tions, this example shows that substituted acroleins can be synthesized readily by the dithiane method.

We have encountered several limitations to the $HgO-BF_3$ procedure. Thus, attempted hydrolysis of 2-benzoyl-1,3-dithiane to the α-ketoaldehyde afforded benzoic acid (73%) as the only isolable product. Also, the dithianes of enolizable ketones could not be hydrolyzed successfully by our method. Poor material balance was obtained, and yields of only 20–30% of the ketone could be isolated from cyclohexanone or cyclopentanone dithianes.[7] However, 2,2-diphenyl-1,3-dithiane was hydrolyzed readily to benzophenone (86%).

Experimental Section

With the exception of II, the dithianes in Table I were prepared according to ref 1 and literature cited therein. Commerical red mercuric oxide and tetrahydrofuran were used directly unless otherwise specified. Boron trifluoride etherate was distilled at reduced pressure from calcium hydride before use.

General Procedure for Hydrolysis of 2-Substituted 1,3-Dithianes.—Red mercuric oxide (2 molar equiv), 2 molar equiv of boron trifluoride etherate, and 15% aqueous tetrahydrofuran (10 ml/g of dithiane) were stirred vigorously in a three-neck flask equipped with a dropping funnel and a nitrogen inlet tube. The dithiane (1 molar equiv) was dissolved in the minimum of tetrahydrofuran and was added *via* the dropping funnel in the course of 10–15 min under nitrogen. Stirring was maintained for 10–20 min after addition was complete. In the course of this time, the red mercuric oxide gradually dissolved and a white precipitate appeared. All hydrolyses were carried out at room temperature except for entry 6, Table I. The latter case required 30 min at reflux to complete the reaction. Ethyl ether (2 vol) was then added, the precipitated salts were filtered, and the ether was washed to pH 10 with saturated sodium carbonate and to neutrality with saturated sodium chloride. After drying over magnesium sulfate, the ether was evaporated under vacuum to yield crude aldehyde. Analysis by nmr indicated complete consumption of starting material and formation of aldehyde (>90% pure) in the yields reported in Table I.

Acetaldiacetates. General Procedure.—The procedure described for hydrolysis was used except that mercuric acetate was substituted for mercuric oxide and dry acetic acid was used as the solvent. A white precipitate appeared immediately upon addition of the dithiane. The same work-up method as before afforded crude acetaldiacetates free of starting material and homogeneous by nmr spectroscopy.

2-(2-Acetoxy-3,3-diethoxypropyl)-1,3-dithiane (II).—2-Lithiodithiane was prepared by the usual method[1] from 8.03 g (0.067 mol) of 1,3-dithiane in 75 ml of dry tetrahydrofuran at −50°. A solution of 1,1-diethoxy-2,3-epoxypropane[6] (9.78 g, 0.067 mol) in 10 ml of dry tetrahydrofuran was then added dropwise at such a rate that the temperature was maintained at −30°. After 3 hr at −35°, the reaction was allowed to warm to room temperature. The reaction mixture was diluted with an equal volume of ether, washed with saturated sodium chloride, dried over magnesium sulfate, and evaporated under vacuum. Removal of residual solvent and unreacted dithiane was accomplished at 0.05 mm, 12 hr at room temperature, to yield 17 g of crude alcohol.

The alcohol was dissolved in pyridine (25 ml) and acetic anhydride (18 ml) was added. After 18 hr at room temperature, the mixture was poured into ice water and extracted twice with ether (100 ml). The ether layer was washed with copper sulfate solution to remove pyridine, dried over magnesium sulfate, and evaporated under vacuum to afford the crude acetate. Molecular distillation at 130° and 0.1 mm afforded 10–12 g of II as a colorless oil, pure by nmr analysis: ($CDCl_3$) δ 5.15 (1 H, d t, J = 5, 7 Hz), 4.45 (1 H, d, J = 5 Hz), 4.04 (1 H, t, J = 7 Hz), 3.62 (4 H, m), 2.81 (4 H, m), 2.13 (4 H, m), 2.05 (3 H, s), 1.20 (6 H, t, J = 7 Hz).

4,4-Diethoxy-2-butenal (III).—The distilled acetate II was hydrolyzed by the usual method (mercuric oxide–BF_3). The crude product, 3-acetoxy-4,4-diethoxybutanal, was homogenous by nmr: ($CDCl_3$) δ 9.72 (1 H, t, J = 2 Hz), 5.52 (1 H, m), 4.55 (1 H, d, J = 4.5 Hz), 3.61 (4 H, m), 2.72 (2 H, m), 2.03 (3 H, s), 1.18 (6 H, t, J = 7 Hz). The crude 3-acetoxy-4,4-diethoxybutanal (6.42 g) was dissolved in chloroform (10 ml) and 1,5-diazabicyclo[5.4.0]undec-5-ene (5.35 g) (Aldrich) was added dropwise with cooling to keep the temperature below 30°. The reaction was stirred 0.25 hr after addition was complete and then was diluted with hexane, washed twice with water, and dried over magnesium sulfate. After evaporation of solvent, the crude product was distilled at 45–50° (0.15 mm) to yield 4,4-diethoxy-2-butenal (3.6 g, 77%) as a colorless liquid. The nmr spectrum was in excellent agreement with that of known material:[8] ($CDCl_3$) δ 9.62(1 H, d, J = 7 Hz), 6.7 (1 H, d d, J = 16, 3 Hz), 6.32 (1 H, d d, J = 16, 7 Hz), 5.15 (1 H, d, J = 3 Hz), 3.60 (4 H, m), 1.22 (6 H, (t, J = 7 Hz).

Registry No.—II, 26958-39-4.

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(7) Tentative explanations for the poor recovery of starting material include acid-catalyzed mercuration of product ketone *via* the enol, and oxymercuration of possible thioenol ether intermediates. Some precedent exists for both reactions: A. Morton and H. Penner, *J. Amer. Chem. Soc.*, **73**, 3300 (1951); W. H. Watanabe and L. E. Conlon, *ibid.*, **79**, 2828 (1957).

(8) Prepared according to the method of L. Yanovskaya, B. Rudenko, V. Kucherov, R. Stepanova, and G. Kogan, *Izv. Akad. Nauk SSSR*, **12**, 2189 (1962).

Anomalous Dimerization of 5,5-Dimethyl-2-cyclohexene-1-one

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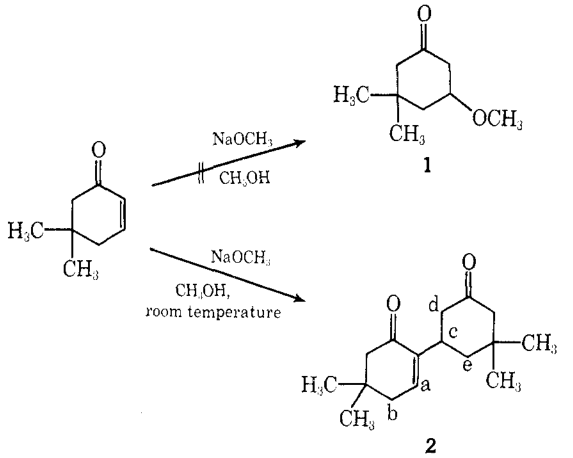
We recently became interested in preparing 3,3-dimethyl-5-methoxycyclohexanone (**1**) by the base-catalyzed addition of methanol to 5,5-dimethyl-2-cyclohexen-1-one utilizing a procedure described by Puetzer[2] for the preparation of 4-methoxy-2-butanone. Addition of 5,5-dimethyl-2-cyclohexen-1-one to anhydrous methanol containing a catalytic amount of sodium methoxide followed by neutralization with glacial acetic acid resulted in the precipitation of a colorless crystalline solid. The product obtained showed twin carbonyl peaks at 5.85 and 6.0 μ ($CHCl_3$) in the infrared. The absence of the $-OCH_3$ signal in the nmr definitely eliminated **1** as the structure. Elemental analysis and the m/e peak at 248 mass units pointed to a dimer of the starting material.



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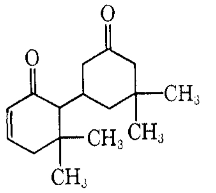
(2) B. Puetzer, C. H. Nield, and R. H. Barry, *J. Amer. Chem. Soc.*, **67**, 832 (1945).

The peak area ratios, chemical shift values, and spin-spin splittings in the 100-MHz nmr spectrum of the reaction product were consistent with the dimer structure 2. The triplet (J = 4.5 Hz) at 6.61 ppm was assigned to proton a of the dimer. In comparison, the chemical shift of the proton at this ring position in the starting material occurred at 6.78 ppm while the olefinic proton α to the carbonyl had a chemical shift of 5.87 ppm. From double irradiation at 6.61 Hz, protons b were identified as a doublet at 2.28 ppm. A complex multiplet at 3.12 ppm, having a peak area equal to proton a, was assigned to methine proton c. Upon double irradiation at 3.12 Hz, protons d were assigned to a doublet (J = 8.5 Hz) at 2.26 ppm and magnetically nonequivalent protons e were assigned to doublets (J = 7.0, J = 9.5 Hz) at 1.58 and 1.57 ppm. The ring methylene protons between the carbonyl and *gem*-dimethyl groups were recorded as singlets at 2.10 ppm for the cyclohexanone ring and at 2.25 ppm for the cyclohexenone ring of the dimer. The methyl groups on the cyclohexanone ring were magnetically nonequivalent and occurred at 1.05 and 0.95 ppm. The methyl groups on the cyclohexenone ring of the dimer were observed as a singlet at 1.00 ppm.

Recently, House[3] isolated a different dimer from the reaction of 5,5-dimethyl-2-cyclohexen-1-one with dilithium tris(1-hexynyl)cuprate. He has assigned structure **3** to this compound. We are postulating that our dimer, **2**, is formed by way of the mechanism of eq 1.



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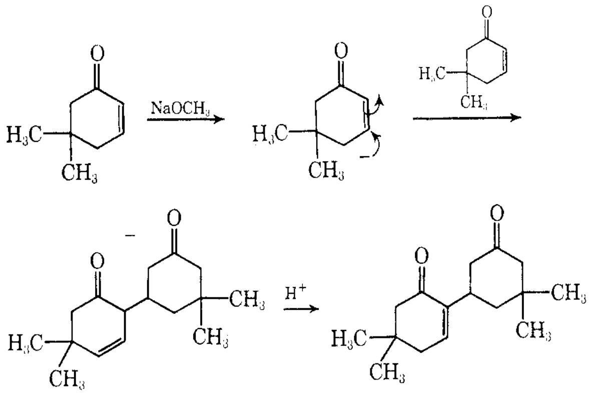

(1)

Alternatively, the dimer could arise by 1,4 addition of methoxide to the cyclohexenone, followed by dimerization, proton transfer, and ultimate loss of methoxide to yield the isolated product. Attempts to dimerize 2-cyclohexen-1-one in this manner were unsuccessful, only starting material or resinous products being obtained.

However, in related work, we have found that methyl mercaptan and propyl mercaptan added normally and in high yield to the double bond of both 2-cyclohexen-1-one and 5,5-dimethyl 2-cyclohexen-1-one in the presence of a basic catalyst (Triton B).

Presumably, the less basic character of the mercaptide anion precluded proton abstraction at the activated 4 position of the ring as depicted for the mechanism of eq 1.

Experimental Section

Boiling points are uncorrected; melting points are corrected. Infrared measurements were carried out with a Beckman IR-8 spectrophotometer. Nmr studies were made with the Varian A-60 and Varian HA-100 instruments.

5,5-Dimethyl-2-cyclohexen-1-one.—The general procedure of Gannon and House[4] was used to prepare this compound. A yield of 107 g (86%) was obtained from 1.0 mol of 3-ethoxy-5,5-dimethyl-2-cyclohexen-1-one after distillation through a 12-in. Vigreux column, bp 61-63° (15 mm).

Anal. Calcd for $C_8H_{12}O$: C, 77.4; H, 9.7. Found: C, 77.2; H, 9.7.

Dimerization of 5,5-Dimethyl-2-cyclohexen-1-one.—To a solution of 6.2 g (0.05 mol) of 5,5-dimethyl-2-cyclohexen-1-one in 10 ml of methanol was added 100 mg of sodium methoxide, and the resulting solution was stirred as the temperature slowly rose from 25 to 35°. The reaction mixture sustained itself at 35° for several hours after which stirring was continued for 3 days at room temperature. Neutralization of the solution with 0.5 ml of glacial acetic acid resulted in the precipitation of 1.2 g of a white solid, which was filtered and washed with water. The filtrate yielded an additional 2.9 g of product; the total yield of dimer was 4.1 g: mp 98-99°; ir ($CHCl_3$) 5.85 (C=O) and 6.0 μ (conjugated C=O); mass spectrum *m/e* 248.

Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.4; H, 9.7. Found: C, 77.3; H, 10.1.

Registry No.—2, 10517-07-4; 5,5-dimethyl-2-cyclohexen-1-one, 4694-17-1.

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[3] H. O. House and W. F. Fischer, *J. Org. Chem.*, **34**, 3615 (1969).

[4] W. Gannon and H. O. House, *Org. Syn.*, **40**, 14 (1960).