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A NOVEL AND USEFUL METHOD FOR THE PREPARATION OF METHYL ESTERS FROM DIMETHYL ACETALS

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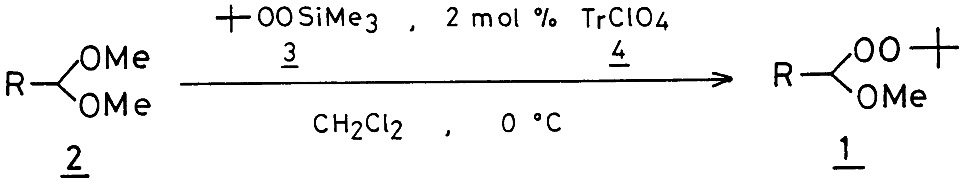
In the presence of a catalytic amount of trityl perchlorate, acetal-type peroxides are successfully prepared from dimethyl acetals and *t*-butyl trimethylsilyl peroxide in good yields. The peroxides thus obtained are converted to the corresponding methyl esters also in good yields.

The oxidation of aldehydes to carboxylic acids is one of the important transformations in organic synthesis, however, the reactions are generally carried out by the use of heavy metal oxides, such as $KMnO_4$, CrO_3, and Ag_2O. Thus, it is desired to develop a useful method for the preparation of carboxylic acids from aldehydes without using such heavy metal oxides. Further, when acetals (the protected aldehydes) are directly converted to the corresponding esters without a deprotection step, the reaction would be a more useful tool in considering synthetic strategies.

Now, we wish to report a convenient and useful method for the transformation of dimethyl acetals to methyl esters by the two-step procedure including i) the acetal exchange of dimethyl acetals to peroxides on treatment with *t*-butyl trimethylsilyl peroxide in the presence of a catalytic amount of trityl perchlorate1) and ii) the decomposition of the intermediate peroxides to methyl esters.

In the first place, the reaction conditions for the acetal exchange of dimethyl acetal of 3-phenylpropanal were investigated. And it was found that the acetal-type peroxide 1 was obtained in good yield when the acetal 2 was treated with 1.4 times molar excess of *t*-butyl trimethylsilyl peroxide (3) in the presence of 2 mol% trityl perchlorate (4) at 0 °C. The acetal exchange of several dimethyl acetals were examined under the similar reaction conditions and the results are shown in Table 1.



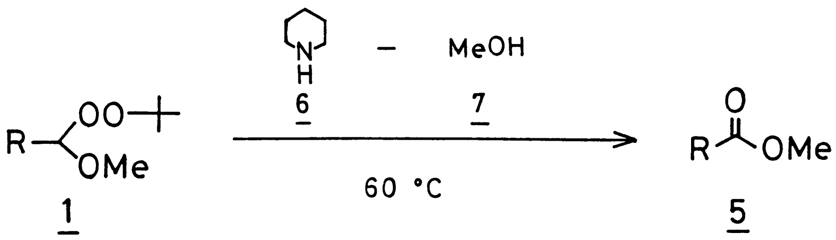
Scheme 1.

Table 1. The Synthesis of Acetal-type Peroxides[a]

Entry	R-	Yield / %
1	$PhCH_2CH_2$-	90
2	$PhCH(CH_3)$-	88
3	$PhCH_2$-	86
4	n-C_8H_{17}-	90
5	n-C_9H_{19}-	85
6	$CH_2{=}CH(CH_2)_8$-	86

a) All the products gave satisfactory ^{1}H NMR and IR spectra.

Next, the reaction conditions for the decomposition of peroxides to the corresponding methyl esters were investigated taking 1-*t*-butyldioxy-1-methoxy-3-phenylpropane as a model. And it was found that the ester 5 was obtained in good yield when the peroxide 1 was heated at 60 ℃ (bath temp) in a mixture of piperidine (6)[2] and methanol (7) as solvents. Then the synthesis of several methyl esters from corresponding peroxides was tried under the same reaction conditions as shown in the Scheme 2 (see Table 2).



Scheme 2.

Table 2. The Synthesis of Methyl Esters[a)]

Entry	R-	Yield / %
7	$PhCH_2CH_2$-	94
8	$PhCH(CH_3)$-	87
9	$PhCH_2$-	85
10	*n*-C_8H_{17}-	84
11	*n*-C_9H_{19}-	94
12	$CH_2=CH(CH_2)_8$-	89

a) All the products gave satisfactory ^1H NMR and IR spectra.

A typical procedure is described for the synthesis of methyl 3-phenylpropionate from 1,1-dimethoxy-3-phenylpropane: Under an argon atmosphere, a CH_2Cl_2 solution (2 ml) of 1,1-dimethoxy-3-phenylpropane (79 mg, 0.44 mmol) and *t*-butyl trimethylsilyl peroxide (0.59 mmol)[3)] was added to a solid trityl perchlorate (3 mg, 0.009 mmol) and the solution was stirred for 5 min at 0 °C. The pH 7 phosphate buffer was added and the organic materials were extracted with ether and dried over Na_2SO_4. After the removal of the solvents under reduced pressure, 1-*t*-butyldioxy-1-methoxy-3-phenylpropane (94 mg, 90%) was isolated by thin layer chromatography on silica gel. ^1H NMR ($CDCl_3$) δ 1.13 (9H, s), 1.6-2.0 (2H, m), 2.4-2.8 (2H, m), 3.37 (3H, s), 4.60 (1H, t, J=6 Hz), 7.07 (5H, s), IR (NaCl) 1000, 880 cm^{-1}. Then, 1-*t*-butyldioxy-1-methoxy-3-phenylpropane (68 mg, 0.29 mmol) was dissolved in a mixture of piperidine and methanol (2 ml, 1:1) and was heated at 60 °C (bath temp) for 3-4 h. The solvent was removed under reduced pressure at room temperature, and methyl 3-phenylpropionate (44 mg, 94%) was isolated by thin layer chromatography on silica gel. ^1H NMR ($CDCl_3$) δ 2.3-3.0 (4H, m), 3.5 (3H, s), 7.03 (5H, s), IR (NaCl) 1730 cm^{-1}.

There have been reported several methods concerning the transformation of acetals to esters, for example, by photolysis[4)] and pyrolysis[5)] of acetals, and by the oxidation of acetals with peracetic acid,[6)] N-bromosuccinimide[7)] and ozone.[8)] However, these reactions have some limitations; that is, the yields are not so good according to the reported data.[4-6)] And some of the reactions are applicable only for acetals of aryl aldehydes (refs. 4 and 7). When ozone is used, esters are obtained in good yields from the corresponding acetals, however, some of the functional groups, such as olefinic group, are incompatible with the reaction conditions.

It is noted that the present reaction is the versatile method for the preparation of carboxylic methyl esters starting from various acetals of aliphatic aldehydes including olefinic group (entries 6 and 12) under mild reaction conditions in good yields.

Further utilization of this useful compound 1 for various synthetic purposes is now in progress.

References

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