Non-rigid Carbon–Carbon Double Bonds: Conformational Assignments of Keten Methyl Trimethylsilyl Acetals

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Summary An n.m.r. study of keten methyl trimethylsilyl acetals shows that substitution effects can permit free rotation of the carbon–carbon double bond at room temperature.

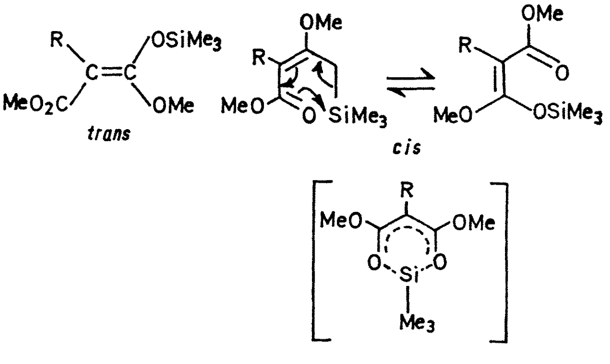
THE preceding communication reported[1] the preparation of the title compounds $R^1R^2C{=}C(OMe)OSiMe_3$ (I; $R^1 = R^2 = H$, Me and Ph, and $R^1 = Ph$, $R^2 = H$ and Me). We find that the related compounds (II; R = H, Me, Et, Ph, and CO_2Me) can be readily prepared from sodium salts of dimethyl malonate[2] or monosubstituted malonates with trimethylchlorosilane (Me_3ClSi). The stereochemistry of

$$R\bar{C}(CO_2Me)_2 \xrightarrow{Me_3ClSi} R(MeO_2C)C{=}C(OMe)OSiMe_3$$

(II)

(I) and (II) is established from a consideration of the spectral data in the Table.

The data show several unusual features. First is the equivalency of the OMe and CO_2Me n.m.r. signals for compounds (II; R=H and Me) and for the major isomer when R=Ph. We attribute this to a low energy tautomerism† (see Scheme) for the isomer designated *cis*, *i.e.*, with CO_2Me and $OSiMe_3$ on the same side of the carbon–carbon double bond. Our findings are similar to those of Pinnavaia[3] who observed a rapid rearrangement of one isomer of trimethylsilylacetylacetonate. For (II; R=H and Me) only the *cis*-isomer was obtained but for (II; R=Ph) about 10% of the *trans*-compound was present.



SCHEME

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† N.m.r. temperature studies at −60° failed to resolve the OMe equivalency of (II; R = Ph).

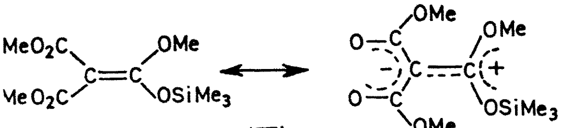
For the *trans*-isomer the OMe and CO_2Me n.m.r. signals are different.

Spectral measurements for $R^1R^2C{=}C(OMe)OSiMe_3$

Compound	N.m.r. (CCl_4) δ values at ambient temperature[a] OSiMe$_3$	OMe	CMe	Ph	CO$_2$Me	H	I.r. (C=C stretch) (cm^{-1})	U.v. (hexane) λ_{max}	$\epsilon \times 10^4$
(I; $R^1{=}R^2{=}Me$)	0·18	3·48	1·48, 1·54q	—	—	—	1708[b]	—	—
(I; $R^1{=}R^2{=}Ph$)	0·03	3·50	—	7·20	—	—	1630[b]	267	1·32
(I; $R^1{=}H$, $R^2{=}Ph$) (a)[c] . .	0·29	3·65	—	6·9—7·4*m*	—	4·62	1640—1660[b]	268	1·42
(b) . .	0·26	3·60	—	6·9—7·4*m*	—	4·52			
(I; $R^1{=}Me$, $R^2{=}Ph$) (a)[d] . .	0·25	3·40	1·86	7·0—7·4*m*	—	—	1650—1670[b]	260	0·84*e*
(b)[d] . .	−0·02	3·60	1·90	7·25	—	—			
(II; R=H) (b)	0·27	3·58	—	—	3·58	4·25	1600	—	—
(II; R=Me) (b)	0·29	3·52	1·66	—	3·52	—	1600 br	—	—
(II; R=Ph) (a)[f]	0·37	3·50	—	7·15	3·50	—	1560 br	—	—
(*b*)[f]	0·02	3·55	—	7·20	3·75	—		—	—
(II; R=CO_2Me)	0·35	3·65	—	—	3·65	—	1530 br	—	—

[a] Spectra recorded using a Varian HA-60A Spectrometer equipped with a variable temperature probe.
[b] Strong band at 860—870 cm^{-1} with overtone at 1720—1740 cm^{-1}. See refs. 2 and 6 for related compounds.
[c] Obtained as a pure isomer. The stereochemistry of (Ia) and (Ib) is not assigned.
[d] Obtained as a mixture.
[e] Contains 30% of isomer (a).
[f] The crude isomer mixture was used since the product underwent change on distillation at reduced pressure.

(II; R=CO$_2$Me) is even more unusual in that all of the OMe signals are equivalent in both carbon tetrachloride and benzene. On cooling a $CDCl_3$ solution to −40°, the OMe singlet signal broadened while the $OSiMe_3$ signal was essentially unchanged. Thus, at room temperature, a major contributor to the structure appears to be the ionic one (III) that permits rotation[4d] and with tautomerism explains the equivalency of the OMe.

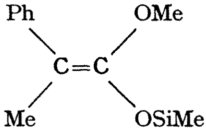


(III)

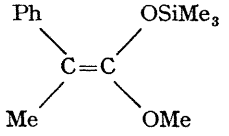
The data in the Table show that whereas (I; $R^1 = R^2 = Me$) has two methyl signals, (I; $R^1 = R^2 = Ph$) has a single phenyl signal. Heating to 140° failed to change the spectrum of the methyl compound, whereas cooling to −60° did not separate the phenyl signals. This is consistent with a stabilization contribution to the dipolar form $Ph_2\overset{-}{C}{-}\overset{+}{C}(OMe)OSiMe_3$ by the phenyl group permitting free rotation and equivalency. Recently, Shvo[4c] has shown that the vinyl ether $(MeO_2C)_2C{=}C(Bu^t)OMe$ has a particularly low energy barrier of rotation (18·3 kcal mol^{-1}) about the carbon–carbon double bond.

Analysis of the $OSiMe_3$ chemical shift data is the key to assigning the stereochemistry of unsymmetrical compounds in the Table. For many of the compounds the chemical shift value is in the δ 0·20—0·35 range but for the diphenyl compound (I) the $OSiMe_3$ shift at δ 0·03 is at relatively high field. This is inconsistent with the dipolar structure. However, in this molecule other factors related to the n.m.r. shift values of $OSiMe_3$ are important. Steric hindrance prevents the phenyl groups from being coplanar with the ene system. This is shown in the n.m.r. spectrum by the phenyl signal appearing as a singlet.[5] The $OSiMe_3$ group is *cis* to the non-coplanar phenyl substituent and Dreiding models show that these methyl groups are above the plane of the phenyl group. Thus the 3Me of the $OSiMe_3$ group are in the positive shielding region of the phenyl ring and the chemical shift is at the high field value of δ 0·03.‡

The isomer assignments in the Table are related to the analysis of the n.m.r. spectrum of the diphenyl compound (I). For form (a) of (I; $R^1 = Me$, $R^2 = Ph$), the phenyl signal is a multiplet, indicating a high degree of electronic



(Ia)



(Ib)

interaction (coplanarity) with the ene system, whereas in form (b) the phenyl signal is a singlet, indicating non-coplanarity and upfield shifting of the $OSiMe_3$ signal by the phenyl group. For (I; $R^1 = H$, $R^2 = Ph$) the methyl signals of the $OSiMe_3$ group of both isomers are at relatively low field values of δ 0·29 and 0·26. We believe this is due to the phenyl being co-planar with the ene system in both isomers. Consistent with this explanation is the finding that the phenyl signal of each isomer is a multiplet. Thus a subtle difference in coplanarity of system (I) exists between (I; $R^1 = H$, $R^2 = Ph$) and (I; $R^1 = Me$, $R^2 = Ph$) due to the steric effect of the methyl group compared with hydrogen.

The i.r.[2,6] and u.v. data are in agreement with the assigned structures. Of particular interest is the extinction coefficient values for compounds (I) shown in the Table. Data for (I; $R^1 = R^2 = Ph$) and (I; $R^1 = H$, $R^2 = Ph$) are in agreement with those for phenylketen acetals that have λ_{max} (cyclohexane) 265 nm (ε 16,000—17,000).[7] The low ε value for (I; $R^1 = Me$, $R^2 = Ph$) is in agreement with the earlier conclusion that this molecule in form (b) (Ph and $OSiMe_3$ *cis*) is not planar.

Correlation of stereochemical assignment by $OSiMe_3$ shift value and tautomerism is illustrated by (II; R = Ph). Thus, the *trans*-isomer (b) (CO_2Me and $OSiMe_3$ *trans*) which does not undergo tautomerism (different shift values

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‡ Diphenylketen bistrimethylsilyl acetal shows the $OSiMe_3$ signal coincident with Me_4Si. $OSiMe_3$ is slightly more electron donating than OMe as seen for the CMe shifts of $MeCO_2Me$ *vs.* $MeCO_2SiMe_3$ (δ 1·95).

for CO_2Me and OMe) has a *cis*-relationship between phenyl and $OSiMe_3$. This relationship where the phenyl is not coplanar (phenyl signal is a singlet) results in a diamagnetic shift of $OSiMe_3$ signal to a value near that of Me_4Si. (IIa; R = Ph) on the other hand displays tautomerism and has the $OSiMe_3$ function *trans* to phenyl with concomitant downfield $OSiMe_3$ n.m.r. signal.

The final compound (I) of the series was obtained from 9-methoxycarbonylfluorene. The n.m.r. signals of the $OSiMe_3$ and OMe occur at δ 0·39 and 3·92, respectively. These are at lower field than any of the corresponding values given in the Table. This is in contrast with (I; $R^1 = R^2 =$ Ph) in which the phenyl groups are not coplanar and the methyl signal of $OSiMe_3$ is at high shift value. Thus, a high degree of ionic character is indicated for the molecule, as would be expected for the fluorenide form.

Spectral data for $R_2C{=}C(OSiMe_3)_2$ compounds were consistent with those of compounds (I) .

Spectral studies of the title compounds lead to the conclusion that freedom of rotation about a carbon–carbon double bond is influenced by the substituents attached to the double bond. The rigidity is decreased as electron-donating groups (*e.g.*, OR) are located on one carbon atom while electron-attracting groups (*e.g.*, CO_2R, Ph) are attached to the other atom of the double bond. The reduction of carbon–carbon double bond character can result in freedom of rotation at room temperature.

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