

Metal Reductions of Malonates and Oxalates. A Convenient Decarboxylation Route for Disubstituted Malonates and Synthesis of Keten Acetals¹

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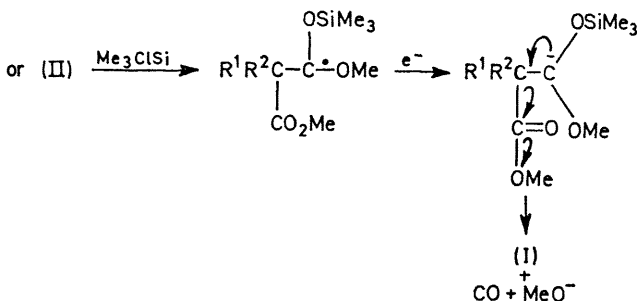
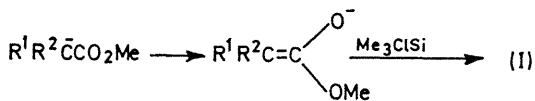
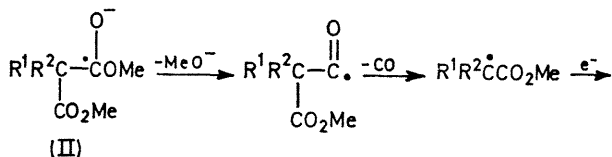
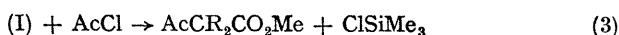
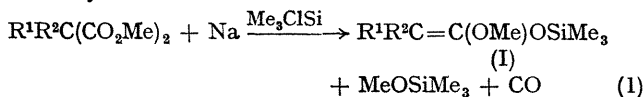
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Summary Alkali-metal reduction of disubstituted malonates or treatment of esters with base in the presence of trimethylchlorosilane gives high yields of the reactive disubstituted keten alkyl trimethylsilyl acetals, while diethyl oxalate, under similar conditions is reduced to 1,2-diethyl-1,2-bis(trimethylsilyloxy)ethylene.

THE alkali-metal reduction of esters (acyloin condensation) in the presence of trimethylchlorosilane (Me₃ClSi) has been shown to lead to 1,2-bis(trimethylsilyloxy)olefins.² The reaction produces high yields of cyclic products from ring sizes of four carbons and greater.^{2b,c} In an attempt to produce cyclopropene derivatives by acyloin-type reduction of disubstituted malonic esters† we have discovered a high yield process that leads initially to keten alkyl silyl acetals and an equivalent amount of carbon monoxide (reaction 1). The keten acetals are readily hydrolysed to the ester (reaction 2) (which thus provides a very convenient and mild dealkoxycarbonylation procedure for disubstituted malonic esters)³ or can be used as intermediates, e.g., acylation (reaction 3).⁴ Table 1 lists malonates reduced in this way.



SCHEME

After initial electron transfer from the metal there are at least two possible routes for the subsequent fragmentation (see Scheme)⁵

TABLE 1

$R^1R^2C(CO_2R^3)_2 \rightarrow R^1R^2C=C(OR^3)OSiMe_3$			
R ¹	R ²	R ³	Yield (%)
Me	Me	Me	87
Me	Me	Et	86
Et	Et	Et	88
Ph	Et	Et	90*
Ph	Ph	Me	85
-(CH ₂) ₃ -		Et	60

* Mixtures of isomers.

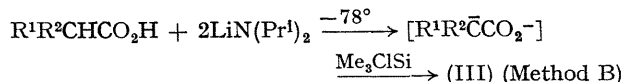
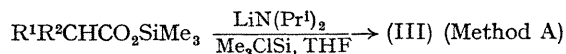
The synthesis of compounds like (I) can also be accomplished by silylation of substituted acetate α-anions.^{6,7} Compounds (I) are mixed keten acetals (alkyl, silyl). The keten bis-silyl acetals, (III), can be prepared (see Table 2) by either Method A or B.

TABLE 2

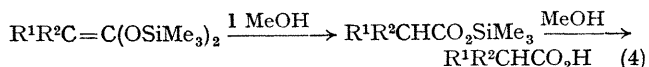
Preparation of keten bis-silyl acetals $R^1R^2C=C(OSiMe_3)_2$ (III)

R ¹	R ²	Method	Yield ^a (%)
H	H	A and B	25, 30
H	Me	A and B	50, 63
H	Bu ^t	B	61
H	Ph	B	71
Me	Me	B	70
Me	Ph	B	83
Ph	Ph	B	85
-(CH ₂) ₄ -		B	50

^a Single runs only.



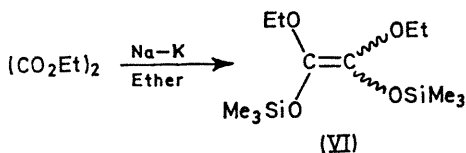
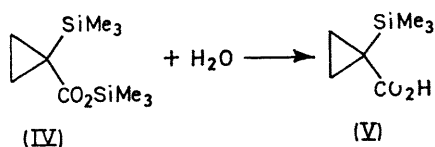
Selective solvolysis of keten acetals (III) is easily attained (reaction 4). With one equivalent of methanol, trimethylsilyl acetates are formed, whereas, with an excess of methanol at room temperature for 1 h the corresponding acid was produced quantitatively.



Cyclopropanecarboxylic acid by Method B formed the C-silylated product (IV) [n.m.r. δ 0.0 (CSiMe₃) and 0.22 (OSiMe₃)] rather than the isomeric compound of type (III).

† Monosubstituted malonates do not reduce but produce the silylated enol.

On hydrolysis (IV) formed the acid (V) [n.m.r. δ 0.06 (CSiMe₃)].



When acyloin reduction conditions are applied to diethyl oxalate a *cis-trans* mixture of 1,2-diethoxy-1,2-bis(trimethylsilyloxy)ethylene (VI) is obtained in 64% yield. Di-isopropyl oxalate behaved in a similar fashion but we have not yet been successful in attempts to reduce dimethyl oxalate. The method constitutes a new synthesis of tetraalkoxyethylenes.

Analytical, i.r., m.s., and n.m.r. data are in agreement with the structural assignments of the compounds described. The stereochemistry of compounds of type (I) is reported in the following communication.

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¹ For previous paper see, J. J. Bloomfield, *Tetrahedron Letters*, 1968, 591.

² (a) U. Schrapler and K. Rühlmann, *Chem. Ber.*, 1964, **97**, 1383, and earlier papers cited therein; (b) K. Rühlmann, H. Seefuth, and H. Becker, *ibid.*, 1967, **100**, 3820; (c) J. J. Bloomfield, *Tetrahedron Letters*, 1968, 587.

³ A decarboxylation procedure for malonates using NaCN in Me₂SO at a high temperature has been described. A. P. Krapcho, G. A. Glynn, and B. J. Grenon, *Tetrahedron Letters*, 1967, 215.

⁴ (a) Cf. U. Schmidt and M. Schwochau, *Tetrahedron Letters*, 1967, 4491; (b) S. M. McElvain and P. L. Weyna, *J. Amer. Chem. Soc.*, 1959, **81**, 2579; (c) S. M. McElvain, *Chem. Rev.*, 1949, **49**, 453.

⁵ Cf. E. Van Heyningen, *J. Amer. Chem. Soc.*, 1955, **77**, 4016.

⁶ (a) C. R. Krueger and E. G. Rochow, *J. Organometallic Chem.*, 1964, **1**, 476; reported only one example of such a reaction. They found that ethyl acetate anion and TMCS gave *C*- and *O*-silation. In the substituted acetate series employed we obtained *O*-silation exclusively; (b) I. F. Lutsenko, Y. I. Baukov, G. S. Burlachenko, and B. N. Khasapov, *ibid.*, 1966, **5**, 20, using the mercuric salt of methyl acetate and triethylsilyl iodide obtained *C*- and *O*-silation depending on the solvent employed; (c) A. D. Petrov, S. I. Sadykh-Zade, and E. I. Filatova, *J. Gen. Chem. (U.S.S.R.)*, 1959, **29**, 2896; (d) It appears likely that C. R. Hance and C. R. Hauser, *J. Amer. Chem. Soc.*, 1953, **75**, 944; obtained keten acetals (I) in addition to the formulated *C*-silyl esters—see ref. 6a.

⁷ α -Anions of carboxylic acids have been studied by P. L. Creger, *J. Amer. Chem. Soc.*, 1967, **89**, 2500; 1970, **92**, 1396, 1397; and P. E. Pfeffer and L. S. Silbert, *J. Org. Chem.*, 1970, **35**, 262.