n_D^{20} 1.4942, d_4^{15} 1.3420, d_4^{20} 1.2565. The only physical constant reported by Claisen and Matthews[2] was the density, with which our value is in exact agreement.

When piperidine was used in catalytic and 0.1 molar amounts, a product yield of 6% was obtained. Like results were observed on employing piperidine acetate in ethanol[4] as a catalyst.

Ethyl α-(2,2,2-trichloro-1-hydroxaminoethyl)acetoacetate (II?). To a solution of 1.3 g. (0.019 mole) of hydroxylamine hydrochloride in 3 ml. of water was added 2 ml. of 10% sodium hydroxide, 0.50 g. (0.0019 mole) of ethyl α-(2,2,2-trichloroethylidene)acetoacetate and enough ethanol (*ca.* 1 ml.) to dissolve the trichloro compound. The solution was refluxed for 10 min. on the water bath, cooled to room temperature, and 5 ml. of water added. The crystalline material that separated was recrystallized from 80% ethanol and from ethyl acetate; yield 0.45 g. (80%), m.p. 152–153°, iodoform test (+), ferric chloride (ethanol) enolic test (−), x-ray powder diffraction data: 7.00[5] −0.9,[6] 5.62–0.4, 4.69–1.0, 4.19–0.5, 3.80–0.6, 3.18–0.5, 2.85–0.5, 2.73–0.1, 2.53–0.2, 2.36–0.2, 2.20–0.8, 2.10–0.2, 1.96–0.1, 1.75–0.1.

Anal. Calcd. for $C_8H_{12}NO_4Cl_3$: C, 32.84; H, 4.13; N, 4.79; Cl, 36.36. Found: C, 32.51; H, 3.99; N, 4.74; Cl, 36.49.

An infrared spectrum of ethyl α-(2,2,2-trichloroethylidene)acetoacetate, in chloroform solution, showed the presence of a carbonyl group (5.8 μ) and a carbon to carbon double bond (6.1 μ). The infrared spectrum of ethyl α-(2,2,2-trichloro-1-hydroxaminoethyl)acetoacetate, in chloroform solution, showed the presence of a carbonyl group (5.7 μ) and no carbon to carbon or carbon to nitrogen double bond.

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(4) R. Kuhn, W. Badstübner, and C. Grundmann, *Ber.*, 69, 98 (1936).

(5) Interplanar spacing, Å, CuK$_\alpha$ radiation.

(6) Relative intensity by visual estimation; 1.0 most intense.

2-Pyrones. XXIV. Derivatives of α,β-Dimethylglutaconic Anhydride

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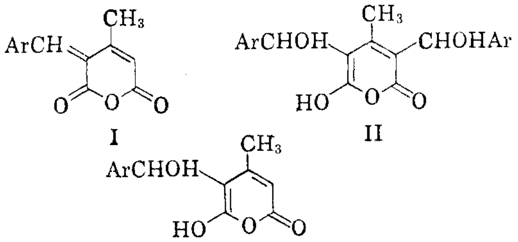
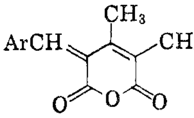
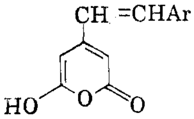
As a part of a continuing study designed to provide additional information about the chemistry of β-methylglutaconic acid and its derivatives which are of current importance as intermediates in the biosynthesis of cholesterol[1] we have extended our previous studies[2,3] in which we noted differences in the behavior of glutaconic anhydride and β-methylglutaconic anhydride in their reactions with aromatic aldehydes. The ease of formation of the arylidene structure (I) from the β-methyl substituted anhydride was attributed to two possible factors: the steric inhibition of further condensation of the aldehyde in the α-position, leading to structures such as II, and increased ease of dehydration of the carbinol III as a result of the electron releasing characteristics of the β-methyl group. In order to evaluate the relative importance of these two factors we have studied the reaction of α,β-dimethylglutaconic anhydride with aromatic aldehydes and diazonium salts. Using techniques described previously,[2-4] this anhydride condensed readily with aromatic aldehydes to give 24–39% yields of arylidene structures (IV). The data are summarized in Table I. Although a refined study of the yields obtainable in these reactions was not made, it appears that this reaction, at least, shows no improvement over the reaction with β-methylglutaconic anhydride. From this it is concluded that the ease of dehydration of the carbinol, through the process illustrated in VI, is a more important factor in determining the course of this reaction than is further condensation of the aldehyde in the ortho position. The latter possibility, completely eliminated in the reaction of the α,β-dimethyl anhydride, results in no marked change in the character of the reaction. It is anticipated, therefore, that replacement of the β-methyl group with a more effective electron release group would result in a marked increase in the ease of formation of structures of the arylidene (I, IV) type.



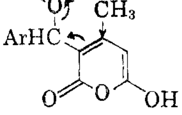
III



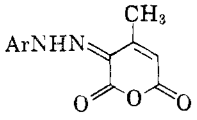
IV



V



VI



VII

There remains a possibility, not previously considered in this series, that the aldehyde con-

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(1) H. Rudney, *J. Am. Chem. Soc.*, **76**, 2595 (1954); **77**, 1698 (1955); J. L. Rabinowitz *et al.*, *J. Am. Chem. Soc.* **77**, 1295 (1955); **76**, 3037, 5168 (1954); K. Bloch, L. C. Clark, and I. Harary, *J. Biol. Chem.*, **211**, 687 (1954).

(2) Richard H. Wiley and H. G. Ellert, *J. Am. Chem. Soc.*, **77**, 5187 (1955).

(3) Richard H. Wiley, E. L. DeYoung, and N. R. Smith, *J. Am. Chem. Soc.*, **76**, 1675 (1954).

(4) Richard H. Wiley and C. H. Jarboe, *J. Am. Chem. Soc.*, **77**, 403 (1955).

TABLE I

γ-Arylidene-α,β-dimethylglutaconic Anhydrides

				Analysis			
				Carbon %		Hydrogen %	
Aryl Group	Color	M.P.,[a] °C.	Yield, %	Calcd.	Found	Calcd.	Found
p-Dimethylaminophenyl	Purple	237–239E	30	70.83	70.15	6.32	6.07
p-Diethylaminophenyl	Purple	163B	24	72.21	71.93	7.07	6.81
3,4-Dimethoxyphenyl	Yellow	159–160E	39	66.66	66.64	5.59	5.54
3,4-Diethoxyphenyl	Yellow	139–141B	37	68.34	67.98	6.37	6.23
1-Naphthyl	Orange	192–194E	33	77.68	77.77	5.07	4.80

[a] E, ethyl acetate; B, benzene.

densation takes place at the β-methyl group to give a structure V. In order for this reaction to occur the methyl group must be considered to be activated by the principle of vinylogy as one would expect the methyl group of ethyl crotonate or ethyl β,β-dimethylacrylate to be activated. Although there are analogies for such activation—for example, the base-catalyzed condensation of ethyl oxalate with ethyl crotonate to give diethyl oxaloacetate[5]—the analogy does not hold for the aldehyde condensations. It has been shown[6] that the base-catalyzed condensation between benzaldehyde and either crotonic acid or β,β-dimethylacrylic acid takes place at the α-carbon atom with rearrangement of the double bond. Thus, crotonic acid gives α-benzylidenevinylacetic acid. If such a reaction occurred with β-methylglutaconic anhydride, the accepted structure IV would result. At present there seems to be no more direct basis than this comparison for eliminating structure V. Positive identification of a band characteristic of the methyl group at 3.5 μ in the infrared is not practical because of the lack of resolution in this region using pellet techniques and the insolubility of the anhydride and its derivatives in solvents such as carbon disulfide and carbon tetrachloride which are transparent in this region. It is further interesting that apparently none of the known transformation and interconversions[7] of products obtained from this aldehyde-anhydride condensation can be used to clearly eliminate the possibility of structure V.

Coupling of α,β-dimethylglutaconic anhydride with a variety of aryldiazonium salts, using techniques previously described,[1-3] has given the γ-arylhydrazono derivatives (VII) listed in Table II.

EXPERIMENTAL

α,β-Dimethylglutaconic anhydride was prepared from the corresponding acid,[8] m.p. 103°, by cyclization with acetyl chloride on heating. In our hands the anhydride, b.p. 138–140°/3 mm, solidified, m.p. 38–42°, but could not be recrystallized. The derivatives listed in Tables I and II were prepared by procedures described in previous reports.[1-3]

TABLE II

γ-Keto-α,β-Dimethylglutaconic Anhydride Arylhydrazones

				Analysis Nitrogen %	
Aryl Group	Color	M.p.,[a] °C.	Yield, %	Calcd.	Found
Phenyl	Orange	167–170H	49	11.47	11.50
p-Nitrophenyl	Yellow	214–218H	62	14.53	14.60
p-Tolyl	Yellow	177–178E	50	10.85	11.07
o-Anisyl	Orange	185–188F	29	10.21	10.31

[a] H, glacial acetic acid; E, ethyl acetate-petroleum ether; F, ethyl acetate or benzene.

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Synthesis of 5,6,7-Trimethoxyindole, a Possible Intermediary Metabolite of Mescaline[1]

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The hypothesis that the currently designated psychotomimetic substances owe their unique physiological activity to an indole nucleus has been proposed by several investigators.[4-8] This has

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[2] Battelle Memorial Institute.

[3] Fels Research Institute.

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