Preparation of Ethylene Acetals (1,3-Dioxolanes) from 2-Methoxyethyl Carboxylates via 1,3-Dioxolanium Ions

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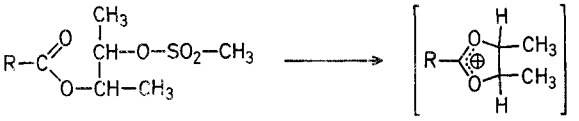
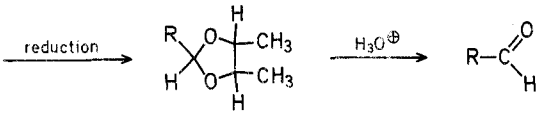
Aldehydes are often prepared only with considerable difficulty[1]. Since they are intermediate in oxidation state between carboxylic acids and primary alcohols, they are in principle accessible from either of these precursors by straightforward oxidation or reduction reactions. However, in many cases the reactivity of the aldehyde is comparable to or greater than that of the starting material, and further oxidation or reduction takes place. One of the attempts to resolve this problem has utilized the reduction of dioxolanium ions[2] (**2**), obtained by intramolecular alkylation of 3-mesyloxy-2-butyl carboxylates (**1**), and hydrolytic cleavage of the 1,3-dioxolanes **3** to give the aldehydes **4**.



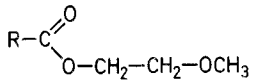
1 **2**



3 **4**

We report here an extension of this approach which affords a general method by which the reduction of carboxylic acid derivatives can be stopped at the aldehyde stage.

We have found that the most conveniently generated dialkoxycarbenium ions are the unsubstituted 1,3-dioxolanium ions **7** which are easily prepared by treatment of the readily available 2-methoxyethyl carboxylates (**5**) with triethyloxonium tetrafluoroborate in dichloromethane[3]. In general, the 1,3-dioxolanium tetrafluoroborates (**7**) are crystalline compounds and may be purified by recrystallization, although we have not found this to be necessary. The formation of the dioxolanium ion involves initial alkylation of the methoxy oxygen of **5** to give a new oxonium ion (**6**) which then undergoes cyclization to **7**[4,5].



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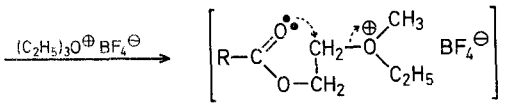

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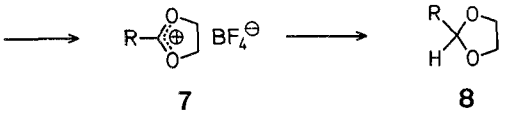

7 **8**

Difficulties resulting from insolubility of the dioxolanium salts in etheral solvents and from Lewis acidity of various reducing agents were overcome by the use of tetrabutylammonium borohydride. This reagent is conveniently prepared[6]

Table. Conversion of 2-Methoxyethyl Carboxylates (**5**) to 1,3-Dioxolanes (**8**).

R	Yield (%)[a]	b.p.[f]/torr (Lit.)	Purity (%)[b]
a C_6H_5	82	120°/5 (107–108°/13)[13]	99
b *c*-C_6H_{11}	76[c]	100°/3 (103–104°/15)[14]	94[d]
c C_6H_5—CH_2—	91[c]	110°/5 (98–99°/1)[15]	92
d *i*-C_3H_7	85[c]	120°/760 (123°/760)[13]	90
e *n*-C_7H_{15}	86[c]	100°/5 (117–119°/34)[16]	90
f C_6H_5—CH=CH—	80	110°/5 (84°/0.1)[17]	95
g C_6H_5—CO—$(CH_2)_2$	76[c]	140°/2	97

[a] Isolated yields for two steps after Kugelrohr distillation of the acetal.

[b] By G.L.C. Conditions: 10% Carbowax 20 M on Chromosorb W; 5 ft × 1/8 in.

[c] The crude reaction mixture was added dropwise to a solution of reducing agent in this case as the dioxolanium salt is quite soluble in dichloromethane.

[d] The crude product was subjected to rapid chromatography on alumina using ether/petroleum ether (1:1) as eluent.

[e] The reducing agent was added as a solution in acetone (see text).

[f] Bath temperature.

from sodium borohydride and tetrabutylammonium salts and is readily soluble in dichloromethane. Using this mild reducing agent we have been able to effect conversion of the esters **5** to the acetals **8** in overall isolated yields of ~75–85% after Kugelrohr distillation; the aldehydes are readily obtained from the acetals by mild acid hydrolysis. The Table summarizes the results for a series of esters; in all cases, the acetals (or their hydrolysis products) were shown to be identical with authentic samples by G.L.C., N.M.R., and I.R. A detailed procedure is given for the preparation of 2-styryl-1,3-dioxolane (**8f**).

Although both the isolation[4,5,10,11] and reduction[2,10–12] of dioxolanium ions have been reported, previous procedures have been of distinctly limited synthetic value. The procedure reported here affords a general method for the preparation of the dioxolanium ions from carboxylic acids and utilizes a mild and selective new reducing agent to avoid the problems of heterogeneous reactions.

The isolable 1,3-dioxolanium salts **7** may also be subjected to reaction with a variety of nucleophiles other than hydride, including those which would react with the starting ester **5** to give undesired products. For example, we have found in preliminary studies that the reaction of the dioxolanium ions **7** with alkyllithium reagents leads to good yields of ketone ethylene acetals.

The last two entries in the Table reveal a noteworthy feature of our method for the preparation of aldehydes. Thus, although borane is necessarily produced in the transfer of a hydride ion from borohydride to the organic cation, the double bond of the styryl group in derivative **7f** is unaffected; neither hydroboration of the unsaturated acetal **8f** nor conjugate addition[2] to dioxolanium ion **7f** is observed. In the case of the 1,3-dioxolanium salt **7g** which possesses a free carbonyl group, reduction of this group can be suppressed by adding the reducing agent as a solution in acetone: thus, the ketonic acetal **8g** is isolated in good yield.

2-Styryl-1,3-dioxolane (8f):

A solution of 2-methoxyethyl *trans*-cinnamate[7] (**5f**; 2.0 g, 10 mmol) and triethyloxonium tetrafluoroborate[8] (4.0 g, 21 mmol) in anhydrous dichloromethane (10 ml) is heated at reflux under nitrogen for 20 h in a flask equipped with a side arm containing a fritted glass disc. The mixture is cooled to −78°, and the precipitated 1,3-dioxolanium salt **7f** is filtered by forcing the solvent through the fritted disc with a positive pressure of dry nitrogen. The salt is washed with cold dichloromethane (2 × 5 ml), and dichloromethane (10 ml) is added to the flask[9]. To the mixture is then added dropwise a solution of tetrabutylammonium borohydride (3.0 g, 12 mmol) in dichloromethane (20 ml) while the mixture is cooled in a dry-ice/acetone bath with stirring under a nitrogen atmosphere. The resultant solution is poured into 10% aqueous sodium hydroxide (50 ml) at 0°. The layers are separated, and the organic solution is extracted with 1 *N* aqueous sodium hydroxide (2 × 25 ml), dried with potassium carbonate, and evaporated at reduced pressure. The crude product is taken up in ether (100 ml), the insoluble tetrabutylammonium salts are removed by filtration, and the ether is removed at reduced pressure. Short-path (Kugelrohr) distillation of the residue gives **8f** with a purity of 95%; yield: 1.37 g (80%); b.p. 120° (bath temperature)/5 torr.

This work was supported by grants from the Research Corporation and from the Petroleum Research Fund, administered by the American Chemical Society.

Received: July 23, 1974

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