zene followed by vacuum sublimation at 170° (0.05 mm.), m.p. 285–286°.

Anal. Calcd. for $C_{22}H_{32}O_2$: C, 80.55; H, 9.83. Found: C, 80.93; H, 9.56.

Infrared absorption in potassium bromide pellet was 2941, 2882 (C—H), 1715 cm.$^{-1}$ (C=O).

Dehydrogenation of Ib.—A mixture of isobisadduct, 100 mg., and 100 mg. of palladium black were heated at 300° for 1 hr. During the heating process a white solid sublimed on the side of the tube; subsequently the green fluorescence of dibenz[*a,h*]anthracene appeared. The product was extracted with benzene and chromatographed on activated alumina to give several fractions. Dibenz[*a,h*]anthracene, m.p. 264–265°, was eluted with benzene, 14 mg. (yield 16.2%), melting point undepressed on admixture with an authentic sample.

Acknowledgment.—This work was supported by Grant C5946 from the National Cancer Institute, National Institute of Health, U. S. Public Health Service, and by Grant L-46 of the American Cancer Society, New York, New York.

A Reinvestigation of the Condensation of Ethyl Tricarballylate with Benzaldehyde

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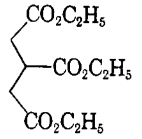
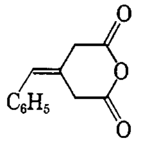
Received March 31, 1964

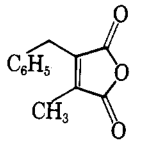
Müller[1] observed that ethyl tricarballylate (1,2,3-tricarboethoxypropane, I), benzaldehyde, and sodium ethoxide reacted to give a mixture of acidic esters which, upon saponification, followed by acidification and steam distillation, yielded an acid anhydride, $C_{12}H_{10}O_3$, m.p. 44–45°. This compound could not be converted to the free acid as acidification of its salts gave only the anhydride. On the basis of the elemental analysis, the neutralization equivalent and the elimination of several isomeric structures, Müller proposed that the compound was β-benzylideneglutaric anhydride II. In this paper evidence is presented which shows the compound to be benzylmethylmaleic anhydride III.



I



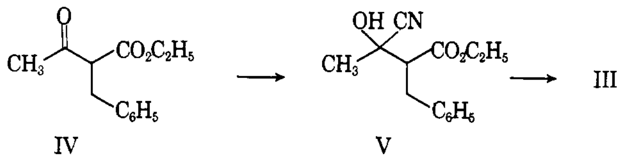
II



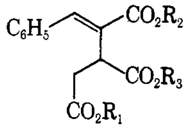
III

The anhydride was prepared according to Müller's directions,[1] except that the base-catalyzed condensation was effected by sodium hydride in benzene.[2] The product (m.p. 42.5–43.0°), isolated in 2% yield, had the elemental composition reported by Müller. The infrared spectrum showed bands at 1850, 1810, and 1760 cm.$^{-1}$, typical of a maleic anhydride moiety[3]; the ultraviolet spectrum in cyclohexane showed a maximum at 243 mμ (ϵ 5400); and the nuclear magnetic resonance spectrum consisted of three singlets at τ 2.87, 6.34, and 8.08 of relative areas 5.0:2.0:3.0. These spectra are clearly inconsistent with the structure of β-benzylideneglutaric anhydride and indicate the correct structure is that of benzylmethylmaleic anhydride III.

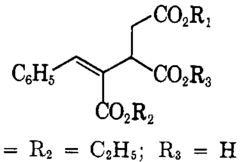
In order to confirm the structural assignment, benzylmethylmaleic anhydride III was synthesized by an alternate route. Triethylamine-catalyzed addition of hydrogen cyanide to ethyl 2-benzylacetoacetate (IV) afforded a mixture of the diastereomeric cyanohydrins V along with some unreacted keto ester IV. This mixture on being heated at reflux with concentrated hydrochloric acid afforded as neutral products, 4-phenylbutan-2-one (presence inferred from infrared band at 1720 cm.$^{-1}$) and the anhydride III which was separated by fractional crystallization. The latter was shown by mixture melting point determination and comparison of the ultraviolet and infrared spectra to be identical with the anhydride prepared according to Müller's directions.



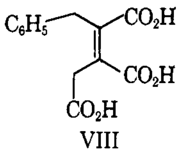
The reaction sequence which is considered to account best for the formation of III is shown below. Benzaldehyde condenses with ethyl tricarballylate in the manner of the Stobbe condensation[2] to give a mixture of acidic esters VIa and VIIa. Migration of the double bond of VIa or VIIa under the conditions of the condensation (or during the subsequent saponification) gives after saponification the triacid VIII which readily decarboxylates. Loss of water gives the anhydride III. It should be noted that the anhydride is derived from a "normal" Stobbe product (condensation occurring at a *methylene* carbon of ethyl tricarballylate).



VIa, $R_1 = R_2 = C_2H_5$; $R_3 = H$
b, $R_1 = H$; $R_2 = C_2H_5$; $R_3 = H$
c, $R_1 = C_2H_5$; $R_2 = H$; $R_3 = H$
d, $R_1 = H$; $R_2 = C_2H_5$; $R_3 = C_2H_5$



VIIa, $R_1 = R_2 = C_2H_5$; $R_3 = H$
b, $R_1 = H$; $R_2 = C_2H_5$; $R_3 = H$
c, $R_1 = C_2H_5$; $R_2 = H$; $R_3 = H$
d, $R_1 = H$; $R_2 = C_2H_5$; $R_3 = C_2H_5$



VIII

An alternative scheme for the formation of the anhydride III involves the formation of the acidic esters VId and VIId by the intermediacy of a six-membered lactone in the Stobbe condensation. These compounds would be at best only minor products of the condensation because of the known preference for the formation of five rather than six-membered lactonic intermediates

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(1) H. Müller, *Ber.*, **39**, 3590 (1906).

(2) W. S. Johnson and G. H. Daub, *Org. Reactions*, **6**, 1 (1951).

(3) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p. 45.

during Stobbe condensations.[4] However, the migration of the double bond of VId or VIId (yielding VIII after saponification) should be more favored than the case of VIa or VIIa since the proton which must be abstracted is further removed from the carboxylate anion.

A second crystalline compound [m.p. 191–192°; $C_{15}H_{16}O_6$; $\lambda_{\max}^{\mathrm{EtOH}}$ 263 mμ (ε 19,700); $\nu_{\max}^{\mathrm{KBr}}$ 3400–2600, 1745, 1715, and 1700 cm.$^{-1}$], also derived from a "normal" Stobbe product, was isolated from the saponification products in 17% yield (based on benzaldehyde). The nuclear magnetic resonance spectrum of this compound is summarized in Table I. On the basis of the spectral and analytical data it may be formulated as VIb, VIc, VIIb, or VIIc. However, the fact that the compound is completely unchanged after treatment with (a) boiling aqueous potassium hydroxide for 5 hr. or (b) boiling 7% sulfuric acid for 1 hr. eliminates VIc and VIIc from consideration. No attempt was made to distinguish between VIb and VIIb although VIIb seems to be the more likely since it has the more hindered ester function.

TABLE I

N.M.R. SPECTRUM[a] OF VIIb (OR VIb)

Assignment[b]	τ	Relative area	Multiplicity	J (c.p.s.)
$-\mathrm{C}H{=}\mathrm{C}<$	1.90	1	1	
C_6H_5-	2.65	5	1	
$-\mathrm{CH}<$	5.27	1	4	8.2, 5.5
$-\mathrm{C}H\mathrm{H}-$	6.60	1	4	8.2, 17.2
$-\mathrm{CH}H-$	7.31	1	4	5.5, 17.2
$\mathrm{O{-}C}H_2\mathrm{CH_3}$	5.62	2	4	7.0
$\mathrm{O{-}CH_2C}H_3$	8.63	3	3	7.0

[a] Spectrum was measured in trifluoroacetic acid. [b] The acidic protons were indistinguishable from the protons of the solvent.

Compounds resulting from condensation at the methyne carbon of ethyl tricarballylate were not found, but the conclusion that such compounds were not formed cannot be drawn since the two compounds isolated account for only 19% of the benzaldehyde used in the condensation.

Experimental

Condensation of Benzaldehyde and Ethyl Tricarballylate.—The condensation was effected by sodium hydride in benzene according to the method described[2] using 5.79 g. (0.0547 mole) of benzaldehyde, 21.33 g. (0.082 mole) of ethyl tricarballylate, and 1.96 g. (0.082 mole) of sodium hydride. The mixture of acidic esters obtained was dissolved in 5% aqueous sodium hydroxide and heated to boiling for 30 min. The reaction mixture was cooled, acidified with dilute hydrochloric acid, and extracted with ether. The ethereal solution was dried over sodium sulfate, filtered, and evaporated *in vacuo*. A portion of the residue crystallized and was collected on a filter and washed with ether. The crystals (compound VIIb or VIb) weighed 2.54 g. and melted at 188–191°. Repeated recrystallization from methanol–water gave crystals melting at 191–192°. This compound was recovered unchanged after treatment with boiling 20% potassium hydroxide or boiling 7% sulfuric acid. The spectra are described in the above discussion.

Anal. Calcd. for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.78; H, 5.61.

The noncrystalline mixture was steam distilled until the distillate was clear (750 ml.), and the distillate was extracted with ether which was then dried over sodium sulfate, filtered, and evaporated *in vacuo*. The resulting oil (210 mg.) crystallized on cooling to −10°. The crystals were twice recrystallized from pentane yielding 140 mg. of benzylmethylmaleic anhydride III, m.p. 41–42°. Sublimation at 70° and 0.08 mm. of Hg raised the melting point to 42.5–43.0°. The spectra are described in the above discussion.

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.26; H, 4.98. Found: C, 71.22; H, 5.16.

Benzylmethylmaleic Anhydride III (from Ethyl 2-Benzylacetoacetate).—Hydrogen cyanide was prepared[5] from 50.0 g. (1.02 mole) of sodium cyanide and collected in a flask cooled to −70°, then transferred to an ice–salt bath. Ethyl 2-benzylacetoacetate (10.0 g., 0.045 mole), prepared by the general procedure described,[6] was dissolved in 30 ml. of dry benzene, cooled to −5°, and added to the hydrogen cyanide. Triethylamine (1.0 ml.) was added and the mixture was stirred for 5 hr. at −5°. The reaction mixture was washed four times with ice-cold water, once with 4% sodium hydroxide solution, once with 2% hydrochloric acid, and finally with saturated sodium chloride solution. The benzene solution was dried over magnesium sulfate, filtered, and the benzene removed *in vacuo* to give 11.15 g. of an oil; $\nu_{\max}^{\mathrm{CHCl_3}}$ 3460, 2250 (very weak), 1740, and 1720 cm.$^{-1}$. Thin layer chromatography indicated that the oil consisted of a 9:1 mixture of diastereomeric cyanohydrins and starting material. A portion of the oily mixture (9.91 g.) was heated to reflux with 150 ml. of concentrated hydrochloric acid for 4 hr. The cooled reaction mixture was diluted with water and extracted with ether. The ether solution was washed several times with saturated sodium bicarbonate solution, once with water, then dried over sodium sulfate, filtered, and evaporated to give 1.00 g. of an oil which has all the infrared bands of methylbenzylmaleic anhydride and a band at 1720 cm.$^{-1}$ corresponding to 4-phenylbutan-2-one. The oil was steam distilled and 600 mg. of material was reisolated from the steam distillate by extraction with ether. After four recrystallizations from pentane there was obtained 140 mg. of benzylmethylmaleic anhydride, m.p. 42.5–43.0°. The ultraviolet and infrared spectra were identical with those of the anhydride prepared by the condensation, and the melting point of a mixture of the two materials was undepressed.

Acknowledgment.—The author wishes to thank Professor E. E. van Tamelen for valuable discussions and the National Science Foundation for a predoctoral fellowship. This research was supported by the U. S. Public Health Service through Grant No. AI-5102-02.

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[4] The condensation of diethyl glutarate with benzophenone fails under the same conditions which promote condensation of diethyl succinate with benzophenone in 90% yield; see W. S. Johnson, A. L. McCloskey, and D. A. Dunnigan, *J. Am. Chem. Soc.*, **72**, 514 (1950).

[5] K. H. Slotta, *Ber.*, **67**, 1028 (1934).

[6] H. E. Zaugg, D. A. Dunnigan, R. J. Michaels, L. R. Swett, T. S. Wang, A. H. Sommers, and R. W. DeNet, *J. Org. Chem.*, **26**, 644 (1961).

The Preparation of Parabanic Acids from 1,1,3-Trisubstituted Ureas *via* a Hofmann Elimination Reaction

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Received April 2, 1964

Previously we reported[1] a novel intramolecular cyclization of propynyl ureas to 2-imidazolones *via* an isolable intermediate imidazolinium salt. Cyclization was achieved with a variety of strong acids and chlorinating agents.[1c] Since the reaction of amides with oxalyl chloride[2] has been studied in our laboratories

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[1] (a) P. J. Stoffel and A. J. Speziale, *J. Am. Chem. Soc.*, **84**, 501 (1962); (b) P. J. Stoffel and A. J. Speziale, *J. Org. Chem.*, **27**, 3079 (1962); (c) P. J. Stoffel and A. J. Speziale, *ibid.*, **28**, 2917 (1963).

[2] A. J. Speziale and L. R. Smith, *ibid.*, **27**, 4361 (1962); **28**, 1805 (1963).