-benzyl-6-hydroxy-3(2*H*)-pyridazinone (*1*) was formed in about 40 % yield. A similar product is also formed from azo(1-phenylethane) and dimethylmaleate. The mechanism of this reaction is obscure and will be investigated further.

Experimental. Methylidimine and acetylenedicarboxylic acid. Potassium hydroxide (1.2 g), potassium hydrogen acetylenedicarboxylate (1.5 g), methylhydrazinehydrosulfate (1.4 g) and a trace of copper(II) acetate were dissolved in water (20 ml) and hydrogen peroxide (30 %, 1.2 ml) added over a period of 20 min. Nitrogen (180 ml) was evolved. The solution was evaporated to dryness, acidified with hydrochloric acid and extracted with ethyl acetate. The solvent was removed to give a residue which contained mainly acetylenedicarboxylic acid. After methylation with diazomethane dimethyl methylmaleate (7 parts), methylmaleic anhydride (7 parts), and dimethyl methylfumarate (3 parts) were detected by means of GLC. The total yield was less than 1 %.

Azo(2-propane) and dimethyl maleate. A solution of azo(2-propane) (2.0 g) and dimethyl maleate (4.0 g) in methanol (50 ml) was irradiated for 25 h with pyrex filtered UV light (Hanau; 75 W). The solvent was removed and the product distilled to give an air sensitive oil (1.8 g) which contained nitrogen. The oil was chromatographed on alumina to give a small ester fraction (0.05 g) which contained mainly dimethyl diisopropylsuccinate in an *erythro:threo* ratio of 3:1. The main product appeared to decompose on the column. Practically identical products were obtained when dimethyl fumarate was used in place of dimethyl maleate.

Photoreaction of azophenylmethane and dimethyl maleate. Azophenylmethane⁵ (0.2 g) in dimethyl maleate (2 ml) was irradiated for 24 h at 350 nm in a Rayonet reactor. Dibenzyl, stilbene, and polymeric material was formed but no dimethyl dibenzylsuccinate (GLC).

Thermal reaction of azophenylmethane and dimethyl maleate. A solution of azobenzyl (0.5 g) in dimethyl maleate (2 ml) was held at 150° for 6 h. Only about 5 ml of nitrogen was formed. Dibenzyl, stilbene, and a trace of dimethyl dibenzylsuccinate were formed (GLC) but the main product was 2-benzyl-6-hydroxy-3(2H)pyridazinone (*1*) (0.18 g), m.p. 205–207°, lit.⁶ 206°. NMR, IR, and masspectral data are in accordance with the proposed structure. (Found: C 64.8; H 5.0; N 13.0. Calc. for C₁₁H₁₀N₂O₂: C 65.0; H 4.9; N 13.9).

Thermal reaction of azo-(1-phenylethane) and dimethyl maleate gave a similar product as azophenylmethane probably 2(1-phenylethyl)-6-hydroxy-3(2H)pyridazinone, m.p. 180–182°. (Found: C 66.6; H 5.6; N 13.0. Calc. for C₁₂H₁₂N₂O₂: C 66.8; H 5.6; N 13.0).

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The Photo Reaction between Azoester and Olefins

1. Cyclohexene, 1-Hexene, and Styrene

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In an attempt to photochemically dialkylate methyl maleate with azo(2-propane) only a trace of methyl 1,2-di-(2-propyl) succinate was obtained.¹ No other defined product could be isolated, but it seemed possible that part of the product was a diazetidine formed by addition of the azocompound and maleate. With the hope to obtain a more stable diazetidine, diethyl azodicarboxylate was photochemically reacted with cyclohexene and 1-hexene. No diazetidins could be isolated from these reactions. Instead, the major products were the alkylated hydrazoesters (*1*) and (*3*), respectively. To rule out the possibility that diazetidins (*e.g.* *2*) were first formed which then rearranged to the hydrazoesters