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ORGANIC TRANSFORMATIONS VIA METAL SILANE REAGENTS: SYNTHESES OF VINYL ETHERS FROM DIMETHYL KETALS AND $(CO)_5MnSi(CH_3)_3$

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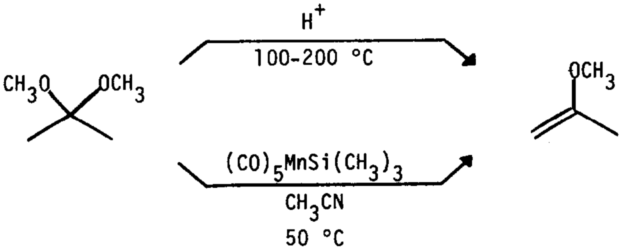
Summary: The reaction of dimethyl ketals with $(CO)_5MnSi(CH_3)_3$ (1) at 50 °C in CH_3CN affords methyl enol ethers, generally in 75-95% yields.

Methyl enol ethers are conventionally synthesized by treatment of the corresponding dimethyl ketals or acetals with protic acids at temperatures in the 100-200°C range (eq i).[2,3] Such conditions are not compatible with the presence of many types of functional groups, and some important classes of vinyl ethers, such as allyl vinyl ethers, spontaneously rearrange above room temperature. On the basis of our previous studies of organic molecule/metal silane reactions,[4] we considered the possibility that an appropriate transition metal trialkylsilane might effect the ketal → enol ether transformation under milder conditions. In this communication, we report that the readily available silane $(CO)_5MnSi(CH_3)_3$ (1)[5] cleanly converts dimethyl ketals to vinyl ethers at moderate (50 °C) temperatures and without added acid or base.

(i)



Acetonitrile solutions of dimethyl ketal and 1.0-2.0 equiv of 1 (see Table) were heated at 50 °C under N_2 for 2-4 hr. Methyl enol ethers formed in good yields (generally 75-95% based upon starting ketal), as determined by ^1H NMR (CD_3CN solvent) and GLC. In each case, product identity was confirmed by comparison with independently prepared authentic samples. Isolated yields were determined for three representative substrates; after separating the volatile $CH_3OSi(CH_3)_3$ and manganese by-products (initially $(CO)_5MnH$; see below), 74-81% yields of distilled methyl enol ethers were obtained (Table).

The data in the Table provide a fair representation of the strengths and limitations of our procedure. Yields are uniformly good, but entries 6 and 7 show that equilibrium mixtures of regioisomers (from unsymmetrical ketals) and geometric isomers (from acyclic ketals) can form; similar product distributions are obtained when conventional conditions for enol ether synthesis are utilized (eq i).[6] By-product $(CO)_5MnH$ (which undergoes conversion to $Mn_2(CO)_{10}$ and $Mn_2(CO)_9(CH_3CN)$ as the reaction proceeds) is a weak acid ($pK_a \cong 7$)[7] and may affect product ratios. We have previously shown the $(CO)_5MnH$ can catalyze (albeit slowly) the interconversion of trimethylsilyl enol ether regioisomers.[4f] However, product ratios at 10-20% conversion did not significantly differ from those at 90% conversion, and similar results were obtained from reactions conducted with added 2,6-di-*t*-butylpyridine. $(CO)_5MnH$ is also capable of hydrogenating activated olefins via a free radical mechanism.[8] Thus extension of reaction times beyond the recommended 2-4 hr can lead (particularly for entry 8) to detectable amounts of saturated products. By using ca. 2 equiv of **1** (which accelerates initial enol ether formation), this problem is largely avoided.

We suggest that enol ether formation occurs as shown in the Scheme. This mechanism accounts for the reaction stoichiometry and is related to pathways previously proposed for reactions of **1** with aldehydes, ketones,[4a,f] and cyclic ethers.[4b] The initial step is believed to be silylation of a ketal oxygen to give the ion pair **2**. A related ion pair, $(CH_3)_3N\overset{+}{S}i(CH_3)_3$ $(CO)_5Mn^-$, can be isolated from the reaction of **1** with $(CH_3)_3N$.[3a] Subsequently, extrusion of $CH_3OSi(CH_3)_3$, leading to the new ion pair **3** (Scheme) is proposed. Conversion of **3** to the enol ether may take place via direct proton transfer, electron/H· transfer, or via the manganese

Scheme. Proposed Mechanism of Vinyl Ether Formation

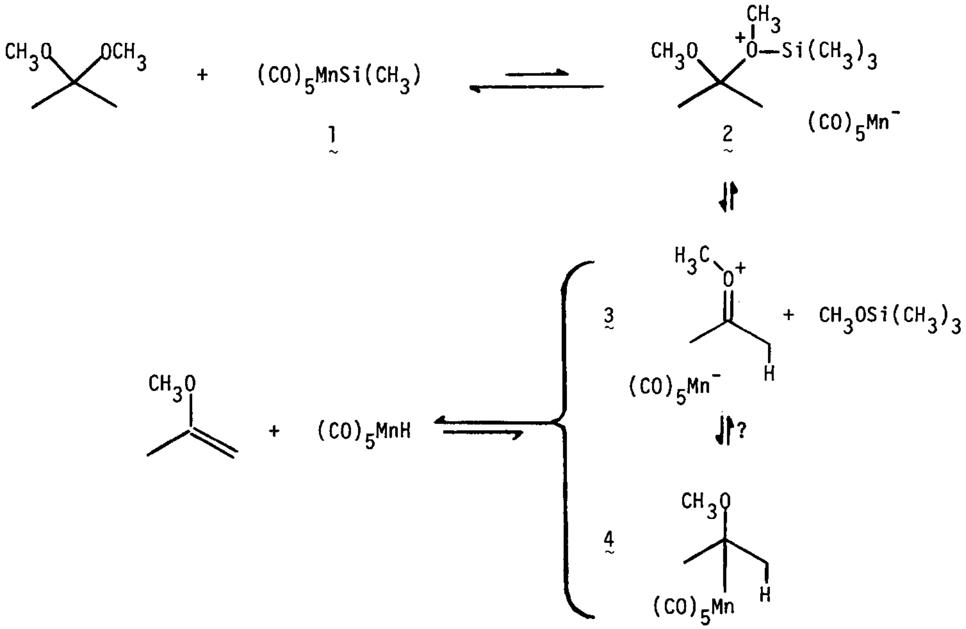
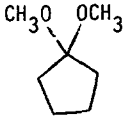
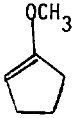
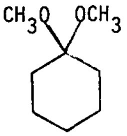
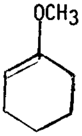
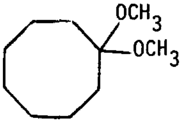
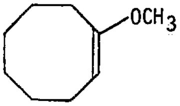
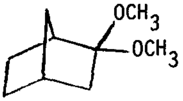
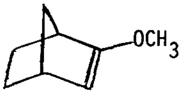
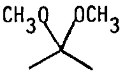
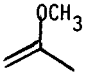
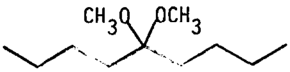
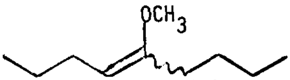
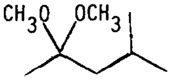
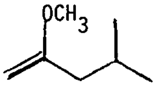
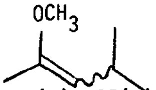
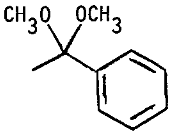
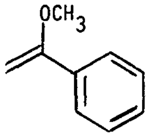


Table. Vinyl Ethers Synthesized from Dimethyl Ketals and 1[a]

entry	starting ketal	product[b]	yield data(%) GLC[c]	NMR[d]	isol[e]
(1)			93	95	-
(2)			97	95	-
(3)			89	95	79
(4)			56	60	-
(5)			78	77	-
(6)		 25(Z): 75(E)	88	95	74
(7)		 71  4(Z): 25(E)	97	93	-
(8)			93	97	81

(a) Reaction stoichiometries were as follows: entries 1,2,3,7: 1.0-1.3 equiv 1; entries 4,5,6, 8: 1.7-2.0 equiv 1. Enol ether concentrations were 0.5-1.0 M.

(b) Assigned by GLC coinjection with and ^1H NMR comparison to authentic samples.

(c) GLC yields are corrected for detector response factor and are the average of at least three injections.

(d) ^1H NMR yields were determined by comparing the integral of the product $-OCH_3$ with that for the entire $-Si(CH_3)_3$ region.

(e) Products were isolated via simple atmospheric and reduced pressure distillation.

alkyl **4**. These possibilities are not readily distinguished by experiment; however, when dimethyl acetals are reacted with **1** under CO, manganese acyls derived from the carbonylation of **4** can be isolated.

The reaction of **1** with dimethyl ketals contrasts with that of $(CH_3)_3Si\text{-}I$. The latter reagent affords ketones exclusively.[9] These reactions likely diverge at the point of ion pair **3** (Scheme). Although transition metal anions are strong nucleophiles,[10] attack of $(CO)_5Mn^-$ upon the oxygen-bound methyl group of **3** (which would irreversibly yield ketone) clearly does not occur. However, when I^- is the anion of **3**, dealkylation takes place readily.

Reactions of **1** with dimethyl acetals are somewhat more complex. These, and several synthetically useful extensions of the methodology described in this communication, will be reported in a subsequent full paper.

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References and Notes

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(2) For some representative syntheses, see (a) Meerwein, H. in Houben-Weyl "Methoden der Organischen Chemie", E. Müller, ed., vol 6/3, Georg Thieme Verlag, Stuttgart, p 97, p 199ff; (b) Taskinen, E. *Acta Chem. Scand.*, **1974**, *B28*, 357; (c) Newman, M.S.; Vander Zwan, M.C. *J. Org. Chem.*, **1973**, *38*, 2910; (d) Wohl, R.A. *Synthesis*, **1974**, 38; (e) House, H.O.; Kramer, V. *J. Org. Chem.*, **1963**, *28*, 3362; (f) Norris, R.O.; Verbanc, J.J.; Hennion, G.F. *J. Am. Chem. Soc.*, **1938**, *60*, 1160.

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