Anal. Calcd. for $C_{26}H_{23}NO$: C, 85.44; H, 6.35; N, 3.83. Found: C, 85.59; H, 6.46; N, 3.95.

m-Tritylanisole. The product from the tritylation of *o*-anisidine was deaminated by dissolving 4 g. of this material in 150 ml. of acetic acid and adding 120 ml. of 50% hypophosphorous acid. This clear solution was cooled to 0° and 4 g. of sodium nitrite was added. The mixture was allowed to stand for 2–3 hr. and thus reach room temperature. A solid precipitated which was removed by filtration and recrystallized from a mixture of toluene and petroleum ether. Sublimation gave *m*-tritylanisole with a melting point of 169°–170°. The yield was *ca.* 60%.

Anal. Calcd. for $C_{26}H_{22}O$: C, 89.10; H, 6.33. Found: C, 89.45; H, 6.60.

m-Tritylphenol. The ether prepared above was cleaved with hydrobromic acid in a conventional manner to yield *m*-tritylphenol with a melting point of 278°–280°. The infrared spectrum of this material had a fairly strong absorption peak at 12.8 μ, characteristic of a meta disubstituted benzene. The yield was ca. 60%.

Anal. Calcd. for $C_{25}H_{20}O$: C, 89.24; H, 5.95. Found: C, 89.11; H, 6.21.

Structure proof for m-tritylanisole. Aniline was tritylated in the usual way with *m*-methoxyphenyldiphenylcarbinol (from *m*-bromoanisole and benzophenone, *via* the Grignard reagent). The resulting *m*-methoxyphenyl-*p*-aminophenyldiphenylmethane was deaminated in the same manner described for *o*-methoxy-*p*-tritylaniline to give *m*-tritylanisole. The latter gave no depression in a mixed melting point with material obtained from the tritylation product of *o*-anisidine. The infrared spectra of the two materials were identical. Both could be cleaved to yield *m*-tritylphenol.

Tritylphenetoles. The tritylphenetoles were isolated from their respective reaction mixtures obtained from the rate studies. The *para*-ethyl ether melted at 189°–190°.

Anal. Calcd. for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found: C, 89.21; H, 6.76.

The *meta* ethyl ether melted at 139°–140°.

Anal. Calcd. for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found: C, 88.84; H, 6.60.

Acknowledgment. The authors are grateful to the National Science Foundation whose financial assistance made this work possible.

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Reaction of Hydroxylamine with Ethyl α-(2,2,2-Trichloroethylidene)acetoacetate

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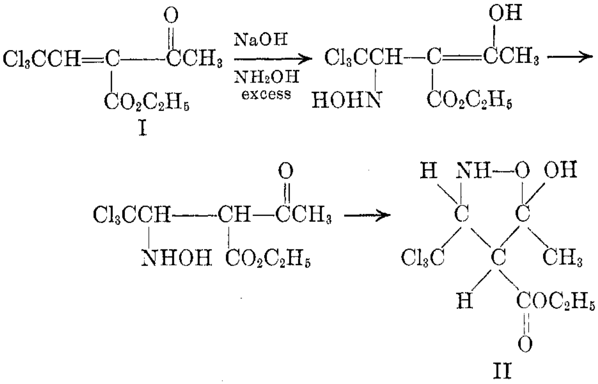
The preparation of ethyl α-(2,2,2-trichloroethylidene)acetoacetate (I) by the reaction of chloral with ethyl acetoacetate in the presence of acetic anhydride, was reported by Claisen and Matthews.[2]

$$Cl_3CCHO + H_2C(CO_2C_2H_5)COCH_3 \xrightarrow{Ac_2O} Cl_3CCH{=}C(CO_2C_2H_5)COCH_3 + H_2O$$

We have found that the use of basic catalysts, to effect the condensation, results in considerably lower yields. In an effort to prepare an oxime of this substance, we obtained a crystalline derivative which exhibited the analysis required for an addition rather than a condensation reaction product. An infrared study of the hydroxylamine addition product showed no apparent carbon to carbon or carbon to nitrogen double bonds while the ethyl α-(2,2,2-trichloroethylidene)acetoacetate (I) did show a band (6.1 μ) for the carbon to carbon double bond. It was therefore concluded that no oxime was present in the reaction product but that a probable 1,4-addition of hydroxylamine to ethyl α-(2,2,2-trichloroethylidene)acetoacetate had occurred to form a single racemate of ethyl α-(2,2,2-trichloro-1-hydroxaminoethyl)acetoacetate. To our knowledge, such an exclusive addition of hydroxylamine to an α,β-unsaturated ketone is unique. The probable reactions occurring are shown below.



Ethyl α-(2,2,2-trichloroethylidene)acetoacetate (I) showed a rather broad and complex carbonyl band at 5.8 μ whereas its addition product with hydroxylamine exhibited a simple and very sharp carbonyl band at 5.7 μ. In the absence of predictable[3] evidence for both ester and ketonic (possibly enolized) bands in the final product, a cyclic structure (II) is suggested tentatively for it.

By arrangement with the Chemical-Biological Coordination Center, 2101 Constitution Ave., Washington 25, D. C., the trichloroketo ester and the hydroxamino ester, herein described, were tested for various types of biological activity, but no significant results were obtained.

EXPERIMENTAL

Ethyl α-(2,2,2-trichloroethylidene)acetoacetate (I). The method briefly described by Claisen and Matthews[2] was employed. A solution of 200 ml. (301 g. or 2 moles) of chloral, 254 ml. (260 g. or 2 moles) of ethyl acetoacetate and 190 ml. (204 g. or 2 moles) of acetic anhydride was refluxed for 18 hr. The ethyl α-(2,2,2-trichloroethylidene)acetoacetate distilled at 99–100° at 1 mm. on a 10-inch Widmer column; yield 203 g. (39% based on ethyl acetoacetate),

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(1) Bristol Laboratories Research Associate (R. M. H.) and Research Fellow (J. R.) of The Ohio State University Research Foundation (Project 224).

(2) L. Claisen and F. E. Matthews, *Ann.*, **218**, 175 (1883).

(3) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen Co., Ltd., London, 1954, p. 157.

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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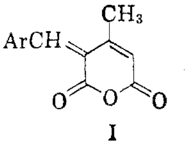
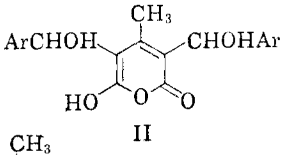
As a part of a continuing study designed to provide additional information about the chemistry of β-methylglutaconic acid and its derivatives which are of current importance as intermediates in the biosynthesis of cholesterol[1] we have extended our previous studies[2,3] in which we noted differences 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.



I



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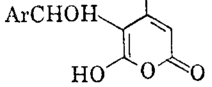

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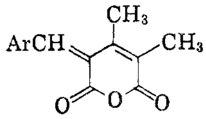
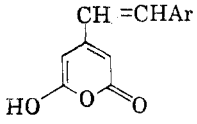
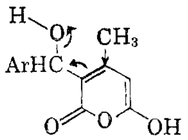


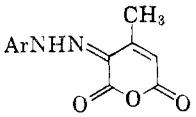
IV



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).

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