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ELECTROGENERATED ACID AS AN EFFICIENT CATALYST FOR ACETALIZATION OF CARBONYL GROUP WITH 1,2-BISTRIMETHYLSILOXYETHANE

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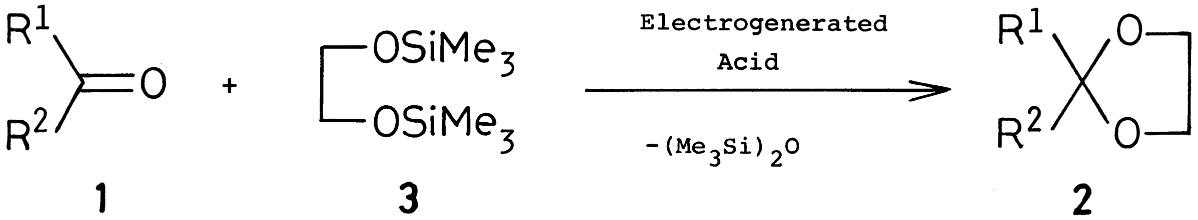
Electrolysis of a mixture of carbonyl compounds and bistrimethylsiloxyethane in CH_2Cl_2-$LiClO_4$-(Pt) readily gave the corresponding acetalized products in good yields.

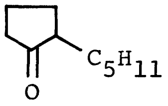
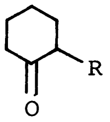
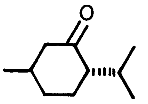
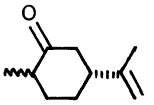
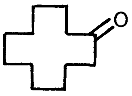
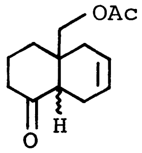
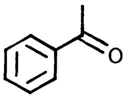
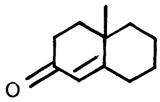
Protection of carbonyl function as a form of 1,3-dioxolane is one of the key operations in organic transformation. Although many practical methods have been devised for this purpose, a simple one which can be performed under mild conditions within a short reaction period is still required.$^{1)}$ Using an electrogenerated acid which can be produced by the electrolysis with lithium perchlorate in an aprotic solvent,$^{2)}$ we developed a convenient procedure for acetalization of aldehydes and ketones (1) with 1,2-bistrimethylsiloxyethane (3). Due to its easy operation and high efficiency, the present electrochemical method constitutes a viable alternative to the reported one which employs the powerful, but highly moisture sensitive reagent, trimethylsilyl trifluoromethanesulfonate, as an acid-catalyst.$^{3)}$



Typical electrochemical procedure is as follows. A mixture of 2-methylcyclohexanone (1.0 mmol), 3 (1.4 mmol), and $LiClO_4$ (20 mg, 0.19 mmol) in CH_2Cl_2 (5 ml) was electrolyzed with platinum electrodes (1.5 cm^2) in an undivided cell at an applied voltage of 10 V (current: 0.4-0.5 mA). TLC monitoring revealed that the reaction has completed after passing 0.0058 F/mol of electricity. After the addition of pyridine (0.3 ml), concentration and chromatography (SiO_2, hexane-AcOEt 10:1) gave the ethylene acetal 2d in 90% yield. Other results of electrochemical acetalization of carbonyl compounds are listed in Table 1.

Except for the conjugated enone 1k, most of aliphatic and aromatic carbonyl compounds could be transformed into the corresponding acetals 2, readily. Noteworthy is the fact that the electrochemical acetalization can be achieved by use of a small amount of $LiClO_4$ (sufficient for about 20 mol% equiv.) and a catalytic amount of electricity. Another application of such an electrogenerated acid for the selective transformation of functional groups is now in progress.

Table 1. Electrochemical Acetalization of Carbonyl Compounds 1.a)

	Carbonyl compd 1	3, equiv.	Time/min (F/mol)b)	Yield of 2/%	Bp Ob/°C(Torr)d) Mp/°C
a	$CH_3(CH_2)_5COR$ R = H	1.6	40(0.0085)	96	107(16)
b	R = Me	1.5	20(0.0041)	97	103(22)
c		1.5	10(0.015)	98	111(17)
					
d	R = Me	1.4	3(0.0058)	90	129(18)
e	R = $CH_2CH_2CO_2Me$	1.5	20(0.0085)	99	162(16)
f		1.5	40(0.0097)	91	107(16)
g		1.5	40(0.012)	97	105(19)
h		1.6	60(0.075)	95	66-68 (hexane)
i		1.6	80(0.03)	91(9)e)	193(18)
j		1.5	12(0.0138)	93	56.5-59 (hexane)
k		1.5	120(0.307)	39(46)e)	125-127(19)

a) Carried out using 1 (1.0 mmol) and 3 (1.4-1.7 mmol) in CH_2Cl_2 (5 ml) under an applied voltage of 10 V (current: 0.4-0.5 mA) at room temperature. b) Electricity based on 1. c) Isolated yield. d) Indicated by an air-bath temperature without correction. e) Numbers in parentheses indicate the unchanged 1.

References

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2) K. Uneyama, A. Isimura, K. Fujii, and S. Torii, Tetrahedron Lett., in press.
3) T. Tsunoda, M. Suzuki, and R. Noyori, Tetrahedron Lett., 21, 1357 (1980).

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