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NOVEL CLEAVAGES OF BENZYL- AND *m*-METHOXYBENZYL-TRIMETHYLSILANE BY TRIFLUOROACETIC ACID

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Summary

Benzyltrimethylsilane is cleaved slowly by trifluoroacetic acid at 70°C to give, in addition to the expected trimethylsilyl trifluoroacetate and toluene, mainly *o*- and *p*-trimethylsilylmethyldiphenylmethane (I and II) along with smaller amounts of dibenzyl, *o*- and *p*-methyldiphenylmethane, and benzyl trifluoroacetate. Addition of benzyl trifluoroacetate substantially increases the yields of I and II, and it is suggested that they are formed by benzyl trifluoroacetate benzylation of benzyltrimethylsilane, and that the benzyl trifluoroacetate is formed from methylenecyclohexadiene intermediates themselves produced by ring-protonation of benzyltrimethylsilane followed by loss of the Me_3Si^+ entity. Addition of water up to about 5 wt.-% increases the rate of cleavage and diverts the reaction towards formation of toluene and hexamethyldisiloxane. *m*-Methoxybenzyltrimethylsilane is much more readily cleaved by trifluoroacetic acid, which is consistent with reaction via a methylenecyclohexadiene type of intermediate, and *m*-methylanisole is the sole aromatic product.

Introduction

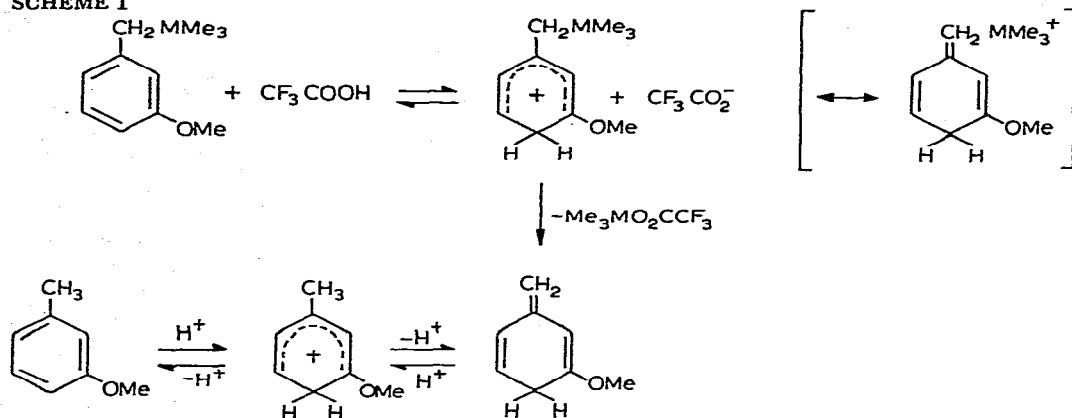
Two groups of workers recently independently observed that the benzyl-tin bonds in some $\text{XC}_6\text{H}_4\text{CH}_2\text{-SnMe}_3$ compounds can be cleaved by acids to give $\text{XC}_6\text{H}_4\text{Me}$ compounds by an unusual mechanism, involving ring protonation followed by loss of the Me_3Sn^+ entity to give a methylenecyclohexadiene intermediate, as represented in Scheme 1 [1,2]**. This mechanism appears to operate for $\text{X} = m\text{-MeO}$, and probably also for $\text{X} = m\text{-Me}$, in both aqueous-methanolic

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** For simplicity, the corresponding sequences initiated by protonation *ortho* to the Me_3MCH_2 group are omitted.

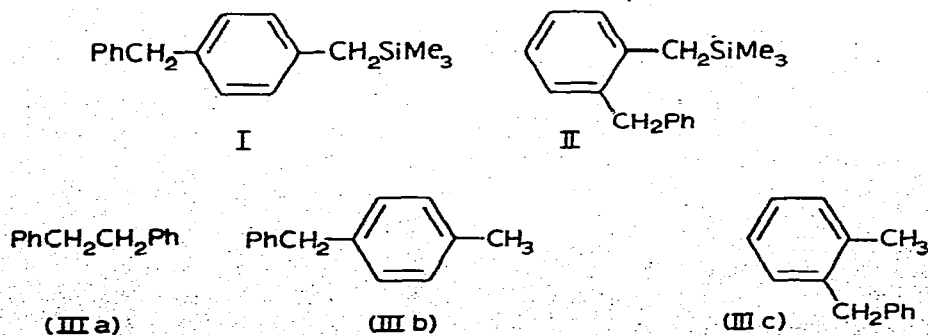
perchloric acid [1] and benzene containing trifluoroacetic acid [2], but for benzyltrimethylsilane itself, and its derivatives with X = *o*- and *p*-Me, -F, -Cl, *o*-Br, *m*- and *p*-CF₃, *p*-t-Bu and *p*-OMe direct cleavage of the benzyl-Sn bond seems to occur, at a rate not much greater than that of the Sn-Me bonds [1,2]. Silicon compounds of the type Ph(CH₂)_nSiMe₃ are known to undergo slow cleavage of both Si-Me and Ph(CH₂)_n-Si bonds for n = 2-4 in trifluoroacetic acid at 70°C [3], and we have now examined the rather more rapid cleavage in this medium of the benzyl-silicon bonds in benzyl- and *m*-methoxybenzyltrimethylsilane.

SCHEME 1



We have found that for the silicon as for the tin compounds, there is a clear difference in behaviour between the benzyl and *m*-methoxybenzyl derivatives. The methoxy compound is quite readily cleaved; in a 1 : 10 (molar ratio) mixture of the compound and trifluoroacetic acid, *m*-methylanisole is formed in about 20% yield after 1 h at room temperature (ca. 20°C). After 18 h at 70°C no starting material remains, and *m*-methylanisole is the sole aromatic product revealed by GLC analysis.

The parent benzyltrimethylsilane reacts much more slowly, and when a 1 : 10 (molar ratio) PhCH₂SiMe₃/CF₃CO₂H mixture was kept at 70°C for 24 h about 70% of unchanged benzyltrimethylsilane remained (see Experimental), and this was the greatly dominant component of the mixture as revealed by GLC (Table 1). The expected trimethylsilyl trifluoroacetate was present, along with some toluene, but there were greater amounts of higher molecular weight products, which were shown to be *p*- and *o*-trimethylsilylmethyldiphenylmethane



(I and II). There were also small amounts of benzyl trifluoroacetate, and a mixture (III) of dibenzyl (IIIa) with its isomers *o*- (IIIb) and *p*-methyldiphenylmethane (IIIc). (Small amounts of products of higher molecular weight were also present, and these probably include compounds of the type $\text{Me}_3\text{SiCH}_2 - \text{C}_6\text{H}_3(\text{CH}_2\text{Ph})_2$ (see below).) Hydrogen was also formed, but the quantity was not determined.

We must emphasize the qualitative nature of the results of the determination of the product compositions, since there was not even approximate quantitative agreement between the analysis carried out (on mixture kept for 3 h at 70°C) in the U.S.S.R., and those carried out (on mixtures kept for 24 h at 70°C) in the U.K. In the former analyses the mixtures were injected directly on to the GLC column, whereas in the latter the samples were usually obtained by hexane extraction after addition of water. (This converts the trimethylsilyl trifluoroacetate into hexamethyldisiloxane, which was not separated from the hexane in the GLC analysis.) However, for the purpose of the qualitative discussion below the differences are unimportant. Reactions were usually conducted in sealed ampoules after evacuation; some reactions carried out in the U.S.S.R. without this removal of air appeared to take place substantially more slowly, but in the absence of further investigation this possibility is ignored in the discussion below.

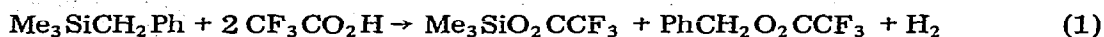
Additional features, mainly apparent in Table 1, are as follows: (a) The amount of toluene relative to that of the other products shows a marked increase in the reaction time. There is no apparent increase in the yields of I and II between 24 and 96 h reaction. (b) Addition of benzyl trifluoroacetate markedly increases the yields of I and II, and probably also of the isomer mixture III, and more surprisingly, apparently also leads to more toluene and the production of some hexamethyldisiloxane. (c) Addition of a little sulphuric acid has a larger and mainly similar effect, but the yields of the mixture III and toluene are much increased. (d) Addition of toluene has little effect. (e) When 5 wt.-% of water is initially present, the rate of disappearance of the benzyltrimethylsilane is somewhat raised and the yield of toluene substantially increased. With a few per cent of water present, when toluene forms a substantial proportion of the products, it is possible to measure the rate of conversion of the starting material to toluene very roughly by monitoring the absorption at 273.5 nm [1,4,5]. (At lower water concentrations, where toluene is a minor product, formation of I and II leads to an increase instead of a decrease of optical density at this wavelength.) The rate of the reaction to give toluene appears to pass through a maximum at about 5 wt.-% water. (f) Toluene was shown to be readily benzylated by benzyl trifluoroacetate, to give IIIb and IIIc, and probably dibenzyltoluenes.

Discussion

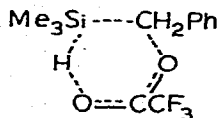
The ready reaction of *m*-methoxybenzyltrimethylsilane is consistent with the operation for this compound of the mechanism shown in Scheme 1. Cleavage of benzyltrimethylsilane is much more complex, since benzyl trifluoroacetate and hydrogen are formed in addition to the expected toluene. The other abnormal products, I, II and III, can be readily accounted for once the formation of benzyl trifluoroacetate is recognised, since this compound acts as an effective

benzylating agent in the medium concerned, and thus benzyltrimethylsilane, which is quite strongly activated towards attack by electrophiles [3,4] is readily converted into I and II. Formation of IIIb and IIIc can be accounted for mainly in terms of subsequent 'normal' cleavage of the $\text{Me}_3\text{Si}-\text{CH}_2\text{Ar}$ bonds of I and II which should occur at a fairly similar rate to that of $\text{Me}_3\text{Si}-\text{CH}_2\text{Ph}$ bonds, though benzylation of product toluene may make a minor contribution. The marked increase in production of I, II, IIIb and IIIc (and also of IIIa, see below) in the presence of added benzyl trifluoroacetate, and especially of IIIb and IIIc in the presence of the more powerful cleavage reagent sulphuric acid, is confirmation of these proposals.

The abnormality of the cleavage thus lies essentially in the formation of benzyl trifluoroacetate and hydrogen, in the overall process represented by eqn. 1.



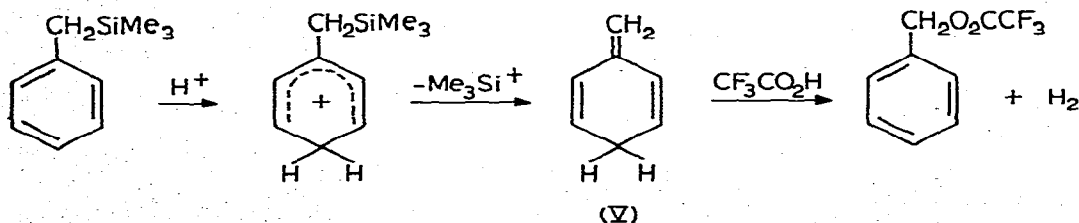
The simplest mechanism one can envisage for this overall process is direct cleavage of the PhCH_2-Si bond in the abnormal direction represented in IV, to give benzyltrifluoroacetate and trimethylsilane, since the latter would readily undergo solvolysis to give trimethylsilyl trifluoroacetate and hydrogen. However



(IV)

cleavage of the $\text{Si}-\text{C}$ bond in the direction Si^-C^+ is contrary to general experience [6], and no special factors are apparent which should favour it in this particular case*. We suggest instead that the initial attack of acid results in the formation of methylenecyclohexadiene (V). (For simplicity the corresponding isomeric intermediates produced by initial protonation at the *ortho*-position are again neglected.) Some of this then undergoes the usual acid-catalysed aromatization to give toluene, but rather more, we suggest, is converted into benzyl trifluoroacetate. This latter reaction, for which possible route is outlined in Scheme 2, is closely analogous to the formation of *p*-methylbenzyl acetate (VI)

SCHEME 2

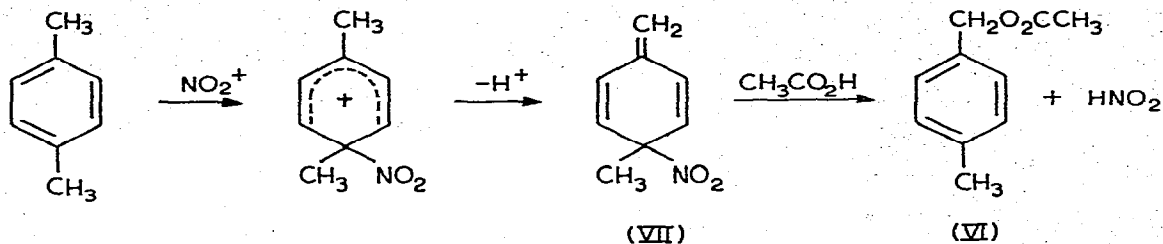


during nitration of *p*-xylene by acetyl nitrate in acetic anhydride, which is

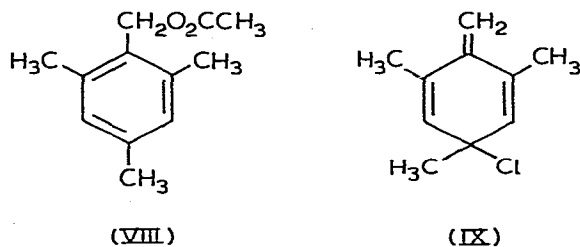
* We note that breaking of the $\text{Si}-\text{C}$ bond in the direction shown in IV involves formation of $\text{Si}-\text{H}$ and $\text{C}-\text{O}$ bonds rather than the markedly stronger $\text{Si}-\text{O}$ and $\text{C}-\text{H}$ bonds produced by normal cleavage.

believed to proceed by the route shown in Scheme 3 [7]*. It has, in fact, been

SCHEME 3

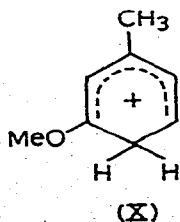


shown that the methylenecyclohexadiene derivative (VII) gives *p*-methylbenzyl acetate on thermolysis or on treatment with acetic acid containing acetic anhydride [7]. Formation of 2,4,6-trimethylbenzyl acetate (VIII) during chlorination of isodurene is thought to go through the analogous intermediate (IX) [8]. (But see [9].)



The favoured mechanism for the conversion of VII into VI and of IX into VIII involves attack of acetic acid at the methylene group and departure of the NO_2^- and Cl^- respectively, in $\text{S}_{\text{N}}2'$ processes [7], and this has the somewhat unattractive implication that hydride ion is the leaving group in the conversion of methylenecyclohexadiene into benzyl trifluoroacetate in trifluoroacetic acid, but free hydride ion is probably not involved, of course, synchronous proton transfer from the solvent, with formation of hydrogen, providing electrophilic assistance to the breaking of the C—H bond. Furthermore, the aromatization provides a powerful driving force in these reactions.

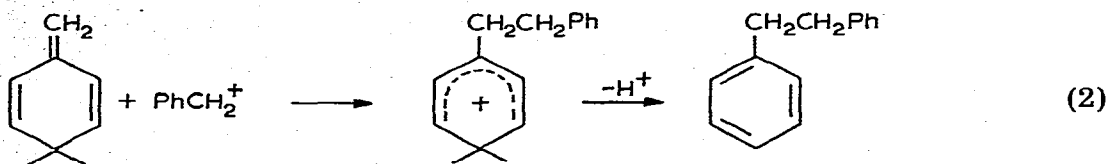
The absence of this "abnormal" reaction in the cleavage of *m*-methoxybenzyltrimethylsilane can be attributed to the fact that carbonium ion (X), which will lose a proton to give *m*-methoxytoluene, is greatly stabilized; thus,



* We note that an electron-transfer process leading via a radical cation to a benzyl radical and a benzyl carbonium ion [9] would account for some features of the reaction, but we do not consider it further because of the apparent absence of a suitable electron-acceptor to initiate such a process.

the electronic influence of the *m*-OMe group which greatly facilitates the formation of the methylenecyclohexadiene intermediate by Scheme 1 also greatly facilitates the conversion of the latter into the normal toluene derivative.

Formation of dibenzyl from benzyltrimethylsilane can be accounted for in terms of benzylation of the methylenecyclohexadiene, as in eq. 2.



The absence of any detectable build-up in the amounts of products I and II as the reaction progresses can reasonably be attributed to a balance between the formation of these products and their removal by further benzylation to give di- and tri-benzylated compounds which would have escaped detection. The ratio of toluene to products I and II thus increases as reaction proceeds.

The presence of water promotes the production of the normal cleavage product, toluene. We cannot at present say whether this is because of a more effective direct cleavage of the benzyl-silicon bond (cf. that of benzyl-tin bonds [1,2]), or, as we favour, diversion of the methylenecyclohexadiene intermediate towards simple aromatization. The rate maximum at about 5 wt.-% of water corresponds with similar maxima observed for aromatic hydrogen exchange and for cleavage of aryl-SiMe₃ bonds in CF₃CO₂H/H₂O mixtures [5], and similar explanations probably apply.

Experimental

Reagents

Benzyltrimethylsilane had b.p. 186–188°C, n_D^{20} 1.4937 and *m*-methoxybenzyltrimethylsilane had b.p. 33°C/1 mmHg, n_D^{20} 1.5013. Less than 1% of impurity was revealed in each case by GLC.

Trifluoroacetic acid (500 ml) was distilled from silver oxide (5 g), and then fractionated from concentrated sulphuric acid (50 ml).

Preparative scale reaction

A mixture of benzyltrimethylsilane (21.6 g, 0.144 mol) and trifluoroacetic acid (164.1 g, 1.44 mol) was heated at 72–75°C under a reflux condenser for 3 h. Trifluoroacetic acid and trimethylsilyl trifluoroacetate were distilled off, and the residue was fractionated at reduced pressure to give unchanged benzyltrimethylsilane (13.8 g, 64%) and a mixture (4.4 g) of I and II, b.p. 155–175°C/3 mmHg, n_D^{20} 1.5508, which was shown by GLC to contain I and II in a ratio of 60 : 40. This mixture was separated by preparative scale GLC (10% SE-30 on Chromosorb AW-HMDS) to give *p*-trimethylsilylmethyldiphenyl methane (I), n_D^{20} 1.5516 (Found: C, 79.6; H, 8.3; Si, 11.1. C₁₇H₂₂Si calcd.: C, 80.3; H, 8.7; Si, 11.0%) and *o*-trimethylsilylmethyldiphenyl methane (II) containing about 10% of I, n_D^{20} 1.5461 (Found: C, 80.6; H, 8.8; Si, 10.7%). The assignments of the *p*- and

o-structure to I and II, respectively, were based on ^1H NMR chemical shift and integration data (Dr. B.D. Lavrukhin).

Reaction of toluene and benzyl trifluoroacetate in trifluoroacetic acid

A mixture of toluene (4.6 g, 0.05 mol), benzyl trifluoroacetate (10.2 g, 0.05 mol), and trifluoroacetic acid (17.1 g, 0.15 mol), was kept for 10 h at 72–75°C beneath a reflux condenser. Unchanged toluene, trifluoroacetic acid and a little benzyl trifluoroacetate were removed, and the residue was fractionally distilled to give two fractions. The first (3.8 g), b.p. 109–110°C/3 mmHg, n_D^{20} 1.5729, was shown by GLC to consist of a mixture of *o*- and *p*-tolyl(phenyl)-methane (Found: C, 91.6; H, 8.3. $\text{C}_{14}\text{H}_{14}$ calcd.: C, 92.3; H, 7.7%), and the second (2.9 g), b.p. 200–210°C/3 mmHg, n_D^{20} 1.6022, was thought to consist of isomeric dibenzyltoluenes (Found: C, 92.7; H, 7.2. $\text{C}_{21}\text{H}_{20}$ calcd.: C, 92.65; H, 7.35%).

Benzyl trifluoroacetate and trifluoroacetic acid

A 1 : 10 mixture of benzyl trifluoroacetate and trifluoroacetic acid was kept in a sealed ampoule at 70°C for 24 h. GLC analysis showed that very little if any reaction had occurred, and no products were detected.

Sealed-tube reactions between benzyltrimethylsilane and trifluoroacetic acid

(1.) *Experiments in the U.S.S.R.* Samples (1–5 g) of the reaction mixtures (Table 1) were placed in ampoules, which were evacuated with cooling in liquid nitrogen and then sealed. They were kept at 70°C for 3 h then opened, and samples were injected on to the GLC columns (10% SE-30 on Chromosorb-W). The compositions in Table 1 are based on peak areas, and are assumed to correspond roughly with wt.-% values. Experiments were conducted at least in duplicate.

(2.) *Experiments in the U.K.* (i) The samples in sealed ampoules, as above, were usually kept at 70°C for 24 h, then broken under a mixture of water and 2 ml of *n*-hexane. The mixture was shaken, then the *n*-hexane layer was separated, washed 3 times with water, and dried (Na_2SO_4). Samples were analysed on a 5% Carbowax 20 M column programmed from 85–200°C at 6°C/min. In some experiments samples of the reaction mixture were injected directly into the GLC system. Authentic samples of benzyl trifluoroacetate, dibenzyl, and *o*- and *p*-methyldiphenylmethane were available to establish retention times, and use of a combined GLC—mass spectral system confirmed the nature of products I and II. (ii) In order to obtain some measure of the extent of reaction, after 24 h a 1 ml sample of the mixture was added to 1 ml of a *n*-hexane solution containing an appropriate concentration of *n*-hexadecane. After several washings, the hexane extract was analysed by GLC as above. With the aid of appropriate calibrations it was shown that ca. 70% of the benzyltrimethylsilane remained. (iii) From one set of sealed tubes containing quantities of reactants, the gas evolved on opening after 24 h was allowed to flow into a suitable evacuated gas-sampling vessel. GLC revealed the presence of hydrogen.

*Interaction of *m*-methoxybenzyltrimethylsilane and trifluoroacetic acid*

(Experiments in the U.K.). A solution of *m*-methoxybenzyltrimethylsilane

TABLE I
INTERACTION OF PhCH₂SiMe₃ (A) AND TRIFLUOROACETIC ACID (B) AT 70°C^a

B:A (molar ratio)	Other reagents ^b	Product composition ^a						Notes					
		Time (h)	PhCH ₃	A	Me ₃ SiO ₂ CCF ₃	PhCH ₂ O ₂ CCF ₃	I ^c		II ^d	III ^e	(Me ₃ Si) ₂ O		
<i>Analyses on reaction mixture^f</i>													
10:1		3		78	4		1	13	9				
3:1				76	5			14	10				
3:1	H ₂ O ^g		15	66				11	7	1	8		
1:1	H ₂ SO ₄ :0.2		5	37			1	27	17	14	2		
3:1	PhCH ₂ O ₂ CCF ₃ :1		9	47			1	26	16	2	2.5		
<i>Analyses on reaction mixture^h</i>													
10:1		24	4	83	<i>i</i>		1	4.5	3.5	0.5	<i>j</i>	<i>j</i>	
10:1		96	14	71	<i>k</i>		2.5	4.5	3.5	1	<i>k</i>	<i>j</i>	
<i>Analyses after extraction^h</i>													
10:1		24	5	76			2	9	4	2	<i>l</i>	<i>m</i>	<i>n</i>
10:1	PhCH ₂ O ₂ CCF ₃ :1		2	23			6	35	30	4	<i>l</i>	<i>m</i>	
10:1	PhCH ₃ :0.6		33	93				25	2	2	<i>o</i>	<i>m</i>	<i>p</i>
10:1	H ₂ SO ₄ :one drop		14	14			3	12	32	25	<i>q</i>	<i>m</i>	

^a Except where indicated, the product composition is expressed in relative peak areas, the total of aromatic compounds detected being taken as 100%. The preponderance of unchanged benzyltrimethylsilane in most cases leads to considerable uncertainty in the amounts of this compound relative to those of the products, and more significance should be attached to the ratios of the products than to the apparent extent of reaction. ^b Molar ratio indicated unless otherwise specified. ^c *p*-Me₃SiCH₂C₆H₄CH₂Ph. ^d *p*-Me₃SiCH₂C₆H₄CH₂Ph. ^e Mixture of PhCH₂CH₂Ph with *o*- and *p*-MeC₆H₄CH₂Ph. ^f Experiments in the U.S.S.R. ^g 5 wt.-% H₂O in the trifluoroacetic acid. ^h Experiments in the U.K. ⁱ Me₃SiO₂CCF₃ + (Me₃Si)₂O = ca. 7%. ^j Higher boiling products, ca. 3% were also detected. ^k Me₃SiO₂CCF₃ + (Me₃Si)₂O = ca. 12%. ^l PhCH₂CH₂Ph: MeC₆H₄CH₂Ph = ca. 1:3. ^m Not sought. ⁿ Higher boiling products, ca. 2%, were also detected. ^o PhCH₂CH₂Ph: MeC₆H₄CH₂Ph = ca. 1:10. ^p Toluene is not included in taking the total aromatics as 100%. ^q Only trace of PhCH₂CH₂Ph.

in trifluoroacetic acid (1 : 10 molar ratio) was sealed into ampoules as above. The ampoules were kept (a) at room temperature (ca. 20°C) for 1 h, (b) at 70°C for 24 h and (c) at 70°C for 48 h. Extraction and GLC analysis as described under (2), above, revealed for (a) a 23 : 100 peak area ratio of *m*-MeOC₆H₄Me : *m*-MeOC₆H₄CH₂SiMe₃, and for (b) and (c) only *m*-MeOC₆H₄Me, with no unchanged *m*-MeOC₆H₄CH₂SiMe₃ and no other volatile products. (Hexamethyl-disiloxane was not sought since it came off with the n-hexane).

Acknowledgement

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