

THE PREPARATION OF BIS- AND TRIS-(TRIMETHYLSILYL)ACETIC ACID

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SUMMARY

Contrary to an earlier report, lithiation of tris(trimethylsilyl)methane followed by carbonation does not yield the acid $(\text{Me}_3\text{Si})_3\text{CCO}_2\text{H}$, (I), if an alkali extraction step is included in the work up; the product is actually the acid $(\text{Me}_3\text{Si})_2\text{CHCO}_2\text{H}$, (II). The acid (I) can be obtained if the alkali extraction is omitted. Separate experiments have confirmed that (I) is rapidly converted into (II) by aqueous or methanolic base.

INTRODUCTION

In a paper dealing with reactions of tris(trimethylsilyl)methylithium, Cook and his colleagues reported that carbonation gave tris(trimethylsilyl)acetic acid $(\text{Me}_3\text{Si})_3\text{CCO}_2\text{H}$ (I)¹. They described this acid as having a m.p. of 105°, showing singlets in the NMR spectrum (in CCl_4) at τ 9.86, and 8.43, and giving the elemental analysis and molecular weight expected for (I). Work by two of us (O.W.S. and J.S.J.) has now shown that if the exact procedure for isolation of the acid described by Cook *et al.*, involving extraction with base then re-acidification, is followed, the product is mainly bis(trimethylsilyl)acetic acid, $(\text{Me}_3\text{Si})_2\text{CHCO}_2\text{H}$, (II), and it appears that the m.p. and NMR spectrum given by Cook *et al.* referred to (II), while the analysis and molecular weight referred to a sample of (I) obtained by them from an experiment in which the base-extraction step was omitted.

RESULTS AND DISCUSSION

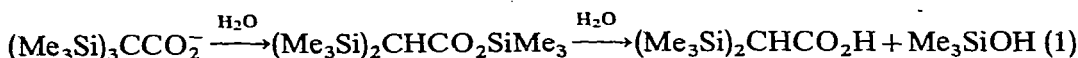
A solution of tris(trimethylsilyl)methylithium in ether was poured on to solid carbon dioxide, and the resulting slurry was added to aqueous hydrochloric acid. Extraction with ether, was followed by shaking of the ethereal extracts with aqueous sodium hydroxide and reacidification of the aqueous solution. Several recrystallizations followed by sublimation gave an acid of m.p. 100–102°, which was shown by its elemental analysis, neutral equivalent, molecular weight, and NMR spectrum to be (II). The NMR spectrum (in CCl_4) showed singlets at τ 9.83, 8.43 and -2.08 , attribu-

table, respectively, to the Me_3Si proton, the $\alpha\text{-C-H}$ proton, and the CO_2H proton; the intensities were close to the expected ratios of 18/1/1. The peak at $\tau - 2.08$ collapsed when a solution in carbon tetrachloride was shaken with deuterium oxide.

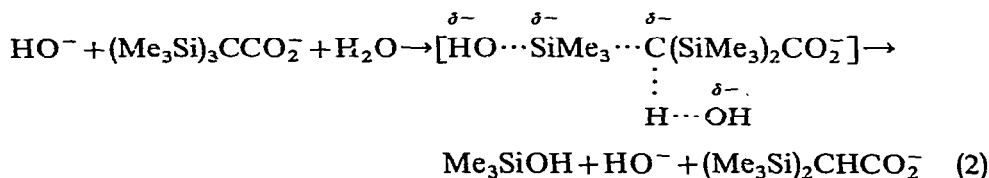
On the other hand, when the base-extraction step was omitted after the carbonation, a mixture of acids was obtained, from which by chromatography on silica gel (I) was isolated pure, m.p. 128–130°, in 30% yield, along with a mixture of (I) and (II). That the pure acid in this case was (I), was shown by satisfactory analytical and molecular weight data, and by the NMR spectrum, which showed peaks at τ 9.73 (Me_3Si) and -1.95 (OH), in the intensity ratio of 27/1*.

That base readily removes one trimethylsilyl group from (I) was confirmed by dissolving a sample of (I) containing 25% of (II) in 5% aqueous sodium hydroxide and extracting with ether after 2 h. The acid (II) was isolated in 85% yield, the NMR spectrum confirming that none of the tris-compound, (I), remained; hexamethyldisiloxane was also identified as a product. Again, when (I) and (II) were separately dissolved in methanol-*d* containing sodium methoxide, and the NMR spectra were recorded within 1 min, the peaks due to the Me_3Si groups appeared in both solutions at τ 9.84, showing that (I) had been completely converted into (II).

We cannot at present decide between two possible mechanisms. The first, (1), would involve migration of an Me_3Si group within the carboxylate ion, followed by rapid hydrolysis of the ester formed (*cf.* ref. 3):



The second would involve direct cleavage of an $\text{Me}_3\text{Si-C}$ bond under attack of the hydroxide ion at silicon, possibly in a synchronous process such as that represented by (2)²:



It has been argued that cleavages of the latter type are unlikely³, since they involve reactions between two anions, and (notional) generation of di-anionic species. However, the anions, *o*-, *m*-, and *p*- $\text{Me}_3\text{SiCH}_2\text{C}_6\text{H}_4\text{CO}_2^-$ are all cleaved by base more readily than the parent $\text{Me}_3\text{SiCH}_2\text{C}_6\text{H}_5^4$; the influence of delocalization of π -electrons into the carboxylate ion group outweighs the deactivating effect of the negative pole, and the activating effect of the *p*- CO_2^- group, in particular, is very substantial. The (incipient) carbanion $(\text{Me}_3\text{Si})_2(\text{CO}_2^-)\text{C}^-$ could thus be stabilized by the Me_3Si groups [through ($p_\pi \rightarrow d_\pi$) bonding] and by the CO_2^- group (through conjugation of the lone pair with the C=O bond), and even though the stability of the potential carbanion is not the only factor governing the ease of cleavage of a C-Si

* A check on laboratory notebooks showed that Cook *et al.* had sometimes worked up the products after carbonation of tris(trimethylsilyl)lithium by a base-extraction, as they reported¹, and sometimes by omitting this step. Unfortunately they did not realize that they were dealing with two distinct products.

bond², ready base cleavage of one Me₃Si-C bond of (I) would be easily explicable. It would also be consistent with the very rapid base cleavage of Me₃Si-C bonds in the compound (Me₂HSi)₄Si^{5*}. The question should be resolvable by kinetic studies, and by examination of an ester such as (Me₃Si)₃CCO₂Me, which should undergo direct cleavage more readily, but rearrangement much less readily, than the carboxylate ion derived from (I).

EXPERIMENTAL

General

All experiments with organolithium reagents were conducted under nitrogen.

NMR spectra were recorded at 60 MHz on a Varian A60 spectrometer, with carbon tetrachloride solutions containing tetramethylsilane as internal standard. IR spectra were recorded in carbon tetrachloride on a Beckman IR-20 instrument. Molecular weights were determined at 70 eV with an LKB-9000 combined gas chromatograph-mass spectrometer.

Preparation of bis(trimethylsilyl)acetic acid (II)

An ethereal solution (25 ml) of methyllithium (100 mmol) (prepared from bromomethane and lithium) was injected into a flask containing tris(trimethylsilyl)methane⁶ (9.85 g, 42 mmol) in tetrahydrofuran (100 ml). The mixture was refluxed for 7 h then poured on to powdered solid carbon dioxide. The resulting slurry was added to 5% hydrochloric acid (150 ml), and the mixture was extracted several times with ether (1000 ml). The combined extracts were shaken thoroughly with 3 × 100 ml portions of 5% aqueous sodium hydroxide, and the combined aqueous extracts were acidified. Ether extraction (500 ml), followed by removal of the ether under reduced pressure gave crude bis(trimethylsilyl)acetic acid (6.8 g, 79%). After several crystallizations from ethanol, and sublimation, a sample of high purity was obtained, m.p. 100–102°. (Found: C, 47.13; H, 9.94%; neutral equivalent 200; mol.wt., 204. C₈H₂O₂Si₂ calcd: C, 47.00; H, 9.86%; neutral equivalent and mol.wt., 204.) The IR spectrum showed a C=O absorption at 1668 cm⁻¹, and the NMR spectrum showed resonances at τ 9.83, 8.43, and -2.08, in the intensity ratio of 19/1/1. When a solution in carbon tetrachloride was shaken with deuterium oxide, the peak at τ -2.08 collapsed, while the peaks at τ 9.83 and 8.43 were unchanged.

Preparation of tris(trimethylsilyl)acetic acid, (I)

A solution of methyllithium (66 mmol) in ether (40 ml) (supplied by Alpha Products) was injected into a flask containing tris(trimethylsilyl)methane (11.8 g, 51 mmol) in tetrahydrofuran (100 ml). The mixture was refluxed for 8 h then poured on to powdered solid carbon dioxide. The resulting slurry was added to 5% hydrochloric acid (150 ml), and the mixture was extracted several times with ether (750 ml). The ethereal extract was dried over Drierite, and the solvent removed under reduced pressure to give impure tris(trimethylsilyl)acetic acid (8.45 g, 59%). The crude product

* The stability towards base of tetrakis(trimethylsilyl)methane^{1,5} remains anomalous. It is known that proton transfer from the solvent to the separating carbon atom is of importance in at least some base-cleavages of Si-C bonds², and possibly this process is seriously sterically hindered in (Me₃Si)₄C.

was transferred to a chromatographic column (20 mm \times 280 mm; silica gel, grade 950, 60–200 mesh, Fisher Scientific Co.) using petroleum ether, b.p. 38–50°. Petroleum ether (500 ml) was passed through the column followed by methanol (500 ml). Removal of the solvent from the methanol fraction gave a mixture of acids (4.1 g); NMR analysis showed that it contained approximately equal amounts of tris-, and bis-(trimethylsilyl)acetic acid. Removal of the solvent from the petroleum ether fraction gave tris(trimethylsilyl)acetic acid (4.3 g, 30%), m.p. 128–130° (Found: C, 47.92; H, 10.07%; Si, 30.18%; mol.wt. 276. $C_{11}H_{28}O_2Si_3$ calcd.: C, 47.76; H, 10.20; Si, 30.47%; mol.wt. 277).

The IR spectrum showed a C=O absorption at 1645 cm^{-1} , and the NMR spectrum showed resonances at τ 9.73 and -1.95 in the intensity ratio of 27/1.

Base cleavage of tris(trimethylsilyl)acetic acid

(a) A sample (0.28 g) of tris(trimethylsilyl)acetic acid containing 25% bis-(trimethylsilyl)acetic acid, as revealed by NMR analysis, was dissolved in 5% aqueous sodium hydroxide (40 ml). The solution was stirred for 2 h then extracted with ether (100 ml). This liquid remaining after removal of the ether under reduced pressure was shown to be hexamethyldisiloxane by its NMR spectrum, which showed a peak at τ 9.94 (lit.⁷, τ 9.94).

The basic solution was acidified and extracted several times with ether (500 ml). Evaporation of the ether left a white solid (0.19 g), which was shown by its NMR spectrum to be bis(trimethylsilyl)acetic acid (85%); no resonances due to tris-(trimethylsilyl)acetic acid could be detected.

(b) *Sodium methoxide-methanol-d*. Samples of tris(trimethylsilyl)acetic acid (0.017 g) and bis(trimethylsilyl)acetic acid (0.016 g) were dissolved in methanol-*d* containing sodium methoxide (1 ml) [prepared by dissolving sodium (0.284 g) in 99% methanol-*d* (10 ml)]. The resulting solutions were placed in NMR tubes, and the spectra of the anions were recorded within 1 min. The positions of the peaks due to the Me_3Si protons were identical (τ 9.84) in the two samples. Solvent interference prevented examination of the peak due to $-Si_2CHCO_2^-$, which should be absent in the cleavage product because of deuteration.

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