almost immediately upon completion of the addition. Heat was applied to maintain the temperature at 60° for 0.5 hr. The lower fluorocarbon layer (50 g) collected in the Dry Ice trap showed a major peak and a few minor peaks in the gas chromatographic analysis. Infrared analysis indicated the presence of terminal olefin (5.6 μ, weak) and internal olefins (5.75 and 5.85 μ). The major component (80%) was identified as a mixture of *cis*- and *trans*-butene-2 (5.75 μ).[14]

Registry No.—Perfluoroheptyl bromide, 375-88-2; perfluoro-2,3-dichlorobutane, 355-20-4; methylmagnesium chloride, 676-58-4.

Acknowledgments.—The author is indebted to Dr. J. D. Readio for the instrumental analyses and Mr. J. Krushnowski for laboratory assistance.

An Improved Aldehyde Synthesis from 1,3-Dithianes

E. Vedejs* and P. L. Fuchs

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

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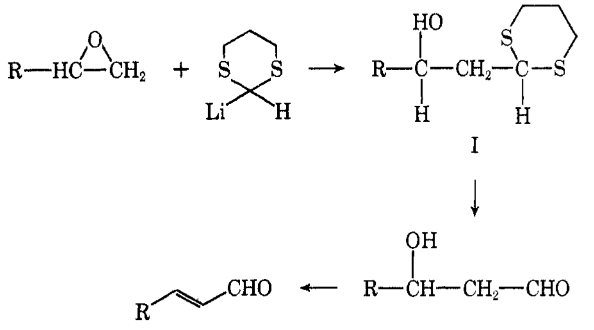
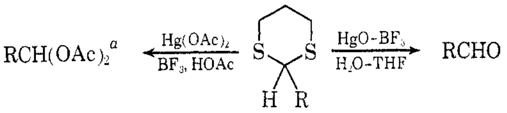
As part of a synthetic project, we required a general route to substituted acroleins. The dithiane method seemed to hold considerable promise in this direction since 2-(hydroxyalkyl)dithianes are readily available from epoxides,[1] and hydrolysis followed by dehydration should result in the desired products.



However, it became apparent that hydrolysis of I would pose difficulties. A thorough search of the literature for experimental details revealed only one example of hydrolysis of a 2-substituted 1,3-dithiane to an aldehyde, 2-phenyl-1,3-dithiane to benzaldehyde.[2,3] Accordingly, we examined the hydrolysis of some simple 2-alkyl-1,3-dithianes under conditions which hydrolyze 2,2-dialkyl-1,3-dithianes to ketones. Disappointingly low yields (20–40%) of heptanal were obtained from 2-*n*-hexyl-1,3-dithiane using $HgCl_2$ with HgO or $CdCO_3$ in refluxing aqueous methanol. Other published conditions[1a] such as the *N*-bromosuccinimide method or the silver nitrate method were even less successful and initial experiments failed to produce any aldehyde (nmr analysis) from 2-isopropyl-1,3-dithiane. Poor material balance was the rule in the various experiments, and in the mercuric chloride reactions, 30–40% of the starting material was lost, presumably due to the formation of insoluble mercury derivatives.

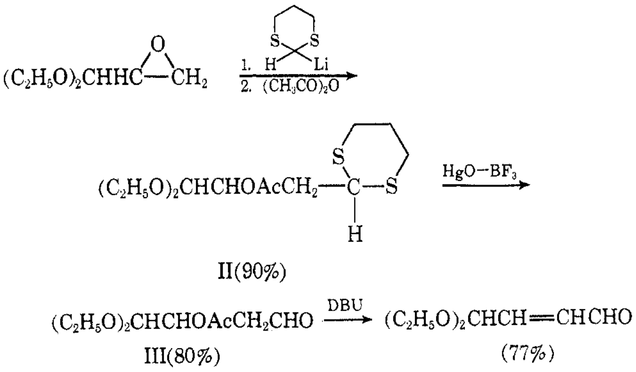
After screening a number of potential reagents,[4] we examined the combination of mercuric acetate and boron trifluoride etherate. Remarkably, a solution of this reagent in acetic acid effected the transacetalization of several 2-substituted 1,3-dithianes into the known acetaldiacetates (Table I) within a few minutes at room temperature. Under similar conditions, red mercuric oxide and boron trifluoride etherate in aqueous tetrahydrofuran hydrolyzed 1,3-dithianes to the corresponding aldehydes[5] in high yield. This method proved to be especially advantageous in the case of II, which was prepared from the epoxide of acrolein diethyl acetal.[6] The $HgO-BF_3$ reagent afforded the aldehyde in 80% yield, while $HgCl_2$ served only to destroy starting material. In addition to demonstrating the mildness of our condi-

Table I



Entry no.	Yield of acetal-diacetate, %	R	Registry no.	Yield of aldehyde, %
1	76[b]	C_6H_5-	5425-44-5	90[c]
2	73[b]	$C_6H_5CH{=}CH-$	26958-41-8	86[c]
3	78[c]	*i*-C_3H_7-	6007-25-6	78[e]
4		*n*-$C_6H_{13}-$	26958-42-9	60[d]
5		$(C_2H_5O)_2CHCHOAcCH_2-$		80[c]
6		$C_6H_5OCOC_6H_{10}-$	26958-43-0	84[c, f]

[a] E. Späth, *Monatsh. Chem.*, **36**, 29 (1915). [b] Yield of recrystallized product. [c] Yield of crude product, homogeneous by nmr. [d] Yield of pure aldehyde isolated by distillation. [e] Yield of aldehyde determined by glpc. [f] 1-Benzoyloxycyclohexanecarboxaldehyde.



DBU = 1,5-diazabicyclo[5.4.0]undec-5-ene

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[1] (a) D. Seebach, *Synthesis*, 17 (1969); (b) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **8**, 639 (1969); E. J. Corey and D. Seebach, *ibid.*, **4**, 1075, 1077 (1965).

[2] D. Seebach, B. W. Erickson, and G. Singh, *J. Org. Chem.*, **31**, 4303 (1966).

[3] Hydrolysis of a 2-alkyl-1,3-dithiane ($HgCl_2$, yield unspecified) is mentioned briefly by J. A. Marshall and H. Roebke, *Tetrahedron Lett.*, 1555 (1970). Transacetalization of a 2-alkyl-1,3,5-trithiane to the methoxyacetal is also reported in ref 1 without experimental details.

[4] Salts of Pb(III), Zn(II), and Tl(I) were tried without success. Copper(II) acetate with BF_3 produced some aldehyde (25% in the case of 2-*n*-hexyl-1,3-dithiane), but 50% of the starting material could not be accounted for.

[5] Aldehydes were also isolated from the reaction of dithianes with $Hg(OAc)_2-BF_3$ in dry *tert*-butyl alcohol, presumably *via* fragmentation of the corresponding *tert*-butyloxonium ion to aldehyde and isobutylene. Thus, cinnamaldehyde (78%) and cinnamaldehyde acetaldiacetate (13%) were produced from the corresponding dithiane, 2 mol of mercuric acetate, and 2 mol of boron trifluoride etherate in 200 mol of dry *tert*-butyl alcohol.

[6] D. I. Weisblat, B. J. Magerlein, D. R. Myers, A. R. Hanze, E. I. Fairburn, and S. T. Rolfson, *J. Amer. Chem. Soc.*, **75**, 5893 (1953).

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

John E. Engelhart*[1] and James R. McDivitt

Esso Research and Engineering Company,
Linden, New Jersey 07036

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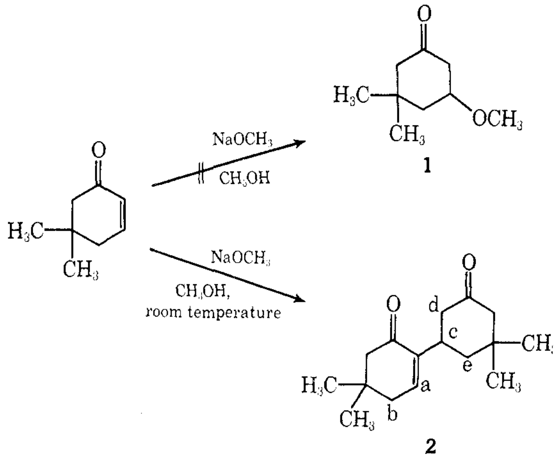
We recently became interested in preparing 3,3-dimethyl-5-methoxycyclohexanone (**1**) by the base-catalyzed addition of methanol to 5,5-dimethyl-2-cyclohexen-1-one utilizing a procedure described by Puetzer[2] for the preparation of 4-methoxy-2-butanone. Addition of 5,5-dimethyl-2-cyclohexen-1-one to 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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[1] Esso Agricultural Products Laboratory. To whom inquiries should be addressed: Union Camp Corp., P.O. Box 412, Princeton, N. J. 08540.

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