40–50%. Their ir, pmr, mass spectra, and elemental analysis (within 0.3% for C, H, and N) provided sufficient evidence for the correct structure and purity. The 60-MHz spectra of 0.5 *M* solutions in CDCl$_3$ were studied in degassed sealed tubes between the temperatures of 40 and 95°. The spectra were obtained on a Varian A-60A spectrometer. Temperatures were calibrated with ethylene glycol according to established procedures.[2]

Registry No.—**2**, 1903-64-6; **3**, 3815-24-5; **4**, 30721-92-7; **5**, 38308-87-1; **6**, 38308-88-2.

The Synthesis of 3,5-Dicarbethoxy-1,2,4-cyclopentanetrione. A Correction

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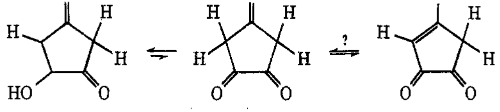
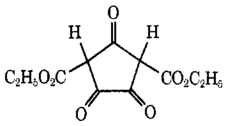
Received October 16, 1972

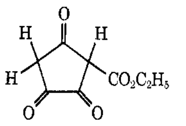
In connection with other work, we required 1,2,4-cyclopentanetrione (**1**), a material of some theoretical interest.[1] A convenient synthesis of **1** from 3,5-dicarbethoxy-1,2,4-cyclopentanetrione (**2**) has been reported.[2] In attempting to prepare **2**,[2-4] however, we encountered some experimental difficulty. In this process we have isolated and characterized 3,5-dicarbethoxy-1,2,4-cyclopentanetrione (**2**), an interesting and relatively unstable material with properties that differ considerably from those previously reported.[2-4] Furthermore, we would like to suggest that the properties previously reported for the title compound, **2**,[2-4] appear to best fit those for 3-carbethoxy-1,2,4-cyclopentanetrione (**3**), a hydrolysis product of **2**.



1

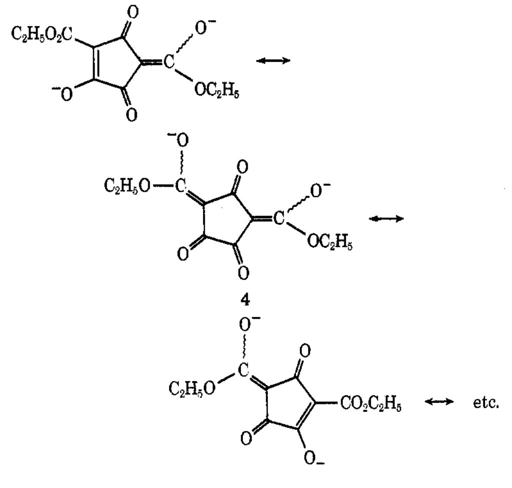


2



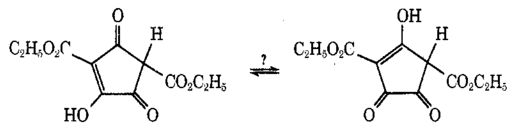
3

Treatment of diethyl acetonedicarboxylate, ethyl oxalate, and sodium or potassium ethoxide as reported[2,4] afforded a yellow salt which, following hydrolysis, could be converted to a viscous material which slowly crystallized. Trituration with a small amount of anhydrous ether gave **2** as a crude yellow solid. Recrystallization from anhydrous ether at 0° gave pure **2**, mp 107–109° dec. The nmr spectrum contained absorptions consistent with two nonequivalent ethoxy groups and a single methine hydrogen. The mass spectrum contained a parent peak at *m/e* 256 (calcd, 256). A neutralization equivalent of 127 (calcd, 128) was obtained by potentiometric titration. Two end points were clearly observable, with pK_a values of 2.1 and 5, estimated from the titration curve. In view of the similar enolic behavior of acylcyclopentanetriones[1c,5a] and related substances,[5b] the structure of this bis sodium or potassium salt, **4**, appears to be best represented as the following resonance hybrid.



4

The nmr spectrum of **4** in D$_2$O consisted of a single ethoxy resonance. Acidification of **4** regenerated the nmr spectrum of **2**, which appears to exist mainly in the diketone form **5** both in deuteriochloroform and in the solid phase (see Experimental Section).



5

In ethyl acetate, **2** readily dissolved and, upon standing, the solution darkened and a crystalline solid precipitated out, mp 145–147°. This new material, compound **3**, appears to be the material previously identified as the title compound.[2-4,6] The nmr and infrared spectra of this substance (**3**), which was isolated earlier by Wislicenus and Schöllkopf,[7] differs considerably from those of **2**. The nmr spectrum in acetone-d_6 consisted of a triplet and a quartet, characteristic of a single ethoxy group, and a singlet methine resonance which integrated as two protons, consistent with the enol form, **6**. In wet dimethyl-d_6 sulfoxide, two ethoxy resonances and a vinyl hydrogen were observed, suggesting an equilibrium between **6** and **7** or possibly **8** in this solvent. Compound **3** titrated (to a pH of 7) as a monoprotic acid, pK_a = 2.1, neut equiv 186 (calcd, 184). The mass spectrum of this material

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(1) (a) C. F. Sheley and H. Schechter, *J. Org. Chem.*, **35**, 2367 (1970); (b) C. H. Depuy and E. F. Zaweski, *J. Amer. Chem. Soc.*, **79**, 3923 (1957); C. H. DePuy and E. F. Zaweski, *ibid.*, **81**, 4920 (1959); C. H. Depuy and P. R. Wells, *ibid.*, **82**, 2909 (1960); (c) K. Hiraga, *Chem. Pharm. Bull.*, **13**, 1300 (1965).

(2) J. H. Boothe, R. G. Wilkinson, S. Kushner, and J. H. Williams, *J. Amer. Chem. Soc.*, **75**, 1732 (1953).

(3) v. P. Ruggli and K. Doebel, *Helv. Chim. Acta*, **29**, 600 (1946).

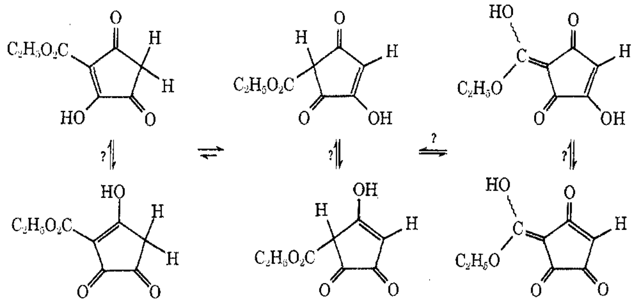
(4) E. Rimini, *Gazz. Chim. Ital.*, **26**, 374 (1896).

(5) (a) J. A. Elvidge and R. Stevens, *J. Chem. Soc.*, 2251 (1965); (b) S. Forsen and M. Nilsson in "Chemistry of the Carbonyl Group," Vol. 2, J. Zabicky, Ed., Interscience, New York, N. Y., 1970, p 157.

(6) We would like to thank Dr. R. G. Wilkinson[2] for kindly providing an infrared spectrum (solid phase) which confirmed the identity of the two materials.

(7) W. Wislicenus and K. Schollkopf, *J. Prakt. Chem.*, **95**, 269 (1917).

contained a parent peak at *m/e* 184 (calcd, 184). Upon standing at room temperature **3** slowly decomposes.



6 **7** **8**

When either **2** or **3** is refluxed in concentrated hydrochloric acid, **1** is obtained in good yield (70%), indicating that both **2** and **3** have the same gross structural features. The low yield in hydrolysis of **4** reported by earlier workers[3] is probably the result of **2** converting to **3**, which is accompanied by some decomposition. However, since **2** can easily be isolated in crude form and the hydrolysis to **1** proceeds in good yield, this represents an efficient synthesis of **1** (overall yield ~30%). Compound **3** (or **1**) could not be isolated from room-temperature hydrolysis of **2** in water.

Experimental Section

Melting points were taken on a Thomas Hoover melting point apparatus and are uncorrected. Microanalyses were determined by Galbraith Laboratories. Nmr spectra were recorded on a Varian T-60 spectrometer. Infrared spectra were measured using a Perkin-Elmer Model 137 spectrophotometer. Mass spectra were obtained on an Associated Electrical Industries MS12 instrument.

3,5-Dicarbethoxy-1,2,4-cyclopentanetrione (**2**).—Compound **2** was synthesized both according to the procedures of Rimini[4,8] and Boothe, *et al.*[2] Thus, potassium (2 g) was dissolved in absolute ethanol (7 g) in ether (50 ml), and ethyl oxalate (3.7 g) was added to the ice-cold solution. After a few minutes, diethyl acetonedicarboxylate[9] (5.2 g) was added dropwise and the mixture was stirred at room temperature for 24 hr. The reaction mixture was filtered and a yellow salt was isolated (9 g). A portion of this salt (2.3 g) was hydrolyzed with dilute sulfuric acid and immediately extracted with ethyl acetate. After drying ($MgSO_4$) and removal of the ethyl acetate under vacuum, the residue (1.33 g) slowly crystallized.[3] The nmr spectrum of this material in $CDCl_3$ indicated the presence of **2**, some diethyl acetonedicarboxylate, and a small but variable amount of **3** (*vide infra*). Washing the residue with a small amount of anhydrous ether afforded crude **2** (0.73 g), mp 85–90° dec. Additional amounts of **2** could be isolated by refrigerating the ether washings.

Hydrolysis of the yellow salt according to the method described by Ruggli and Doebel[3] gave similar results. Thus the potassium salt (2.6 g) in ether was ground up using a mortar and pestle and a few drops of concentrated hydrochloric acid were added. The ether layer was filtered and this process was repeated until the ether layer was colorless and the potassium salt was completely converted to potassium chloride. Evaporation of the ether, as before, afforded a residue similar in composition as previously reported.

Alternatively, sodium ethoxide [from sodium (1.6 g)], ethyl oxalate (5 cc), diethyl acetonedicarboxylate in benzene (200 cc), and anhydrous ether (50 cc) were refluxed under nitrogen for 1.75 hr.[2] The cooled solution was hydrolyzed with dilute sulfuric acid, the aqueous layer was extracted with ethyl acetate, and the organic fraction was distilled under reduced pressure. After standing under vacuum, the residue (6.78 g) solidified. The composition of this residue based on its nmr spectrum was basically the same as isolated above. Washing with anhydrous ether afforded crude **2** (3.22 g), mp 85–90° dec. An additional amount of **2** was isolated from the ether wash (0.5 g).

Compound **2** could be purified by recrystallizing from ether at 0°: mp 107–109°; nmr ($CDCl_3$, TMS) τ 8.24 (t, $J = 7$ Hz), 8.59 (t, $J = 7$ Hz, total of 6 H), 6.05 (s), 5.79 (q, $J = 7$ Hz), 5.56 (q, $J = 7$ Hz, total of 5.1 H), 0.23 (broad s, 0.9 H); ν_{max} (Nujol) 3105, 1770, 1740, 1710, 1680, and 1610 cm^{-1}; *m/e* 256 (calcd, 256); neut equiv 127 (calcd, 128, two end points observed potentiometrically). A yellow disodium salt was isolated after evaporation of the water: ν_{max} (Nujol) 1630, 1540 cm^{-1}; nmr (D_2O) τ 1.23 (t, 3 H, $J = 7$ Hz), 5.92 (q, 2 H, $J = 7$ Hz). Acidification of this salt regenerated **2** as identified by its nmr and infrared spectrum. Also present was a small amount of **3** (~10%).

The two preparations[2,4] gave, by the procedures outlined above, the same material, **2**, as determined by nmr, infrared, and melting point behavior.

Anal. Calcd for $C_{11}H_{12}O_7$: C, 51.56; H, 4.72. Found: C, 51.47; H, 4.68.

3-Carbethoxy-1,2,4-cyclopentanetrione (**3**).—Compound **2** (0.428 g, crude) was dissolved in ethyl acetate, or in an ether–ethyl acetate solution, and then allowed to stand. The solution gradually darkened, and after some 24 hr or more, crystals were deposited (200 mg). This material was recrystallized from ethyl acetate and sublimed: mp 145–147° dec, 145–158° ($CHCl_3$) (lit. mp 159–162°,[2,11] 140–156° dec,[4] 140° dec,[3] 145–150° dec[8]); pyridine salt mp 95–97° (lit.[8] mp 98°); nmr (acetone-d_6, TMS) τ 8.67 (t, $J = 7$ Hz, 3 H), 6.95 (s, 1.9 H), 5.67 (q, $J = 7$ Hz, 1.9 H), 1.45 (broad s, 1.07 H); nmr (wet DMSO-d_6, TMS) τ 8.77 (t), 7.0 (s), 5.85 (q), 8.84 (t), 5.94 (q), 3.63 (s). Based on the area ratio of the methine hydrogen (τ 7.0, 8) to the vinyl hydrogen (τ 3.63, 1), approximately 75% of the material is in the form of **2** in this solvent: ν_{max} (Nujol) 3210, 1760, 1710, 1670, and 1610 cm^{-1}; *m/e* 184 (calcd, 184). This material turned yellow and appeared to decompose upon standing at room temperature. It may also be hydroscopic. Attempts to obtain a satisfactory elemental analysis were not entirely successful. We obtained analysis for a hydrate of **3**, similar to those reported in the literature (for **2**)[2-4] when recrystallized from ethyl acetate.

Anal. Calcd for $C_8H_8O_5$: C, 52.17; H, 4.38. Calcd for $C_8H_8O_5 \cdot {}^1/_5H_2O$: C, 51.19; H, 4.47. Found: C, 51.24; H, 4.26.

The following analysis was obtained when a sample was recrystallized from chloroform and analyzed immediately:[10] C, 52.11, 51.79; H, 4.78, 4.55 (duplicate).

Conversion of 2 to 1,2,4-Cyclopentanetrione (**1**).[2]—Compound **2** (1.0 g, 3.9 mmol) was refluxed for 90 min in concentrated hydrochloric acid (80 ml). After the solution was concentrated to dryness, a dark brown material (0.38 g) was isolated. Compound **1** was separated by this material by sublimation (0.3 g, 70%) as reported: mp 172–174° dec (lit.[2] mp 172–173° dec); *m/e* 112 (calcd, 112) with major fragmentation at P − 42 (loss of C_2H_2O), P − 54 (loss of C_3H_2O), P − 57 (C_2HO_2), and a base peak at *m/e* 42 (C_2H_2O); nmr (TMS–DMSO-d_6) τ 7.09 (s, 2 H), 3.82 (s, 0.97 H), 1.17 (broad s, 1.06 H). The conversion of **2** (isolated in crude form) to **1** in 70% yield represents a very convenient synthesis of **1**.

Conversion of 3-Carbethoxy-1,2,4-cyclopentanetrione (**3**) **to 1,2,4-Cyclopentanetrione** (**1**).—Compound **3** (0.15 g) was dissolved in concentrated hydrochloric acid as reported above. A material identical with 1-hydroxy-1-cyclopentene-3,5-dione (**1**) isolated above was isolated in 80% yield.

Registry No.—**1**, 15849-14-6; **2**, 37951-06-7; **2** (2Na), 37950-90-6; **3**, 37950-91-7.

Acknowledgment.—I would like to thank the Research Corporation for a Cottrell Grant and the University of Missouri, St. Louis, for a summer fellowship.

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(8) See also W. Wislicenus and F. Melms, *Justus Liebigs Ann. Chem.*, **436**, 101 (1924).

(9) R. Adams and H. Chiles, "Organic Syntheses," Collect. Vol. I, A. H. Blatt, Ed., Wiley, New York, N. Y., 1964, p 237.

(10) We would like to thank Dr. Craig Warren and The Monsanto Chemical Co., St. Louis, Mo., for the analysis.