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METHYL γ-TRIMETHYLSILYL CROTONATE

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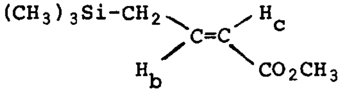
The interaction of silyl centers with the excited states of π-systems has recently attracted considerable interest.[1,2] Despite this interest, compounds such as methyl γ-trimethylsilyl crotonate in which the effect of a trimethylsilylmethyl group on the spectral properties of the α,β-unsaturated ester functionality could be determined have not been previously prepared. Such a system is of interest for several reasons. Zimmerman has calculated that in the π → π* state of an α,β-unsaturated ketone, a charge separation occurs in which the β-carbon becomes partially positively charged while the carbonyl oxygen becomes partially negatively charged. $C{=}C{-}C{=}O \xrightarrow{h\nu} {}^{+\delta}C{-}C{=}C{-}O^{-\delta}$.[3] The fact that a trimethylsilyl methyl group has a much stronger electron releasing inductive effect than a methyl group in aromatic electrophilic substitution reactions led us to expect that a trimethylsilylmethyl group would have a major effect on such a polar excited state.[4,5] In addition to inductive stabilization of a positive charge, silicon has a unique ability to stabilize a carbonium ion center beta to it as shown by the fact that 1-trimethylsilyl-2-chloroethane ionizes as readily as t-butyl chloride.[6,7,8] Clearly, such a silyl center should be able to stabilize a developing positive charge on the beta carbon in the π → π* excited state of methyl γ-trimethylsilyl crotonate.

Methyl γ-trimethylsilyl crotonate was prepared by the Reformatsky reaction of methyl γ-bromo crotonate with trimethylchlorosilane. While the Grignard reaction has often been used to form carbon-silicon bonds, the Reformatsky reaction has not. In fact, there are only two previous examples in the literature. Both report the preparation of α-silyl esters via the Reformatsky reaction of a chlorosilane with an α-bromo ester.[9,10]

$$(CH_3)_3SiCl \;+\; BrCH_2{-}CO_2Et \;+\; Zn \;\rightarrow\; (CH_3)_3Si{-}CH_2{-}CO_2Et$$

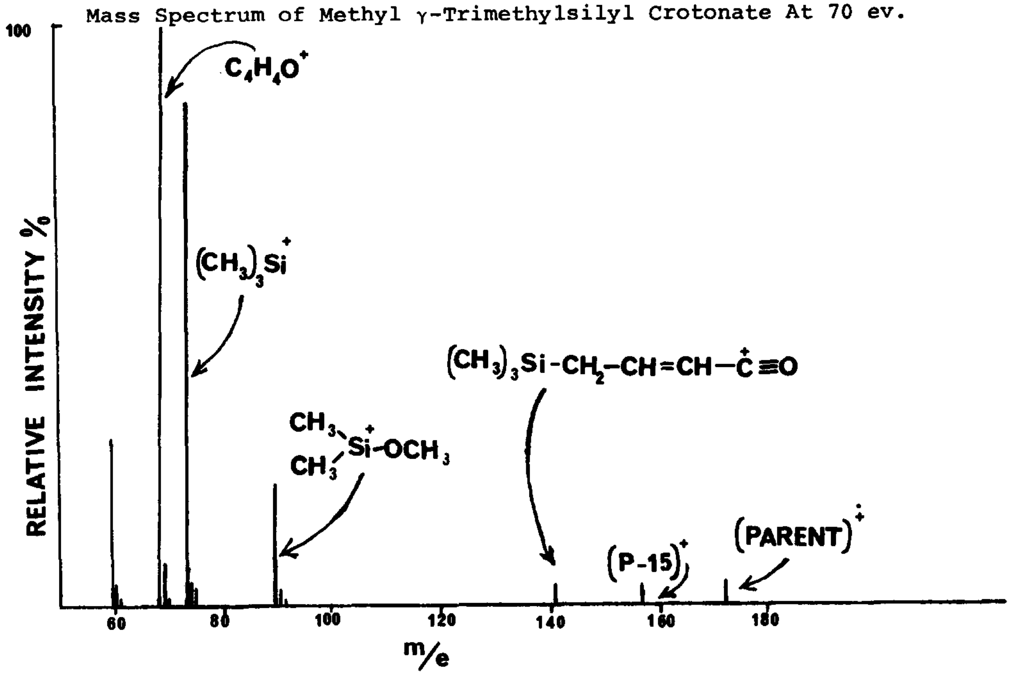
Methyl γ-trimethylsilyl crotonate was prepared by the dropwise addition of a mixture of .1 mole of methyl γ-bromo crotonate and .16 mole of trimethylchlorosilane in 50 ml of dried THF to a rapidly stirred refluxing solution of .12 moles of Mallinkrodt zinc dust in 150 ml of dried benzene.[11] The addition required one hour, after which the reaction was allowed to stir at reflux overnight. After cooling to room temperature the reaction mixture was extracted twice with 50 ml portions of a 20% solution of NH_4Cl and then washed once with 50 ml of cold water.[12] The organic layer was then dried over anhydrous $MgSO_4$, filtered, and the solvents removed by distillation at atmospheric pressure. The residue was then distilled at reduced pressure through a 15 cm Vigreaux column, the fraction bp 80-90°/25 mm was collected; yield 9.3 grams (54%). The product was finally purified by preparative gas chromatography on a ¼" × 15' SE-30 column at 140°. Its nmr is characterized by a singlet at 0.04 δ (9H), a doublet of doublets centered at δ_A 1.66 (2H), J_{ab} = 9 Hz, J_{ac} = 1 Hz, a singlet at 3.60 δ (3H), a pair of triplets centered at 5.55 δ_c (1H), J_{bc} = 16 Hz, J_{ac} = 1 Hz, and finally a pair of triplets centered at 6.89 δ_b (1H), J_{bc} = 16 Hz, and J_{ab} = 9 Hz. The nmr spectrum was run on a Varian HA-100 instrument using cyclohexane as internal standard. The ir spectrum is characterized by a carbonyl stretch at 1718 cm^{-1} and a strong carbon-carbon double bond stretch at 1640 cm^{-1}. The high resolution mass spectrum of the compound was run on an A.E.I. MS-902. In addition to the parent ion at mass 172, a siliconium ion formed by loss of a methyl group from the quarternary silyl center at mass 157 is prominent. Loss of a methoxy group from the ester functionality of the parent ion leads to the corresponding acylium ion at mass 141. The ion at mass 89 is the dimethylmethoxy-siliconium ion formed by rearrangement and fragmentation of the parent-15 ion. The methoxy group of the ester functionality migrates to the siliconium ion center with simultaneous loss of C_4H_4O. The observation of a metastable peak at m/e = 50.5 = $(89)^2/157$ supports this pathway. This type of rearrangement of a methoxy group from an ester functionality to a siliconium ion center has been observed previously in the mass spectrum of 4-trimethylsilyl methyl butyrate.[13] The ion at mass 73 is due to the trimethylsiliconium ion. The base peak at mass 68 has composition C_4H_4O. The observation of a metastable peak at m/e = 26.9 = $(68)^2/172$ indicates that it is formed by rearrangement of the parent ion.



Of great interest is the uv spectrum. The maximum of methyl γ-trimethylsilyl crotonate occurs at 2250 Å, ε = 1.07 × 10^4 in cyclohexane and at 2282 Å, ε = 1.2 × 10^4 in acetonitrile. The bathochromic shift with an increase in solvent polarity is expected for a π → π* transition. By comparison the π → π* maximum in methyl trans crotonate occurs at 2120 Å ε =

1.45×10^4 in ethanol.[14] This shift to longer wavelength of the π → π* transition in methyl γ-trimethylsilyl crotonate amounts to a stabilization of about 9 kcal/mole.

Mass Spectrum of Methyl γ-Trimethylsilyl Crotonate At 70 ev.



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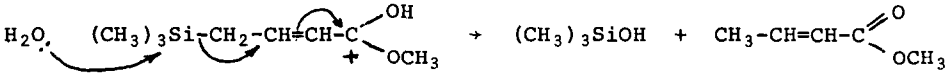
11. This modification of the usual solvent system--benzene--is critical to

the success of the reaction.

12. Both strong acid and base must be avoided in the work-up. A reasonable mechanism for acid catalyzed cleavage of the newly formed carbon-silicon bond can be written yielding methyl crotonate--a product which was indeed detected.



$$H_2O\quad (CH_3)_3Si-CH_2-CH=CH-\overset{+}{C}\begin{smallmatrix}OH\\ OCH_3\end{smallmatrix} \rightarrow (CH_3)_3SiOH + CH_3-CH=CH-C\begin{smallmatrix}\!\!\!=O\\ OCH_3\end{smallmatrix}$$

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