mm).[16] Vpc analysis on a 9-ft 7.5% Carbowax column a 125° and on a 20-ft silicone SE-30 column at 125° showed only one major peak, which, when collected, had λ_{max} 5.93 (shoulder at 5.86) and 6.18 μ; $\lambda_{max}^{95\%\ EtOH}$ 212 mμ; $\delta_{TMS}^{CCl_4}$ 0.93 [6 H, d, J = 6 cps, $(H_3C)_2CH$], 1.9–2.5 (3 H, broad multiplet), 5.61, 5.67, 5.74, 5.80, 6.15, 6.22, and 6.29 ppm [prominent peaks of an ABX pattern for the three vinyl protons very similar to that (5.76, 5.82, 5.89, 5.96, 6.20, 6.27, and 6.34 ppm) of methyl vinyl ketone].

Pure **5** tended to polymerize rapidly;[16] it afforded a 2,4-dinitrophenylhydrazone, mp 104–106.5°.

Anal. Calcd for $C_{13}H_{16}N_4O_4$: C, 53.42; H, 5.52. Found: C, 53.32; H, 5.64.

Crude Mannich base **4** afforded a 2,4-dinitrophenylhydrazone, mp 169–172°. The melting point reported[2] for the 2,4-dinitrophenylhydrazone of the claimed compound **1** prepared *via* this Mannich procedure was 171°. No attempt was made in the present investigation to determine the structure of the 169–172° material.

B. Using Dimethylamine Hydrochloride.—The same procedure described above was followed, using 12.1 g (0.147 mole) of dimethylamine hydrochloride. Distillation of the crude product afforded one main fraction of 12.96 g (56%) of **6**: bp 59–60° (1.25 mm); λ_{max} 5.83 μ; $\delta_{TMS}^{CCl_4}$ 0.90 [6 H, d, J = 6.5 cps, $(H_3C)_2CH$], and 2.14 ppm [s, $(H_3C)_2N$, accurate integration impossible owing to underlying methylene resonances].

Ethyl 2-Isopropyl-3-ethylenedioxybutyrate (9).—According to a procedure of Corey and Gregoriov,[17] a mixture of *ca.* 0.2 g of *p*-toluenesulfonic acid monohydrate, 5.0 ml of ethylene glycol, bp 63–66° (0.2 mm), and 5.01 g (0.0250 mole) of ethyl isopropylacetoacetate (**8**)[18] in 300 ml of dried benzene was refluxed for 48 hr attached to a water separator, cooled, and partitioned between 5% sodium bicarbonate solution and ether. The ether–benzene layer was washed with water and dried over magnesium sulfate. Evaporation of the solvents afforded 6.33 g of slightly yellow oil (theoretical yield of **9**: 6.28 g). Vpc analysis of this material on a 20% Carbowax column at 135° showed only one major component plus a very small amount of what was probably ethylene glycol (by retention time). The purified ketal **9** collected by vpc had λ_{max} 5.75 μ; $\delta_{TMS}^{CCl_4}$ 0.84 and 0.97 (2 d, each 3 H with J = 6 cps, $H_3C\underset{H}{C}CH_3$), 1.21 (3 H, t, CH_3CH_2), 1.36 (3 H, s, CH_3COO), *ca.* 2.1 [1 H, broad m, $HC(CH_3)_2$], 3.86 (4 H, bunched multiplet, OCH_2CH_2O), and 4.04 ppm (2 H, q, OCH_2CH_3).

Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 60.92; H, 9.31.

2-Isopropyl-1-butenone-3 (1). A. ***Via*** **Reduction of Ketal 9 with Lithium Aluminum Hydride.**—The 6.33 g of crude **9** prepared above was dissolved in 50 ml of anhydrous ether and the resulting solution was added dropwise to a stirred mixture of 2.07 g (0.0546 mole) of lithium aluminum hydride and 100 ml of anhydrous ether. After the addition was completed, the solution was allowed to stand at room temperature for 15 min, and then was refluxed for 30 min. Cold water (10 ml) was added cautiously, followed by 100 ml of 25% sulfuric acid, and the mixture was stirred for 15 min. The aqueous layer was separated and extracted with three 100-ml portions of ether. The combined ether layers were washed with water and saturated sodium bicarbonate solution, and dried over magnesium sulfate. Evaporation of the ether afforded 2.43 g (73% from **8**) of crude **7**: λ_{max} 2.90 and 5.82 μ; $\delta_{TMS}^{CCl_4}$ 0.92 [6 H, d, $(H_3C)_2CH$], 2.13 (3 H, s, H_3CC), and 3.94 ppm (1 H, s, OH). Attempts to purify **7** by vpc were unsuccessful since it decomposed to **1** on the column.

The procedure of Colonge and Cumet[6] for preparing **1** from **7** by distillation from iodine was used. The reported yield of 63% was not achieved in our hands, although extensive efforts to maximize yield were not made. From a 2.30-g (0.0177 mole) sample of crude **7** prepared from **9** there was obtained, after careful refractionation to remove the eliminated water and other impurities, only 0.39 g (20%) of **1**: bp 132–133° (lit.[5] bp 134–136°); λ_{max} 5.95 and 6.13 (w) μ; $\lambda_{max}^{95\%\ EtOH}$ 221 mμ (ϵ 9200); $\delta_{TMS}^{CCl_4}$ 1.00 [6 H, d, J = 6 cps, $(H_3C)_2CH$], 2.26 [3 H, s, $H_3CC({=}O)$], 2.98 [1 H, m, $HC(CH_3)_2$], 5.63 (1 H, d, J = 1 cps), and 5.90 ppm (1 H, s, ${}^{H}_{H}{>}C{=}C{<}$).

Analytically pure **1** was prepared by vpc on a 20% Carbowax column at 110°.

Anal. Calcd for $C_7H_{10}O$: C, 74.95; H, 10.78. Found: C, 74.73; H, 10.79.

The 2,4-dinitrophenylhydrazone derivative prepared from **1** by the usual procedure had mp 112.5–114°.

A very small amount of another substance appeared on vpc analysis of the distilled **1**. Its infrared spectrum (no OH or C=O stretch bands) and nmr spectrum {$\delta_{TMS}^{CCl_4}$ 1.05 [6 H, d, J = 7 cps, $(H_3C)_2CH$}, 1.39 (3 H, s, $H_3CC{<}^{O}_{O}$), 3.76 (4 H, bunched multiplet, OCH_2CH_2O), and 4.83 (1 H, m), and 5.16 ppm (1 H, d, J = 1 cps, ${}^{H}_{H}{>}C{=}C{<}$)] suggested that it was 2-isopropyl-3-ethylene–dioxybutene-1.

B. ***Via*** **Aldol Condensation of Methyl Isobutyl Ketone with Formaldehyde.**—According to the procedure of Colonge and Cumet,[6] a mixture of 250 ml of methyl isobutyl ketone, 62 ml of 40% aqueous formaldehyde, 1 g of sodium hydroxide, and 100 ml of 95% ethanol was allowed to stir at room temperature for 3 hr. The mixture was acidified to pH 6 with concentrated hydrochloric acid and reduced in volume to *ca.* 100 ml by distillation at aspirator pressure. The residue was filtered from precipitated salt and distilled to afford 20.73 g of crude **7**: bp 82–90° (8 mm); λ_{max} 2.88 and 5.83 μ; $\delta_{TMS}^{CCl_4}$ 0.92 [d, J = 6 cps, $(H_3C)_2CH$] and 2.14 [s, $H_3CC({=}O)$] ppm. Vpc analysis of this product showed three major and four minor components; no attempt was made to separate and identify these.

Distillation of this product from iodine (as described above) and redistillation afforded 7.64 g of **1** contaminated with a small amount of **5** (detected in the nmr vinyl proton region). In another preparation the only contaminant in the **1** was a small amount of **2**. Thus, usefully pure **1** can be prepared conveniently by the base-catalyzed aldol condensation route.

Registry No.—Methyl isobutyl ketone, 108-10-1; **1**, 7576-24-1; **4**, 3400-93-9; **4** hydrochloride, 7634-80-2; **5**, 2177-32-4; **5** 2,4-dinitrophenylhydrazone, 7634-82-4; **6**, 7641-02-3; **7**, 7641-03-4; 2-isopropyl-3-ethylenedioxybutene-1, 7634-83-5.

Acknowledgment.—The authors are grateful for the financial support provided by Public Health Service Research Grant AM-05014.

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[16] Preparation of **5**, bp 62° (52 mm), by the reaction of isoamoyl chloride with ethylene and aluminum chloride has been reported by P. R. Thomas, C. J. Tyler, T. E. Edwards, A. T. Radcliffe, and R. C. P. Cubbon, *Polymer*, **5**, 525 (1964). The product, which polymerized readily, was characterized by reduction to the saturated ketone and preparation of the semicarbazone of the latter.

[17] E. J. Corey and G. A. Gregoriov, *J. Am. Chem. Soc.*, **81**, 3124 (1959).

[18] W. B. Renfrow, Jr., *ibid.*, **66**, 144 (1944).

A Convenient Synthesis of 2-Methylcyclopentane-1,3-dione

VICTOR J. GRENDA, GLENN W. LINDBERG, NORMAN L. WENDLER, AND SEEMON H. PINES

Merck Sharp & Dohme Research Laboratories,
Merck & Company, Incorporated, Rahway, New Jersey 07065

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Previously[1] a number of methods have been described for the preparation of 2-methylcyclopentane-1,3-dione (II), a key intermediate for the total synthesis of steroids.[2] These syntheses suffer from their multiplicity of steps and/or their low over-all yields.

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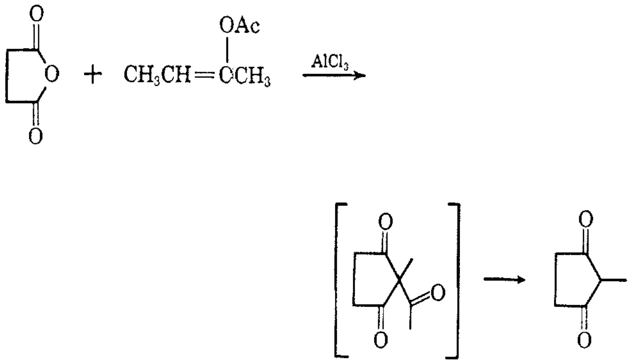
[1] H. Orchin and L. W. Butz, *J. Am. Chem. Soc.*, **65**, 2296 (1943); J. J. Panouse and C. Sannié, *Bull. Soc. Chim. France*, 1036 (1955); C. B. C. Boyce and J. S. Whitehurst, *J. Chem. Soc.*, 2022 (1959).

[2] T. B. Windholz and M. Windholz, *Angew. Chem., Intern. Ed. Engl.*, **3**, 353 (1964).

More recently Bucourt, *et al.*,[3] have reported a more direct approach through the cyclization of diethyl propionylsuccinate.

In this paper we wish to report a convenient, one-step preparation of II in good yield from available starting materials. When succinic anhydride is allowed to react with 2-buten-2-ol acetate (the major enol acetate of methyl ethyl ketone) in the presence of aluminum chloride, a crystalline product (II) is obtained directly after quenching the reaction in cold water. Recrystallization from water provides high quality product in yields of 80–85% of theory.



I II

The analogous reaction of isopropenyl acetate with succinic anhydride has been reported earlier by Merényi and Nilsson[4] to give 2-acetylcyclopentane-1,3-dione. In our reaction, no sign of the corresponding 2-methyl-2-acetylcyclopentane-1,3-dione intermediate (I) could be detected. Direct hydrolysis of the reaction mixture under mild conditions gave product II directly.

Nitrobenzene is the solvent of choice. From a perusal of the variables, optimal yields are obtained with 3.5 moles of aluminum chloride and 1.5 moles of 2-buten-2-ol acetate per mole of succinic anhydride. The reaction is carried out in two stages; the first stage of the condensation is run at low temperature to avoid loss of enol acetate by O → C acyl migration. Ultimately more forcing conditions are required to complete the over-all reaction, as evidenced by measurement of the hydrogen chloride evolved.

Experimental Section[5]

2-Methylcyclopentane-1,3-dione (II).—To a 2-l., three-necked flask protected from moisture by an atmosphere of dry nitrogen and fitted with a stirrer, condenser, and thermometer, there was added 1.0 l. of azeotropically dried nitrobenzene. Anhydrous aluminum chloride (466 g, 3.5 moles) and succinic anhydride (100 g, 1.0 mole) were added with stirring, the temperature being allowed to rise from 45 to 80°. The solution was heated at 110° for 20 min to form the complex and then cooled to room temperature. 2-Buten-2-ol acetate[6] (171 g, 1.5 moles) was added over 15 min while the temperature was maintained near 25° with cooling. After aging for 30 min, the reaction was reheated and aged at 110° for 2 hr. The reaction was cooled to room temperature and quenched by addition to 1.0 l. of water maintained at 5–10°. The addition was carried out with vigorous stirring over a 60-min period. The crude product crystallized from the heterogeneous system and was aged for 3 hr at 5°. The brown product was collected by filtration and washed with two 60-ml portions of nitrobenzene to displace the mother liquors. The residual nitrobenzene was removed by washing the cake with petroleum ether (bp 30–60°). The dried crude product weighed 126 g: $\lambda_{\max}^{0.1\,N\,\mathrm{HCl}}$ 252 mμ (ε 12,670).

Purification.—The crude was dissolved in 3400 ml of hot water (90°) and stirred for 30 min with 13 g of Nuchar C-190N.[7] The clarified filtrate was concentrated *in vacuo* to about 350 ml and aged with agitation at 5° for 1 hr. After filtering and washing with a small quantity of cold water, the product was air dried: 81.2 g; mp 212–214°; $\lambda_{\max}^{0.1\,N\,\mathrm{HCl}}$ 252 mμ (ε 18,000) (lit.[3] mp 210–212°).

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.02; H, 6.92.

From the recrystallization mother liquor there was obtained upon further concentration 2.8 g, mp 207–211°. The aqueous portion of the crude mother liquor was extracted continuously with methyl isobutyl ketone to provide an additional 7.8 g: mp 207–210°; $\lambda_{\max}^{0.1\,N\,\mathrm{HCl}}$ 252 mμ (ε 17,900). The over-all yield amounted to 82%. The product was identical in all respects with that obtained by known methods.[1,3]

Registry No.—II, 765-69-5.

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[3] R. Bucourt, A. Pierdet, G. Costerousse, and E. Toromanoff, *Bull. Soc. Chim. France*, 645 (1965).

[4] F. Merényi and M. Nilsson, *Acta Chem. Scand.*, **17**, 1801 (1963); **18**, 1368 (1964).

[5] Melting points are uncorrected. We are indebted to A. Kalowsky for ultraviolet spectra and to R. N. Boos and associates for elemental analyses.

[6] Available from Eastman Chemical Products, Inc., Kingsport, Tenn.

[7] Trade name for activated carbon available from Industrial Chemical Sales Division of the West Virginia Pulp and Paper Co., New York, N. Y.

Oxidation of β-Lactone Dimer of Dimethylketene

R. Donald Clark

Research Laboratories, Tennessee Eastman Company,
Division of Eastman Kodak Company, Kingsport, Tennessee

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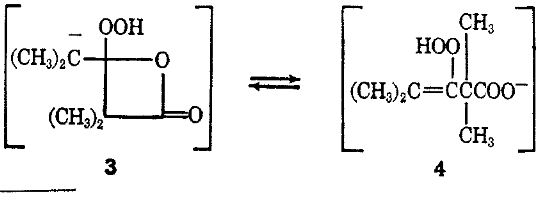
The oxidation of 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid β-lactone (1) with hydrogen peroxide in slightly basic aqueous media yields as final products isopropyl isobutyrate and carbon dioxide. There was evidence of the intermediate formation of sodium isopropyl dimethylmalonate (2).

The results may be interpreted as a nucleophilic attack of the hydroperoxide anion on **1**, resulting in a ring opening which gives the intermediate sodium 2,2,4-trimethyl-3-oxoperoxyvalerate which undergoes an intramolecular Baeyer–Villiger rearrangement (Scheme I). The ring intermediate is favored by the presence of *gem*-dimethyl groups.

This route is proposed because the lactone ring of **1** is easily opened by nucleophilic reagents[1,2] of which the hydroperoxide anion is an example. The alternative mechanism of hydrolysis followed by an intermolecular Baeyer–Villiger reaction was rejected because lactone **1** is relatively stable to hydrolysis under the conditions of the reaction in the absence of hydrogen peroxide.

In another alternative mechanism, the initial attack of the hydroperoxide anion at the isopropylidene double bond of **1** is followed by rearrangement of the intermediate (**3** or **4**) to half-ester **2**. The intermediates **3**



3 **4**

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[1] R. H. Hasek, R. D. Clark, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **27**, 60 (1962).

[2] "2,2,4-Trimethyl-3-hydroxy-3-pentenoic Acid, β-Lactone," Eastman Chemical Products, Inc., Kingsport, Tenn., 1961, Technical Data Sheet No. X-129.