be employed for stage 1; they appear to induce the facile decomposition of β-alkoxyacylsilane **3** initially formed.[9]

For effecting the transformation of stage 2, tetrabutylammonium hydroxide is a preferable reagent of the wide applicability of the facile and relatively clean formation of the product **4.** For efficient conversion, however, it is crucial to use it in an amount as small as possible, because this strong base sometimes catalyzes the polymerization reaction of the aldehyde formed, which results in appreciable decrease of the yield especially when the product is labile to base. For certain β-alkoxyacylsilanes, tetrabutylammonium fluoride (TBAF)[10] is also employable. For example, the acylsilane **3** derived from the diethyl acetal of benzaldehyde or of cinnamaldehyde can be converted into the corresponding product **4** in higher yield under the catalytic effect of TBAF (~0.08 equiv), although the reaction proceeds much more slowly (12 h at room temperature). However, clean conversion can not generally be achieved with TBAF, because the side product **5,** resulting from methyl transfer from silicon to carbon,[2] is often formed in substantial amount. Lithium or sodium alkoxide are also found to be much less effective for the **3** → **4** transformation.

It should be noted that a weaker nucleophile, such as tetrabutylammonium *o*-methoxyphenoxide,[11,12] also catalyzes a conversion of **3** into **4.** This appears to be better reagent, especially for the preparation of base-labile unsaturated aldehydes such as 2-substituted crotonaldehydes, although it is a very slow process.

In contrast to the successful transformation of β-alkoxyacylsilanes into the corresponding unsaturated aldehydes, similar treatment of simple saturated acylsilane leads to the formation of the aldol condensation product of the aldehyde formed,[13] along with the methyl transfer product, even if quaternary ammonium *o*-methoxyphenoxide is employed. Further, the reaction with unsaturated acylsilane is found to give a complex mixture containing a small amount of the corresponding aldehyde[14] during similar procedure with hydroxide or *o*-methoxyphenoxide.

Further elucidation of the reaction mechanism is now under investigation.

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(6) This alkoxyacylsilane exhibited the following spectral data: NMR (CCl_4, methylene chloride as internal standard) δ 0.22 (s, 9 H), 0.52 (d, $J = 7$ Hz, 3 H), 1.03 (t, $J = 7$ Hz, 3 H), 3.0–3.6 (m, 3 H), 4.22 (d, $J = 10$ Hz, 1 H), 7.27 (s, 5 H); IR (neat) 3020, 2963, 1640, 1600, 1490, 1250, 1093, 842, 760 cm^{-1}.

(7) Under forcing reaction condition, the following reaction is observed: $R^1R^2C(OC_2H_5)_2 + R^3CH{=}C(SiMe_3)OSiMe_3 \rightarrow R^1R^2C{=}CHR^3$.

(8) For a facile isomerization of *Z* isomer of this type of aldehyde into its *E* isomer, see, for example, G. Büchi and H. Wüest, *J. Am. Chem. Soc.*, **96,** 7573 (1973).

(9) Depending on the Lewis acid employed, the following two types of decomposition products are obtained: **3** → $R^2CH{=}CHR^1$ or $R^2CH(OH)\text{-}CHR^1SiMe_3$. *These interesting decompositions reactions will be described* in a separate note.

(10) On the specific action of fluoride ion to silicon atom, see I. Kuwajima, *J. Syn. Org. Chem. Jpn.*, **34,** 964 (1976).

(11) Tetrabutylammonium phenoxides are prepared as follows. A slight excess amount of the corresponding substituted phenol is treated with an aqueous solution of tetrabutylammonium hydroxide. Excess phenol is extracted out with ether and most of the water is removed with a rotary evaporator. The remaining solid is used as its solution in methanol.

(12) Various phenoxides were examined for the transformation of **3** ($R^1 = C_6H_5CH_2$; $R^2 = CH_3$; $R^3 = C_2H_5$) into the corresponding aldehyde and the following results were obtained: unsubstituted phenoxide (60% **4,** 3 h for complete disappearance of **3**), *o*-methyl- (67%, 6 h), *m*-methyl- (72%, 42 h), *p*-methyl- (72%, 3 days), and *o-tert*-butylphenoxide (62%, 14 h).

(13) Treatment of 3-phenylpropionyltrimethylsilane with 0.2 equiv of Bu_4NOH at room temperature for 10 min afforded 2-benzyl-5-phenyl-2-pentenal (79%) and 4-phenylbutan-2-ol (7%).

(14) Treatment of 3-phenylpropenoyltrimethylsilane with Bu_4NOH (0.2 equiv, 10 min at room temperature) or *o*-methoxyphenoxide (0.4 equiv, 35 min at room temperature) afforded cinnamaldehyde in 23% and 52% yields, respectively, along with other many unidentified products.

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Cation and Solvent Effects on the Alkylation of Two Alkali β-Ketoenolates

Sir:

In the course of an extended investigation of ion pairing and reactivity of alkali β-diketoenolates, we have observed several phenomena which we think are striking enough to communicate prior to publication of our complete results.

Sodium and potassium dibenzoylmethides (MDBM) are completely carbon alkylated by methyl iodide in Me_2SO, as shown by ^1H NMR and HPLC analysis of the products. Combination of rate data for the process with conductance data[1] shows that the dissociated anions engage in typical S_N2 attack on MeI with a rate constant that is three or four orders of magnitude greater than attack by the alkali enolate ion pair.

When dimethyl sulfate (Me_2SO_4) is used as alkylating agent, clean formation of the oxygen-methylated product (the β-keto vinyl ether) is observed. In dramatic contrast to the kinetics of all other enolate alkylation studies known to us, the reaction *turns out to be only 0.24 order*[2] *in enolate, although still first order in* Me_2SO_4. This suggests that much of the reaction occurs through a highly reactive intermediate generated from Me_2SO_4. This was demonstrated through independent observation of an exothermic reaction[3] between Me_2SO_4 and Me_2SO with a pseudo-first-order rate constant $k_1 = 6.81 \times 10^{-4}\ s^{-1}$ which is roughly comparable to the pseudo-first-order alkylation rates listed in the third column of Table I. The kinetic complications of competing reactions during alkylation (see below) make closer agreement unlikely. The product solution generated after an hour by this process reacted instantly with KDBM and NaDBM to give oxygen-alkylated product. This experiment confirmed the formation of a highly reactive intermediate and showed that it was generated by interaction of Me_2SO_4 with the solvent.

The identity of the intermediate as the dimethylmethoxysulfonium ion[4] Me_2SOMe^+ was substantiated by observation of the ^1H NMR spectrum of a solution of dimethyl sulfate following its solution in $Me_2SO\text{-}d_6$. A single spike at 3.97 ppm was replaced by two peaks of equal heights at 4.02 ppm (assigned to $(CD_3)_2SO^+CH_3$) and 3.44 ppm (assigned to the anion $^-OSO_2OCH_3$). The first-order rate of conversion (at 38 °C) was roughly equivalent to that expected on the basis of the first-order calorimetric rate at 25 °C.

Treatment of the rate data as competing first- and second-order processes[10] led to results typified by the data in Table I, which show (last two columns) that product formation occurs with comparable speed through both pathways under these conditions. More extensive analysis of the results, again using conductance data,[11] confirms the supposition that for the S_N2 process the dissociated enolate anions are the only effective nucleophiles, with essentially no competition from ion pairs.

Table I. Rate Constants for Methylation of Alkali Dibenzoylmethides by Dimethyl Sulfate at 25 °C

	[MDBM] × 10^3 M	k_2, s^{-1} M^{-1}	k_1, × 10^4, s^{-1}	k_2[MDBM], × 10^4, M^{-1} s^{-1}
KDBM	5.015	0.107	3.22	5.366
NaDBM	5.416	0.052	2.44	2.84

Table II. Calorimetric Heats of Methylation with Methylfluorosulfonate of β-Ketoenolates in Propylene Carbonate and Tetrahydrofuran[a]

Compd[b]	ΔH, kcal/mol[c]	ΔH, kcal/mol[d]
HDBM	No rxn	No rxn
LiDBM	No rxn	−29.6
NaDBM	−26.5 ± 1.1 (98% −O)	−32.2 ± 0.4 (67% −C)
KDBM	−25.8 ± 1.0 (98% −O)	−36.5 ± 0.4
CsDBM	−26.3 ± 0.1	−34.9 ± 1.6
HDPM	No rxn	No rxn
LiDPM	No rxn	−36.5 ± 3.5
NaDPM	−34.7 ± 0.6 (<90% −O)	−36.2 ± 0.8
KDPM	−26.5 ± 1.9 (>90% −O)	− 40.3 ± 0.9 (71% C)
CsDPM	−26.1 ± 0.6 (>90% O)	−40.3 ± 1.4 (83% C)

[a] Concentrations: chelate ≈0.02–0.05 M; $MeSO_3F$ ≈0.00309 M. [b] DBM = dibenzoylmethide; DPM = dipivaloylmethide. [c] In propylene carbonate. [d] In THF.

Points of novelty in the present study are, first, the use of dimethyl sulfate for the rapid in situ formation of the oxosulfonium salt and, second, the kinetic evidence for competition of reaction through it with the normal S_N2 reaction of the sulfate.

In propylene carbonate at 25 °C the potent methylating agent methyl fluorosulfonate[12–15] reacts completely within 2 min[16] with sodium, potassium, and cesium DBM and DPM to produce primarily (90–98%) the oxygen-alkylated product[17] and over 26 kcal/mol of heat. Despite the enormous driving force for the alkylation reaction which is implied by this observation, solutions of both lithium compounds evolved no more heat than did the small background reaction with propylene carbonate under the same conditions during a period of at least a half hour.[18]

Table II shows the similar behavior of the lithium chelates and the covalent parent β-diketones, compared with their dramatic difference from the other alkali enolates in propylene carbonate. In contrast, the lithium compounds behave like the other alkali analogues in THF, a solvent which dissociates lithium salts through coordination with the cation. The tabulated results also demonstrate differences in oxygen vs. carbon alkylation as a function of the cation, the anion, and the solvent in conformity with many published observations by other workers.[11,20,21]

The relatively low reactivity of lithium salts compared with those of the other alkali cations has numerous precedents and conforms to their low relative dissociation in dipolar aprotic solvents.[22–25] However, at this point we can only speculate on the thermodynamic or kinetic reasons for it.

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(3) Rate constants reported here were determined calorimetrically following procedures described by D. J. Eatough, J. J. Christensen, and R. M. Izatt ("Experiments in Thermometric Titrimetry and Titration Calorimetry", Brigham Young University, 1973) and V. DePalma (doctoral thesis, University of Pittsburgh, 1977).

(4) Other salts of this ion have been characterized by Smith and Winstein,[5] Kuhn,[6,7] and Cotton et al.[8] and its synthetic utility has been described by Corey and Chaykovsky,[9] all of whom report the gradual isomerism of the highly reactive oxonium ion to a relatively inert sulfonium salt, Me_3SO^+, upon standing of the iodide salt in warm Me_2SO.

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Homogeneous Hydrogenation of Carbon Monoxide

Sir:

We wish to report a homogeneous hydrogenation of carbon monoxide to methane ("methanation"[1]) using $Cp_2Ti(CO)_2$.[2] We also report the serendipitous synthesis and structure of a cluster unprecedented in both cyclopentadienyl chemistry and titanium chemistry.

When a toluene solution of $Cp_2Ti(CO)_2$ is treated with a mixture of hydrogen and carbon monoxide (3:1 mole ratio, total pressure 1 atm at 25 °C) at 150 °C, methane is produced.[3] The solution phase is homogeneous throughout the reaction, and no metal is evident during or after the reaction. When deuterium is used in place of hydrogen, CD_4 is produced; toluene is not detectably deuterated, but some cyclopentadienyl deuteration occurs (infrared evidence). The methanation is not catalytic in titanium, however; methane is produced even under an atmosphere of pure hydrogen (but not under argon). Over a period of 48 h, the color characteristic of $Cp_2Ti(CO)_2$ changes to a royal blue. This blue species is catalytically inactive to a fresh charge of synthesis gas and does not exhibit any infrared bands characteristic of bridging or terminal CO ligands.

We have determined the structure of the intensely blue crystals obtainable from toluene. Using 2730 unique reflections measured with Mo Kα radiation ($2\theta < 50°$), the structure was solved (direct methods) and refined to an agreement factor $R(F)$ of 0.049.[4]