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AMINOSILYLATION OF DIMETHYL ACETYLENEDICARBOXYLATE

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Summary

Nucleophilic addition of *N*-trimethylsilylalkylamines, Me_3SiNHR (where R = Pr and t-Bu), and bis(trimethylsilyl)amine to dimethyl acetylenedicarboxylate occurs via silicon—nitrogen bond cleavage to give dimethyl 2-alkyl-(or trimethylsilyl-)amino-3-trimethylsilyl fumarates as the sole products. These are cleaved by methanol to yield dimethyl 2-(alkyl)aminofumarates. Tris(trimethylsilyl)-amine does not react with dimethyl acetylenedicarboxylate.

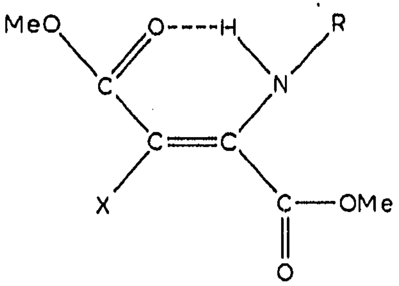
Introduction

Stereochemical aspects of the nucleophilic addition of amines to acetylenedicarboxylic esters have been studied by several workers [1—5]. From spectroscopic data, it has been concluded that stable adducts of primary amines are aminofumarates whereas those of secondary amines are aminomaleates [5]. Triethylamine also adds, to give, surprisingly, the same product as diethylamine [6].

George and Lappert [7] reported the additions of Me_3MNMe_2 (M = Si, Ge and Sn) to diethyl acetylenedicarboxylate involving metal—nitrogen bond cleavage. The IR and NMR spectra of the adducts indicated the presence of only one stereoisomer, which was assumed to be the maleate derivative on the basis of the reported structures of the analogous adducts of secondary amines. Later Rivière-Baudet and Satgé [8] in a detailed study of addition of germylamines, R_3GeNMe_2 (R = Me and Et), to dimethyl and diethyl acetylenedicarboxylates, found evidence (NMR and GLC) for the presence of both maleate and fumarate derivatives. Reactions of secondary organometalamines of the type R_3MNHR have not previously been described and we studied the reactions of Me_3SiNHR (R = Pr and t-Bu) and $(Me_3Si)_2NH$ with dimethyl acetylenedicarboxylate with a view to (a) establishing whether the Si—N bond or N—H bond is cleaved, and (b) determining the stereochemical characterisation of the addition.

TABLE 1

RELEVANT IR AND NMR PEAKS OF

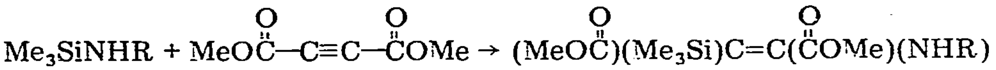


Compound	X	R	IR data (cm^{-1})				NMR data (τ, ppm)		
			NH	ν(C=O)	ν(C=C)	ν(C–O)	X	OMe	Peaks due to R [a]
I	SiMe$_3$	Pr	3250	1745, 1650	1570	1230	9.95	6.25, 6.40	9.10t, 8.50m, 7.05q (J 7 Hz)
II	SiMe$_3$	t-Bu	3250	1740, 1650	1550	1230	9.90	6.25, 6.40	8.70s
III	SiMe$_3$	SiMe$_3$	3160	1750, 1650	1578	1230	9.90	6.25, 6.40	9.80s
IV	H	Pr	3300	1740, 1670	1610	1220	5.00	6.20, 6.40	9.1t, 8.45m, 6.7t, (J 7 Hz)
V	H	t-Bu	3290	1740, 1670	1605	1215	5.25	6.20, 6.40	8.70s
VI	H	s-Bu	3295	1740, 1670	1610	1225	5.05	6.20, 6.40	9.15t, 8.9d 8.6m, 6.1–6.6m
VII	H	i-Bu	3300	1740, 1670	1610	1220	5.00	6.20, 6.40	9.15d, 8.2m, 6.85t (J 7 Hz)
VIII	H	n-Hex	3300	1740, 1670	1610	1220	5.00	6.20, 6.40	8.2–9.3m, 6.65q (J 6 Hz)

[a] s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet.

Results and discussion

Silylamines are markedly less reactive than primary and secondary amines towards dimethyl acetylenedicarboxylate. Thus, whereas amines add exothermally at room temperature, *N*-trimethylsilylalkylamines, Me_3SiNHR (R = Pr, t-Bu) give the adduct in only 10% yield in refluxing ether, while bis(trimethylsilyl)-amine does not react at all under these conditions. However, on heating the reactants neat at 80—90°C for 3—4 hours, the reaction occurs smoothly giving addition products as distillable liquids in quantitative yield. Tris(trimethylsilyl)-amine did not react with dimethyl acetylenedicarboxylate even upon heating the reactants neat at 140—150°C for 10 hours. The order of reactivity, $Me_3SiNHR > (Me_3Si)_2NH \gg (Me_3Si)_3N$, can be related to the nucleophilicity of nitrogen, which decreases as the number of silyl substituents on nitrogen increases.



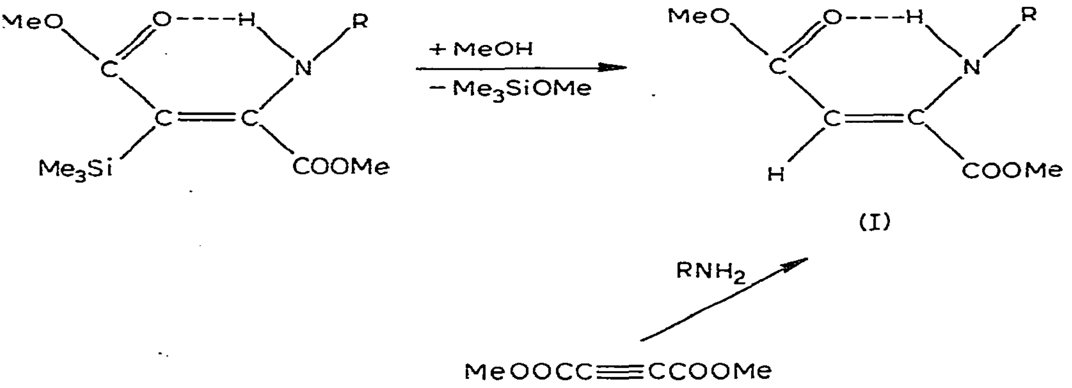
$$Me_3SiNHR + MeO\overset{O}{\overset{\|}{C}}{-}C{\equiv}C{-}\overset{O}{\overset{\|}{C}}OMe \rightarrow (MeO\overset{O}{\overset{\|}{C}})(Me_3Si)C{=}C(\overset{O}{\overset{\|}{C}}OMe)(NHR)$$

(I) R = Pr
(II) R = t-Bu
(III) R = $SiMe_3$

The important peaks present in the IR and NMR spectra (both obtained for neat samples) of the addition compounds are listed in Table 1. That the addition of silylamines to dimethyl acetylenedicarboxylate involves silicon—nitrogen bond cleavage and not nitrogen—hydrogen bond cleavage is clearly demonstrated by the presence of an N—H peak in the IR spectra and the absence of any peak due to a vinylic proton in the NMR spectra, and by the fact that ν(SiNSi), which appears at 935 cm^{-1} in $(Me_3Si)_2NH$ as a strong peak [9], is absent in the adduct. The IR spectra of Me_3SiNHR (R = Me, Et and Ph) have been reported by Berger and Goetze [10], and a peak at about 700 cm^{-1} assigned to the Si—N stretching mode coupled strongly with other vibrations of the molecule. Randall, Ellner and Zuckerman [11] on the other hand, report ν(Si—N) in $Me_3Si^{14}NHPh$ and $Me_3Si^{15}NHPh$ at 899 and 890 cm^{-1}, respectively. In reaction of *N*-trimethylsilyl alkylamines with dimethyl acetylenedicarboxylate, we find that although all other peaks of $Me_3SiNHPr$ and $Me_3SiNHBu$-t in 600—1000 cm^{-1} region are present in the spectra of addition compounds also, the strong peak present at 870 cm^{-1} in both the silylamines is missing in the adducts and, therefore, it may possibly be due to a silicon—nitrogen stretching vibration.

The IR and NMR spectra of the addition compounds further indicate that the distilled product consists of only one stereoisomer, which appears to be the fumarate derivative (structure shown in Table 1). The markedly lower values of ν(N—H) show the presence of strong intramolecular hydrogen bonding. In the addition compound of bis(trimethylsilyl)amine, ν(N—H) is further lowered owing to the presence of the trimethylsilyl group on the nitrogen, and appears at 3160 cm^{-1}. Two strong carbonyl absorptions are present at 1743 ± 5 and 1650 cm^{-1}; the former is due to a free carbonyl group and the latter may be due to a hydrogen bonded carbonyl group. The characteristic peaks of a trimethylsilyl group (δ_s 1255 cm^{-1}; ρ_{as}, 850 cm^{-1}; ρ_s 760 cm^{-1}), are also present in the addition compounds. In the NMR spectra the ester methyls appear as two singlets at τ 6.20 and 6.40 ppm. The former may be due to methyl of a hydrogen bonded ester group and the latter due to methyl of a free ester group. The trimethylsilyl peak appears at 9.9 τ, whereas the N—$SiMe_3$ protons in compound (III) appear as a singlet at τ 9.8 ppm. The N—H proton is highly deshielded because of hydrogen bonding, and is shifted to negative values. In the NMR spectrum of compound I, the N—CH_2 protons of the N—Pr group, appear as a quartet (*J* 7 Hz) because of coupling to the amino proton. This further supports the presence of a hydrogen-bonded amino group. It has been observed before that the NH proton generally couples with protons at the adjoining carbon only when its fast interchange is prevented by hydrogen bonding, as e.g. in β-ketoenamines [12].

The silylamine adducts I—III react exothermally with methanol with ready cleavage of the silicon—vinyl bond. This is consistent with the high reactivity of the corresponding germanium compounds [8] towards water and alcohol. The enamine obtained on removal of the methoxytrimethylsilane, also appears to be exclusively the aminofumarate derivative in each case. Methanolysis of bis-(trimethylsilyl)amine adduct III cleaves off both of the trimethylsilyl groups



giving dimethyl aminofumarate (I, R = H) as a distillable liquid, which was easily identified by its IR and NMR data with those [5] for a sample prepared directly from dimethyl acetylenedicarboxylate.

Compounds IV and V, obtained by the methanolysis of adducts I and II are new; they can also be synthesized by treating dimethyl acetylenedicarboxylate with propylamine or t-butylamine. This reaction has been carried out with three other amines (s-butyl-, i-butyl- and n-hexyl-amines) to give derivatives VI, VII and VIII. Although an excess of the amine was used in all these cases, the reaction stopped after addition of only one mole.

The compounds IV—VIII are distillable liquids, and their IR and NMR spectra (Table 1) show that these are exclusively alkyl aminofumarates. However, in the case of a sample of IV, prepared from dimethyl acetylenedicarboxylate, the NMR spectrum showed the presence of 10% of the dimethyl propylaminomaleate isomer. For the maleate derivative, the vinylic proton appears as a singlet at τ 5.35 ppm and the ester methyl protons give two signals at τ 6.23 and 6.46 ppm. The position of the vinylic proton signal has been utilized by a number of workers [2—5,13] to differentiate between fumaric and maleic acid esters, on the basis of the rule that a β-olefinic proton is deshielded by 0.5 to 0.9 ppm by a *cis*-COOR group [14]. Our results, showing the higher stability of alkyl aminofumarates, are in complete agreement with those of Huisgen et al. [4], who studied the reactions of cyclohexylamine and aromatic amines with dimethyl acetylenedicarboxylate.

A comparison of the ν(N—H) bands in compounds I—VIII (Table 1) clearly indicates that intramolecular hydrogen bonding is stronger in the trimethylsilyl derivatives. Donation of vinylic π-electrons to silicon *d* orbitals is well known [15], and in compounds I—III this will tend to withdraw electrons from the nitrogen attached to the vinylic group, thereby strenghtening the hydrogen bond.

Rivière-Baudet and Satgé [8] have discussed the mechanism of additions of germylamines to acetylenedicarboxylic esters and have proposed a bipolar ion of allenic structure as a common intermediate for the formation of both the stereoisomers. The experimental conditions under which *N*-trimethylsilyl alkylamines and bis(trimethylsilyl)amine add to dimethyl acetylenedicarboxylate are such that only the more stable isomer is obtained. The higher stability of 2-alkyl-(or trimethylsilyl-) amino-3-trimethylsilylfumarates in comparison to the corresponding maleates may be due to intramolecular hydrogen bonding. In the methanolysis of these compounds, it is again the more stable fumarate derivative which is exclusively obtained.

Experimental

Reaction of N-trimethylsilyl propylamine with dimethyl acetylenedicarboxylate

A mixture of *N*-trimethylsilyl propylamine (5.5 g) and dimethyl acetylenedicarboxylate (5.7 g) was heated at 80—90°C for 3 hours. The product distilled at 90°C/0.2 mmHg to give dimethyl 2-propylamino-3-trimethylsilylfumarate as a colourless liquid (8.8 g, 80%) which became yellow after 3—4 hours (Found: Si, 10.1; N, 5.0. $C_{12}H_{23}NO_4Si$ calcd.: Si, 10.3; N, 5.1%).

Reaction of N-trimethylsilyl t-butylamine with dimethyl acetylenedicarboxylate

Dimethyl acetylenedicarboxylate (9.5 g) treated with *N*-trimethylsilyl-t-butylamine (9.85 g) at 80—100°C (3 hours) gave dimethyl 2-t-butylamino-3-trimethylsilylfumarate (16.2 g, 85%), b.p. 80°C/0.2 mmHg (Found: Si, 9.4; N, 4.7. $C_{13}H_{25}NO_4Si$ calcd.: Si, 9.8; N, 4.9%).

Reaction of bis(trimethylsilyl)amine with dimethyl acetylenedicarboxylate

The adduct, formed from bis(trimethylsilyl)amine (9.2 g) and dimethyl acetylenedicarboxylate (8.1 g) by heating the reactants neat at 100—105°C for 6 hours, was identified as dimethyl 2-trimethylsilylamino-3-trimethylsilylfumarate (9.5 g, 55%), b.p. 87—88°C/0.1 mmHg (Found: Si, 18.4; N, 4.5. $C_{12}H_{25}NO_4Si_2$ calcd.: Si, 18.5; N, 4.6%).

Attempted reaction of tris(trimethylsilyl)amine with dimethyl acetylenedicarboxylate

A mixture of tris(trimethylsilyl)amine (9.4 g) and dimethyl acetylenedicarboxylate (5.7 g) was heated at 120—130°C for 12 hours. The IR spectrum of the mixture showed that no reaction had occurred.

Methanolysis of 2-amino-3-trimethylsilyl fumarates

(a) An exothermic reaction occurred on adding methanol (2.0 g) to dimethyl 2-propylamino-3-trimethylsilylfumarate (5.5 g). The mixture was refluxed for 1 hour, then methoxytrimethylsilane and excess methanol were removed in vacuo. The remaining liquid (4.1 g) on distillation gave dimethyl propylaminofumarate (3.6 g 90%) at 80—81°C/0.3 mmHg. (Found: N, 6.9. $C_9H_{15}NO_4$ calcd.: N, 7.0%).

(b) In a similar experiment as above, dimethyl 2-t-butylamino-3-trimethylsilylfumarate (7.2 g) and methanol (2 g) gave dimethyl t-butylaminofumarate (4.7 g, 88%), b.p. 90°C/0.5 mmHg (Found: N, 6.3. $C_{10}H_{17}NO_4$ calcd.: N, 6.5%).

(c) Dimethyl 2-trimethylsilylamino-3-trimethylsilylfumarate (5.7 g), on methanolysis, yielded the dimethyl ester of aminofumaric acid (2.7 g, 90%), b.p. 59°C/0.15 mmHg (Found: N, 8.7. $C_6H_9NO_4$ calcd.: N, 8.8%).

Reactions of primary amines with dimethyl acetylenedicarboxylate

Excess amine (~0.4 mol) was added drop by drop to dimethyl acetylenedicarboxylate (~0.2 mol). An immediate exothermic reaction gave a yellow product. The mixture was heated at 80—100°C (1 hour) and then the excess of amine was removed in vacuo. Distillation under reduced pressure gave the addition compound as a light yellow oil. Only the mono-adduct was formed in all the cases. The following new derivatives were obtained: Dimethyl propylaminofumarate, b.p. 81°C/0.3 mmHg (Found: N, 6.9. $C_9H_{15}NO_4$ calcd.: N, 7.0%), dimethyl s-butylaminofumarate, b.p. 87° C/0.5 mm Hg (Found: N, 6.5. $C_{10}H_{17}NO_4$ calcd.: 6.5%), dimethyl i-butylaminofumarate, b.p. 80° C/0.2 mmHg (Found: N, 6.3. $C_{10}H_{17}NO_4$ calcd.: N, 6.5%), dimethyl t-butylaminofumarate, b.p. 90°C/0.5 mmHg (Found: N, 6.3. $C_{10}H_{17}NO_4$ calcd.: N, 6.5%), and dimethyl n-hexylaminofumarate, b.p. 114°C/0.35 mmHg (Found: N, 5.6. $C_{12}H_{21}NO_4$ calcd.: N, 5.8%).

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