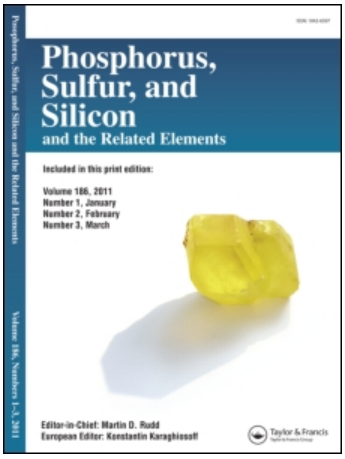

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SYNTHESIS AND GAS CHROMATOGRAPHIC/MASS SPECTROMETRIC STUDY OF SILYLATED HYDROXYQUINONES ON ALL HYDROXYL GROUPS

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SYNTHESIS AND GAS CHROMATOGRAPHIC/MASS SPECTROMETRIC STUDY OF SILYLATED HYDROXYQUINONES ON ALL HYDROXYL GROUPS

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Complete silylation of all hydroxyl groups of hydroxyquinones is reported to be effectively carried out using N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA). The silylated products are studied by gas chromatography/mass spectrometry. A detailed study of their mass spectra provides data for the elucidation of their fragmentation mechanisms as well as the deduction of the hydroxy-group position in the hydroxyquinone backbone.

Key words: Hydroxyquinones; trimethylsilylation of hydroxy-groups; trimethylsilylethers; N-methyl-N-trimethylsilyl-trifluoroacetamide; GC/MS; MS study.

INTRODUCTION

Despite the vast amount of information about hydroxyquinones and their derivatives[1] few studies were aimed at their partially silylated products on their hydroxyl groups. Silylation of only the hydroxyl groups of hydroxyanthraquinones for gas chromatographic analysis (GC)[2,3] or for gas chromatographic/mass spectrometric (GC/MS)[4] analysis has been reported, without fully describing the mass spectra features. Furthermore, up to now the silylations reported are carried out at complex reaction conditions.

We have recently reported[5] a successful application of GC/MS to the study of the progress of the reductive—by the sense of complete silylation of all the functional groups of the molecule, e.g., all hydroxyl and carbonyl ones—silylation reaction of hydroxyquinones as well as to their separation and characterization in synthetic mixtures. Continuing our interest in silylation reaction of hydroxyquinones we thought it advisable to study the complete masking of all their hydroxyl groups without affecting the carbonyl ones, as much for synthetic purposes, since hydroxyquinones are synthetic intermediates of great importance[6,7] as for GC/MS analysis of their mixtures, in case it cannot be carried out, because the molecular ions are beyond the range (10–800 a.m.u.) of the low-cost Quadruple Mass Spectrometers (QMS).

We report here our results concerning a new very efficient and quantitative method of complete masking of the all hydroxyl groups of hydroxyquinones by silyl ether formation with N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA)

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as silylating agent. The mass spectra of the silyl ethers are discussed along with some useful rules based on their extent study. Finally proposed fragmentation mechanisms are presented.

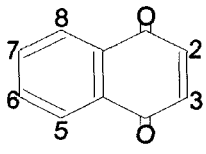
RESULTS AND DISCUSSION

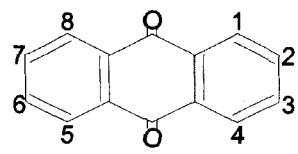
Reaction Conditions Optimization

The silylation reaction was applied to ten different hydroxyquinones, namely: 5-hydroxy-1,4-naphthalenedione [5-HNQ (**1**)], 2-hydroxy-1,4-naphthalenedione [2-HNQ (**2**)], 5,8-dihydroxy-1,4-naphthalenedione [5,8-DHNQ (**3**)], 1-hydroxy-9,10-anthracenedione [1-HAQ (**4**)], 1,4-dihydroxy-9,10-anthracenedione [1,4-DHAQ (**5**)], 5,8-dihydroxy-2(1-hydroxy-4-methyl-3-pentenyl-)1,4-naphthalenedione [5,8-DHHMPNQ (**6**)], 1,5-dihydroxy-9,10-anthracenedione [1,5-DHAQ (**7**)], 2-hydroxymethyl-9,10-anthracenedione [2-HMAQ (**8**)], 1,8-dihydroxy-9,10-anthracenedione [1,8-DHAQ (**9**)], 1,2-dihydroxy-9,10-anthracenedione [1,2-DHAQ (**10**)] (Scheme I).

The silylation reaction may be expressed as in the reaction scheme (Scheme II) for [5,8-DHHMPNQ (**6**)].

Although many silylating agents with different and specific activities are available today, N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA) was chosen as the most suitable silylating agent among the four more active silylamids,[8] e.g., Bis-

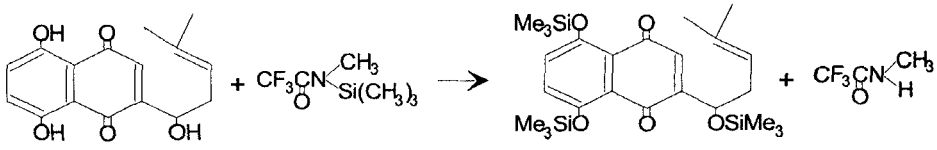




1 5-OH
2 2-OH
3 5,8-$(OH)_2$
6 5,8-$(OH)_2$-2-$CH(OH)CH_2CHC(CH_3)CH_3$

4 1-OH
5 1,4-$(OH)_2$
7 1,5-$(OH)_2$
8 2-CH_2OH
9 1,8-$(OH)_2$
10 1,2-$(OH)_2$

SCHEME I Structures of hydroxyquinones to be silylated.



SCHEME II Reaction scheme for the trimethylsilylation of hydroxyquinones **1–10**.

trimethylsilyl-trifluoroacetamide (BSTFA), Bis-trimethylsilyl-acetamide (BSA), N-methyl-N-trimethylsilyl-acetamide (MSA), because of its greatly reduced R_t (b.p. 132°C) and its volatile by-product N-methyl-N-trifluoroacetamide (MTFA) and it is used as the reaction solvent. MTFA appears as a symmetrical peak before that of MSTFA and doesn't influence the chromatogram. Furthermore, it can be easily removed by blowing a stream of dry nitrogen on the surface of the reaction mixture at room temperature.

The silylation reaction was applied using gradually increasing amounts of the silylating agent (MSTFA), in order to reach the optimal ratio of hydroxyquinone/silylating agent (Figure 1). The completion of the reaction was checked by GC (one peak).

Table I presents the optimum reaction conditions (ratio of hydroxyquinone/MSTFA, reaction time, temperature) and the yields determined. The increased amounts of MSTFA used in some hydroxyquinones may be explained by some strong intramolecular hydrogen bonding.

Gas Chromatographic Properties

The formation of the trimethylsilyl (TMS) derivatives was rapid and well-shaped chromatographic peaks were produced by all the compounds studied. Table II

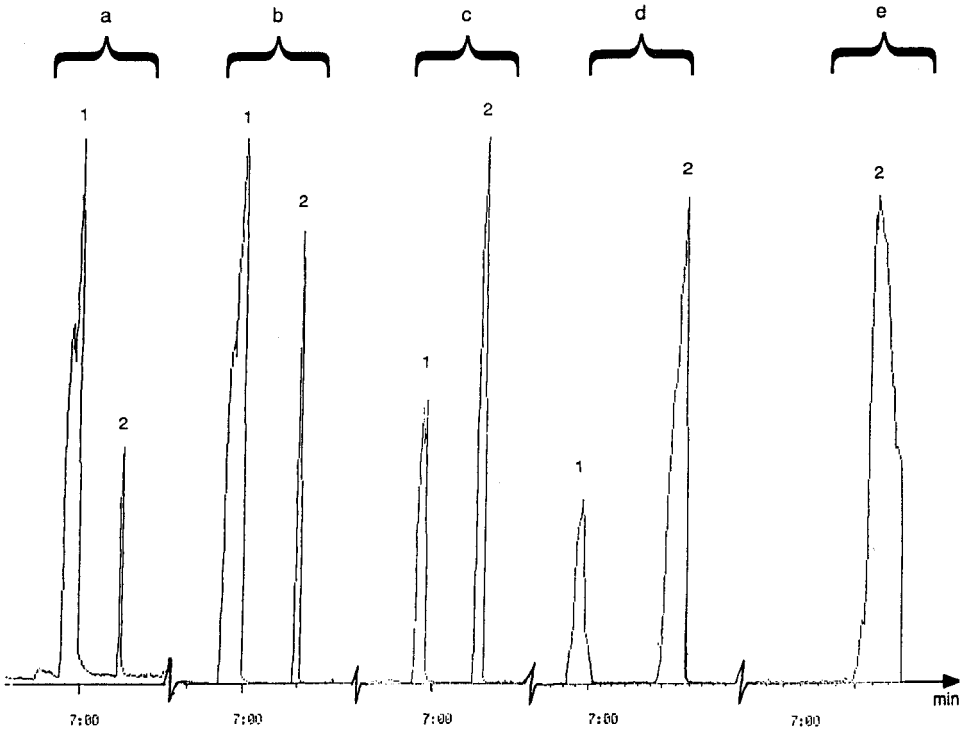


FIGURE 1 5-HNQ (**1**) as an example of optimization process of the ratio hydroxyquinone: MSTFA. Moles of hydroxyquinone/moles MSTFA = 1/3 (a), 1/5 (b), 1/10 (c), 1/12 (d), 1/14 (e). Conditions as in the Experimental section. Peaks: 5-HNQ (1); 5-(TMSO)NQ (2).

TABLE I

Trimethylsilylation of hydroxyquinones **1–10** with MSTFA

Substrate	*Conditions*			*Product* [a,b]	*Yield* [c]
	(°C)	*(min)*	*Quinone/MSTFA*		
(1) 5-HNQ	60	20	1:14	**(1a)** 5-(TMSO)NQ	100
(2) 2-HNQ	60	20	1:14	**(2a)** 2-(TMSO)NQ	100
(3) 5,8-DHNQ	60	20	1:35	**(3a)** 5,8-$(TMSO)_2$NQ	100
(4) 1-HAQ	60	20	1:14	**(4a)** 1-(TMSO)AQ	100
(5) 1,4-DHAQ	60	20	1:56	**(5a)** 1,4-$(TMSO)_2$AQ	100
(6) 5,8-DHHMPNQ	60	20	1:63	**(6a)** 5,8-$(TMSO)_2$-2-[(TMSO)MP]NQ	100
(7) 1,5-DHAQ	60	20	1:56	**(7a)** 1,5-$(TMSO)_2$AQ	100
(8) 2-HMAQ	60	20	1:14	**(8a)** 2-(TMSOM)AQ	100
(9) 1,8-DHAQ	60	20	1:56	**(9a)** 1,8-$(TMSO)_2$AQ	100
(10) 1,2-DHAQ	60	20	1:42	**(10a)** 1,2-$(TMSO)_2$AQ	100

[a]All products showed the expected spectra for the structures assigned.

[b]The silylether of hydroxyquinone n is denoted as na.

[c]Determined by GC.

TABLE II

Gas chromatographic and mass spectrometric data for the trimethylsilyl derivatives of the hydroxyquinones **1–10**

Hydroxyquinone	*Product*	R_t *(min)*	$M^{+\cdot}$ *(m/z, rel.int. %)*	*Principal ions (m/z, rel.[a,b] int.%)*
(1) 5-HNQ	**(1a)** 5-(TMSO)NQ	7:13	246(-)	233(6) 232(14) *231(100)* 203(33) 185(15) 173(20) 129(3) 115(10) 101(12) 94(15) 75(6) 73(7) 45(10)
(2) 2-HNQ	**(2a)** 2-(TMSO)NQ	7:24	246(-)	233(3) 232(18) *231(100)* 203(8) 129(9) 101(12) 75(6) 73(8) 45(10)
(3) 5,8-DHNQ	**(3a)** 5,8-$(TMSO)_2$NQ	8:19	334(-)	319(8) 306(11) 305(20) *304(100)* 274(32) 244(8) 152(5) 137(12) 122(8) 73(12) 45(10)
(4) 1-HAQ	**(4a)** 1-(TMSO)AQ	9:56	296(-)	283(8) 282(28) *281(100)* 266(1) 263(5) 251(15) 235(4) 223(5) 207(1) 165(3) 151(8) 133(5) 119(4) 75(4) 73(3) 45(1)
(5) 1,4-DHAQ	**(5a)** 1,4-$(TMSO)_2$AQ	10:16	384(-)	369(11) 356(10) 355(30) *354(100)* 325(5) 324(17) 294(6) 177(7) 162(8) 147(9) 73(17) 45(5)

shows their retention times as well as the principal ions presented in their mass spectra. The relationships between chemical structures and retention times have been discussed in detail elsewhere[1–5] and are in good agreement with the ones present in Table II.

TABLE II (*Continued*)

Hydroxyquinone	*Product*	R_t *(min)*	$M^{+\cdot}$ *(m/z, rel.int. %)*	*Principal ions (m/z, rel.[a,b] int.%)*
(6) 5,8-DHHMPNQ	**(6a)** 5,8-$(TMSO)_2$-2-[(TMSO)MP]NQ	10:22	504(-)	489(2) 435(15) 421(22) 407(10) 406(16) 405(50) 399(9) 384(4) 332(4) 317(10) *73(100)* 45(20)
(7) 1,5-DHAQ	**(7a)** 1,5-$(TMSO)_2$AQ	10:23	384(-)	370(10) 369(30) 356(11) 355(25) *354(100)* 325(5) 324(20) 294(6) 177(12) 162(10) 147(11) 73(5) 45(5)
(8) 2-HMAQ	**(8a)** 2-(TMSOM)AQ	10:27	310(24)	311(6) 310(24) 295(3) 282(10) 281(14) 280(35) *279(100)* 265(5) 264(6) 235(5) 221(6) 194(5) 193(35) 192(10) 165(30) 164(22) 163(23) 151(6) 147(11) 140(6) 139(9) 126(6) 115(5) 76(8) 75(18) 74(8) 73(56) 63(5) 59(17) 45(20)
(9) 1,8-DHAQ	**(9a)** 1,8-$(TMSO)_2$AQ	10:41	384(-)	371(11) 370(31) *369(100)* 297(4) 268(4) 210(4) 177(3) 74(6) 73(72) 45(20)
(10) 1,2-DHAQ	**(10a)** 1,2-$(TMSO)_2$AQ	10:43	384(-)	371(10) 370(25) 369(80) 177(4) 75(6) 74(8) *73(100)* 45(30)

[a]The base peak is italicised.

[b]Relative to base peak.

Mass Spectra

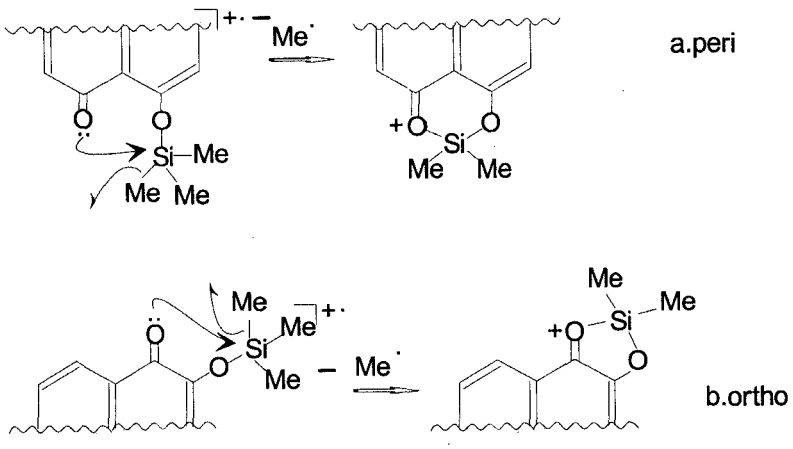
The TMS derivatives of the silylated hydroxyquinones **1–10**, give rise to characteristic fragmentation patterns which, to our knowledge, are first studied in this work. Typical loss of a methyl radical from all molecular ions of the silyl ethers studied is indicated by the unique presence of a [M-15] cation, even though the molecular ion is not observed (Table II).

Formation of a Stable Chelate Structure

An interesting feature dominating the spectra of all TMS derivatives possessing one trimethylsilyloxy substituent in ortho or peri position to the quinonoid oxygen (e.g., **1a**, **2a** and **4a**) is the loss of a methyl radical from each TMS group, which leads to the formation of a stable six or five membered cationic chelate structure, respectively. A proposed structure for this ion is presented in Scheme III.[6] This ion appears as the base peak. The driving force for the expulsion of the methyl radical is the stability of the oxygen-silicon bond in the chelate ring.

Consequently, an aromatization of the quinonoid ring must take place in the case of **3a**, **5a–7a** which contain two such trimethylsilyloxy groups in ortho or peri positions, following the expulsion of the two methyl radicals.

The presence of a trimethylsilyloxy group in such a position so that the previous fragmentation pattern is no longer applicable, e.g., **8a–10a** and the trimethylsilyloxy group on the side chain in **6a**, increases the abundance of the m/z 73 ion, which



SCHEME III Proposed mechanisms for the formation of the chelate ring in hydroxyquinone molecules having a trimethylsilyl group either in peri or ortho position to the carbonyl group.

frequently appears as the base peak (**6a**, **10a**). This pronounced ortho and peri effect is valuable in the interpretation of the unknown position isomers of hydroxyquinones.

Doubly Charged Ions

Of unusual interest is the presence of doubly charged ions. Their nature has been demonstrated by measurement of the exact mass.

The ability of di-TMS derivatives of several compounds to form intense doubly charged ions has been primarily observed by McCloskey and co-workers[9] in long chain trimethylsilylated diols. They have shown that these ions arise from the loss of two methyl radicals and two electrons; one from each TMS moiety. A similar trend has also been observed for the di-TMS derivatives of aromatic amines,[10] amino-hydroxy, dihydroxy and dicarboxy compounds[11] and disubstituted pyridines, quinolines pyrimidines and pteridines.[12] Finally, the presence or lack of these ions has been demonstrated to be position dependent, whereas it is independent of the nature of the functional group.[13]

Similar observations have been made in our study of dihydroxyquinones TMS derivatives. Furthermore, besides the [M-30] doubly charged ions, common in all di-TMS derivatives, two more intense doubly charged ions were observed in the mass spectra. These are the $[M\text{-}60]^{2+}$ and $[M\text{-}90]^{2+}$, the latter being of greater or equal abundance with the corresponding singly charged [M-90].

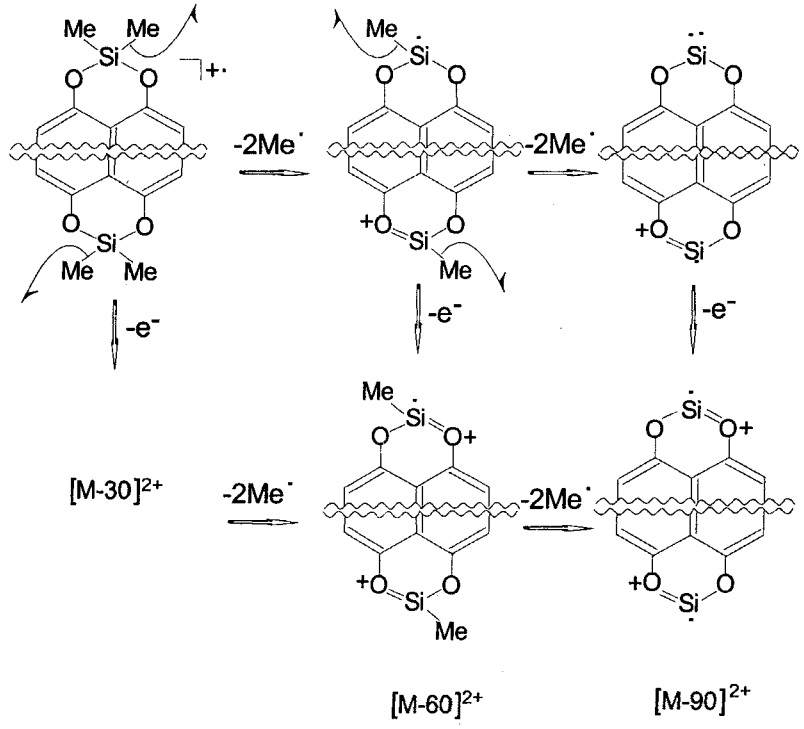
The TMS ethers are listed in Table III, which give rise to doubly charged ions, along with their relative intensities and the corresponding singly charged ones. By careful measurement of exact mass, the identities of even very minor ions (e.g., $[M\text{-}60]^{+}$ of **10a** rel.int. $<0.1\%$) have been deduced and are also reported in Table III.

Inspection of Table III discloses that only **3a**, **5a** and **7a** form intense doubly charged ions [M-30], [M-60] and [M-90]. However, in the mass spectra of **9a** and **10a**, these ions exhibit intensities of only $<4\%$. It is evident that the position of

TABLE III
Doubly charged ions of silylethers **3a**, **5a**, **7a**, **9a** and **10a**

Silyl ether	*Relative intensity %*					
	[M-30]$^{2+}$	*[M-30]$^{+}$*	*[M-60]$^{2+}$*	*[M-60]$^{+}$*	*[M-90]$^{2+}$*	*[M-90]$^{+}$*
(**3a**) 5,8-$(TMSO)_2$NQ	5	100	12	32	8	8
(**5a**) 1,4-$(TMSO)_2$AQ	7	100	8	17	9	6
(**7a**) 1,5-$(TMSO)_2$AQ	12	100	10	20	11	6
(**9a**) 1,8-$(TMSO)_2$AQ	3	0,3	0,8	0,3	0,4	0,9
(**10a**) 1,2-$(TMSO)_2$AQ	4	1	<1	0,1	<1	1

the trimethylsilyloxy groups in the studied compounds is the determining factor for the production of the doubly charged ions. Ortho and peri isomers favour formation of the previously mentioned chelate structures via a cyclization mechanism. Subsequent loss of three pairs of methyl radicals one from each TMS site, leads to the formation of the [M-30], [M-60] and [M-90] doubly charged ions (Scheme IV).



SCHEME IV Proposed mechanism for the formation of the doubly charged ions.

TMS derivatives of monohydroxyquinones, as in the case of **1a**, **2a** and **4a**, also form doubly charged ions but of minor intensity. Exact mass measurements have demonstrated that two doubly charged ions are present in the mass spectra of the

TABLE IV
Doubly charged ions of silylethers **1a–3a**

Silyl ether	*Relative intensities %*			
	$[M-2Me-CO]^{2+}$	*$[M-2Me-CO]^{+}$*	*$[M-3Me-CO]^{2+}$*	*$[M-3Me-CO]^{+}$*
(**1a**) 5-(TMSO)NQ	15	<1	1	20
(**2a**) 2-(TMSO)NQ	3	<1	1	4
(**3a**) 1-(TMSO)AQ	4	0,2	5	3

above compounds. The first one results from the elimination of two methyl radicals and a carbon monoxide molecule along with an electron and the second of one more methyl radical. The relative intensities of both the singly and doubly charged ions for the three silyl ethers (e.g., **1a**, **2a** and **4a**) are reported in Table IV. Therefore the presence or absence of intense doubly charged ions might be helpful in the determination of the substituent position.

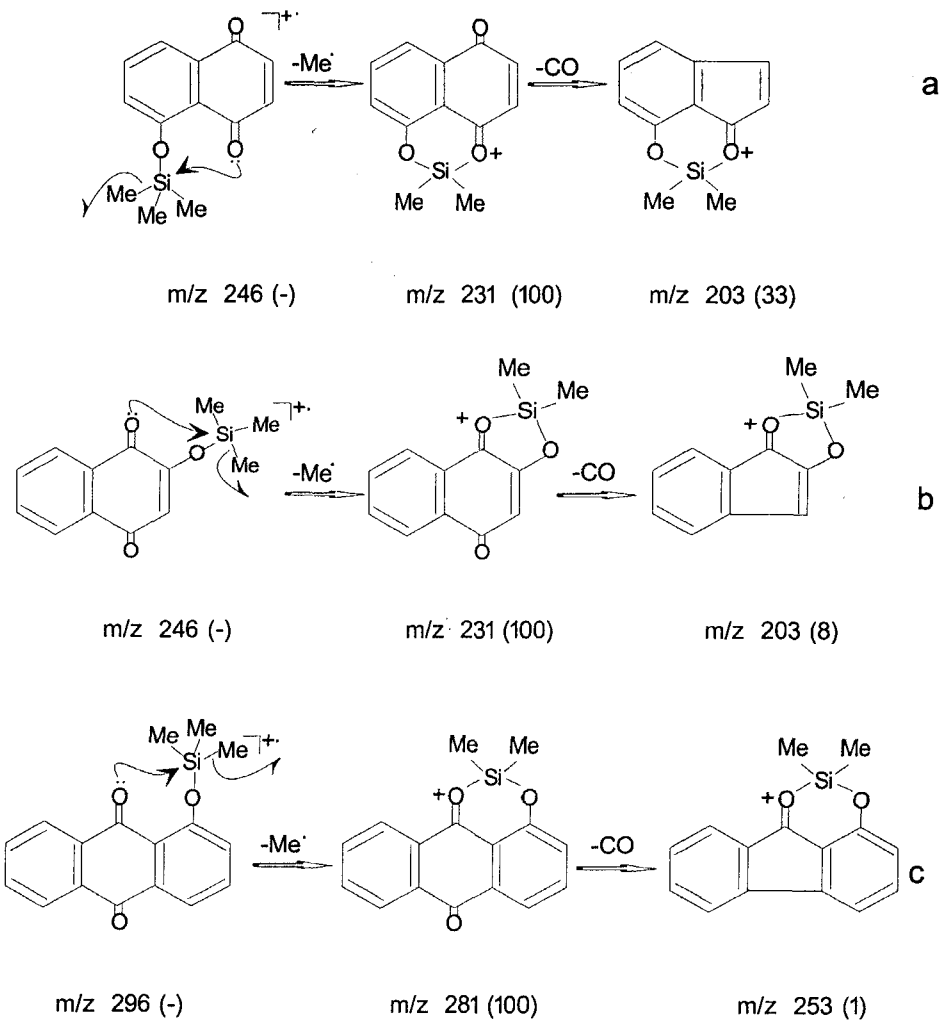
Comparison of the mass spectra enabled us to categorise the TMS compounds studied as follows: a) **1a**, **2a** and **4a** b) **3a**, **5a** and **7a** c) **9a** and **10a**. The mass spectra of **6a** and **8a** appear to follow unique fragmentation pathways.

*Group a: 5-(TMSO)NQ (**1a**), 2-(TMSO)NQ (**2a**), 1-(TMSO)AQ (**4a**)*

No molecular ion is observed while, due to the peri (**1a**, **4a**) or ortho (**2a**) position of the trimethylsilyloxy group, expulsion of a methyl radical from the molecular ion leads to the formation of the stable chelate structure corresponding to the base peak at m/z 231 (**1a**, **2a**) and m/z 281 (**4a**).

Although fragmentation was expected to occur by successive losses of two methyl radicals from the chelate structure, this is observed only in the case of **4a**. Furthermore two doubly charged ions, $[M-2Me]^{2+}$ and $[M-3Me]^{2+}$ are observed by the expulsion of one more electron along with the second or the third methyl radical. It is noteworthy that the $[M-2Me]^{2+}$, of m/z 133 is of higher abundance (5%) than the singly charged one, $[M-2Me]^{+}$ of m/z 266 (1%). In all three silyl ethers the fragmentation of the chelate structure is interrupted by the expulsion of a carbon monoxide molecule. Successive losses of two methyl radicals from the chelate structure follow this expulsion, while the elimination of an electron along with the first or the last radical leads to the formation of two doubly charged ions. As a common feature in all spectra doubly charged ions $[M-2Me-CO]^{2+}$ are of higher abundance than the singly charged ones (Table IV). Both, [M-3Me-CO] ion and $[M-SiMe_3]$ ion, contribute to the formation of the ion of m/z 173 in the case of **1a** and **2a** and m/z 223 for **4a**, a fact which explains their high abundance (20%, 4%, 3%, respectively).

The unique observation of the elimination of water from the [M-Me-CO] ion, at m/z 185 (**1a**, **2a**) and 263 (**4a**) predominating in the case of **1a** and **2a**, seems to proceed by complicated rearrangements[7]. Expected elimination of a trimethylsilyloxy radical leading to a fragmentation pathway identical to the quinone structure, is of minor importance while it is practically absent (~1%).



SCHEME V Proposed fragmentation mechanisms for a: 5-(TMSO)NQ (**1a**) b: 2-(TMSO)NQ (**2a**) c: 1-(TMSO)AQ (**4a**).

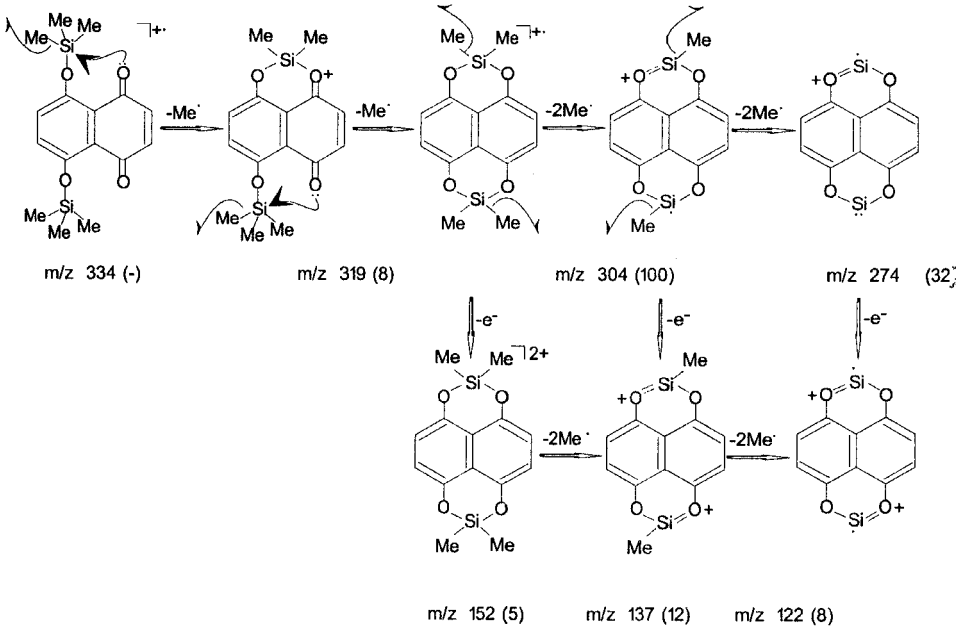
Group b: 5,8-(TMSO)$_2$NQ (**3a**), *1,4-(TMSO)$_2$AQ* (**5a**), *1,5-(TMSO)$_2$AQ* (**7a**)

A high similarity to the previous group with regard to high abundance of the [M-30] ion and absence of the molecular ion was expected and was indeed found. The base peak is attributed to $[M-30]^+$, which seems to be of particular stability. [M-15] ion is also present but to a minor extent.

The governing feature of the mass spectra of this category is the presence of abundant doubly charged ions [M-30], [M-60] and [M-90], resulting from successive losses of three pairs of methyl radicals; each TMS site contributing one methyl radical in every successive step.[9] Both $[M-30]^{2+}$ and $[M-60]^{2+}$ are observed to a lower abundance than the corresponding singly charged ions. The opposite effect is obtained for the $[M-90]^{2+}$ ion, which is of greater abundance (8–11%) than the

$[M-90]^+$ (6–8%). On the contrary loss of the trimethylsilyl or trimethylsilyloxy group from the molecular ions is not observed.

Scheme VI illustrates as an example, the fragmentation pattern of 5,8-$(TMSO)_2$NQ (**3a**).



SCHEME VI Proposed fragmentation mechanism for 5,8-$(TMSO)_2$NQ (**3a**).

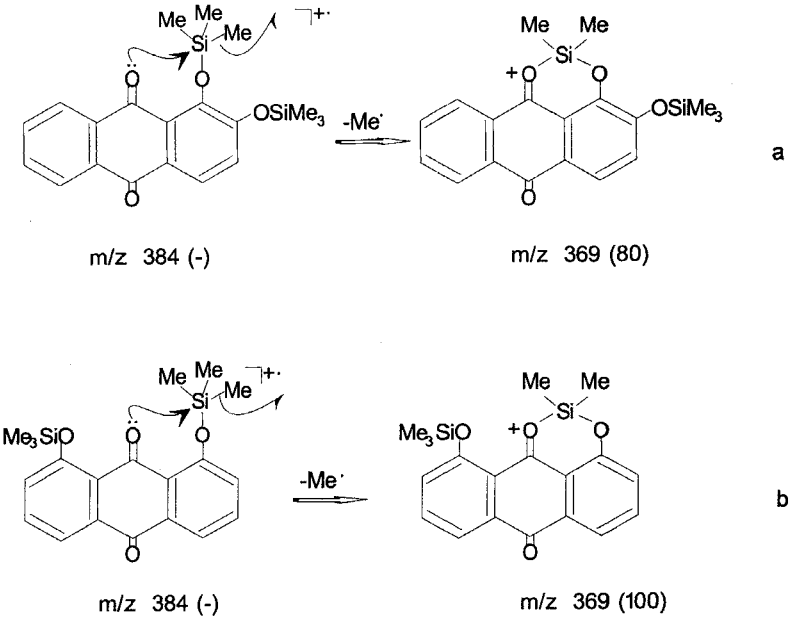
*Group c: 1,8-$(TMSO)_2$AQ (**9a**), 1,2-$(TMSO)_2$AQ (**10a**)*

The two mass spectra differ only in the relative intensity of ions m/z 369 and m/z 73. The first one appears as the base peak in the spectrum of 1,8-isomer, while the second to that of 1,2-isomer.

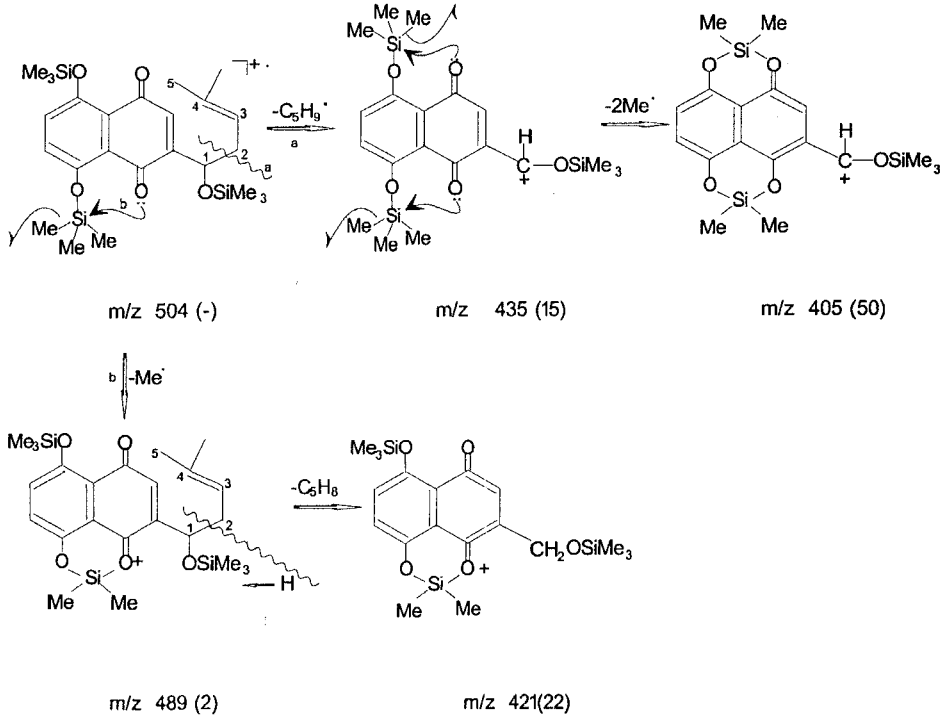
Due to the peri position of the one trimethylsilyloxy group, loss of a methyl radical leads to a stable chelate structure representing by the ion m/z 369. Fragmentation pathways involving elimination either of one trimethylsilyl radical followed by the loss of a carbon monoxide molecule or of a $CH_2{=}SiMe_2$ moiety, are of minor importance as they exhibit ions of very low abundance. These losses are represented by the ions of 296 (<4%), 268 (4%) and 297 (4%), respectively. The structure of the ion of m/z 369 for each silyl ether is depicted in Scheme VII. Furthermore no intense doubly charged ions appear.

*5,8-$(TMSO)_2$-2-[(TMSO)MP]NQ (**6a**)*

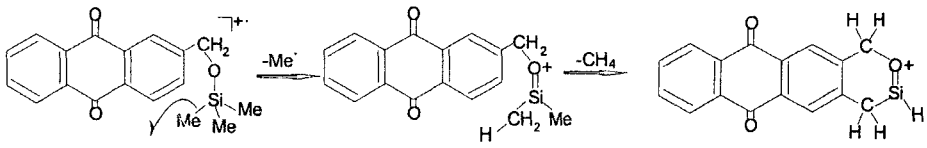
Besides the base peak at m/z 73, few intense peaks are present in the mass spectrum of **6a**. Its fragmentation mechanism results as a combination of the side chain



SCHEME VII Proposed fragmentation mechanisms for a: 1,2-(TMSO)$_2$AQ (**10a**), b: 1,8-(TMSO)$_2$AQ (**9a**).



SCHEME VIII Proposed fragmentation mechanism for 5,8-(TMSO)$_2$-2-[(TMSO)MP]NQ (**6a**).



SCHEME IX Proposed fragmentation mechanism for 2-(TMSOM)AQ (**8a**).

elimination and the formation of the discussed stable chelate structure. Therefore, two different fragmentation pathways are involved.

The first one is concerning a cleavage of the C_1—C_2 bond of the side chain followed by the expulsion of two methyl radicals, leading to the formation of the ions m/z 435 (15%) and 405 (50%). The second consists of successive losses of a methyl radical and the side chain by cleavage of the C_1—C_2 bond possibly via a side hydrogen atom migration, leading to the formation of the ions of m/z 489 (2%) and 421 (22%), respectively.

Proposed structures for the ions discussed may be found in Scheme VIII.

*2-(TMSOM)AQ (**8a**)*

The structure of the m/z 279 might more reasonably be as shown below (Scheme IX).

Of particular interest is the molecular ion, of m/z 310, of moderate abundance (24%), which demonstrates the impossibility of a chelate structure formation, since such a structure frequently excludes an intense molecular ion (Table II).

EXPERIMENTAL

Materials—instrumentation. The hydroxyquinones employed were purchased from Fluka and were reagent grade. Their purity was checked by TLC (one spot with a 20 μg sample). MSTFA was obtained also from Fluka and was of GC quality.

GC/MS analysis was carried out on a Hewlett Packard gas chromatograph, model H.P. 5890 coupled with a VG, TS-250 mass spectrometer. The GC system was fitted with a 25 m × 0.2 mm I.D. column, OV-1, and the end of the column was introduced directly into the mass spectrometer analyser chamber. The system was operated under the following conditions: helium pressure, 5 psi; injector temperature, 280°C; GC temperature, 80°C for 3 min, 80–280°C at 25°C min^{-1}, 280°C for 10 min. The mass spectrometer was set to scan 40–700 a.m.u. per nominal second with an ionising voltage of 70 eV.

Trimethylsilylation reaction. Trimethylsilyl derivatives were prepared by treating of the hydroxyquinone of interest with MSTFA in several ratios (Table I). The reaction was carried out at 60°C for 20 min. Then, samples of the reaction mixture were injected directly into the GC/MS system. All reactions were checked for completion by GC/MS (one peak in GC with the expected $M^{+\cdot}$ in its mass spectrum).

In order to avoid formation of siloxane-by-products, particular care has been taken to protect reactants and products from moisture, even in traces, by persistent drying of all starting materials and apparatus. Thus, the samples of hydroxyquinones after persistent drying in an oven, to a temperature up to 100°C, were kept in a vacuum desiccator. MSTFA was dried with Na_2SO_4 and kept under a nitrogen atmosphere in a desiccator, too. Besides, the appropriate quantities of freshly dried hydroxyquinone and MSTFA were placed in a screw-capped septum vial which was previously blown by a regulated steam of filtered, dry nitrogen and sealed immediately. In order to be dried, nitrogen was passed through gas washbottles with $CaCl_2$ and H_2SO_4.

CONCLUSIONS

The complete silylation of hydroxyquinones on all their hydroxyl groups is reported. The reaction is carried out in a simple, one step, quantitative manner, using MSTFA as both silylating agent and solvent under conditions optimised accordingly.

A detailed study of the TMS-products mass spectra reveals the governing features of the fragmentation patterns and helps in the establishment of useful "thumb rules" for the determination of the hydroxy-group position in unknown hydroxyquinones. Thus, the formation of a stable chelate structure in the fragmentation pattern of the silylether's molecule, corresponding to specific m/z in its mass spectrum, indicates the presence of a hydroxyl group in either a peri or ortho position to one of the two quinonoid oxygens in the hydroxyquinone's molecule. In addition, doubly charged ions reveals the presence of two hydroxyl groups in ortho or peri position to the para carbonyl groups of the hydroxyquinone's molecule.

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