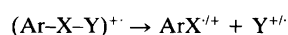


Side-Chain Reactivity of Aromatic Radical Cations*

Enrico Baciocchi

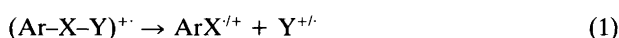
Dipartimento di Chimica, Università 'La Sapienza' P. le A. Moro 5, 00185 Roma, Italy

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The breaking of a side-chain bond β to the aromatic ring according to

is one of the most important reaction modes available to an aromatic radical cation. In this paper, I will discuss the main structural factors influencing the reactivity of this process (when $\text{X-Y} = \text{C-H}$) and the competition between C-H bond cleavage pathway and that involving the breakage of a C-C, C-O, C-S or C-Si bond. Information in this respect comes mainly from product studies concerning chemical, electrochemical and photochemical one-electron oxidation of *p*-alkylbenzyl derivatives, diarylethanes, benzyl ethers and sulphides and benzyltrimethylsilanes.

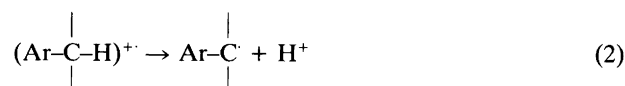
Aromatic radical cations present a rich and interesting chemistry as they undergo a variety of nuclear and (or) side-chain reactions.¹ The latter reactions mostly involve the breakage of benzylic bonds or, more generally, of bonds between an α and a β atom of the side-chain, to give a cation and a free radical [eqn. (1)].



A great number of side-chain reactions is therefore possible, depending on the nature of the bond cleaved. The most common case is C-H bond scission, but also the breakage of a C-C bond and/or various C-Z (Z = heteroatom) bonds can take place. An additional possibility (for example when Z = S, Se, P) is nucleophilic attack at the heteroatom to form heteroatom-functionalised products.

In this paper I will first deal with the main structural factors which influence the reactivity of side-chain reactions involving the cleavage of a C-H bond. Later some systems will be discussed where the rupture of this bond can compete with that of a C-C, C-O, C-S or C-Si bond. The information in this respect comes mainly from product studies on the oxidation of alkylbenzenes, diarylethanes, benzyl ethers and sulphides and benzyltrimethylsilanes by *bona fide* one-electron transfer oxidants, in most cases electrochemical, photochemical and CAN-promoted, [CAN = cerium(IV) ammonium nitrate] oxidations.

Side-chain reactions involving the cleavage of a C-H bond. The most common and useful side-chain reaction of an aromatic radical cation is that where a $\text{C}_\alpha\text{-H}$ bond is broken [eqn. (2)]. In solution, this reaction is often an exergonic process and accordingly alkyl-aromatic radical cations are



generally very strong acids. For the deprotonation of toluene radical cation in MeCN a ΔG° value of $-17 \text{ kcal mol}^{-1}$ can be estimated, corresponding to a $\text{p}K_a$ value of -13 .² The acid strength is decreased by the presence of electron donating groups which increase the stability of the radical cation. Thus, hexamethylbenzene radical cation is a much weaker acid ($\text{p}K_a$ ca. 1) than toluene radical cation.³

The rate of reaction (2) is also very high. Some data are reported in Table 1 for the deprotonation reaction of methylbenzene radical cations in H_2O .⁴ It can be noted that electron-donating groups, which decrease the acid strength of the radical cation, decrease its kinetic acidity as well. It has also been shown that the influence of ring substituents on the kinetic acidity depends upon the relative position (*ortho*, *meta*, *para*) of the side-chain with respect to the substituent itself.

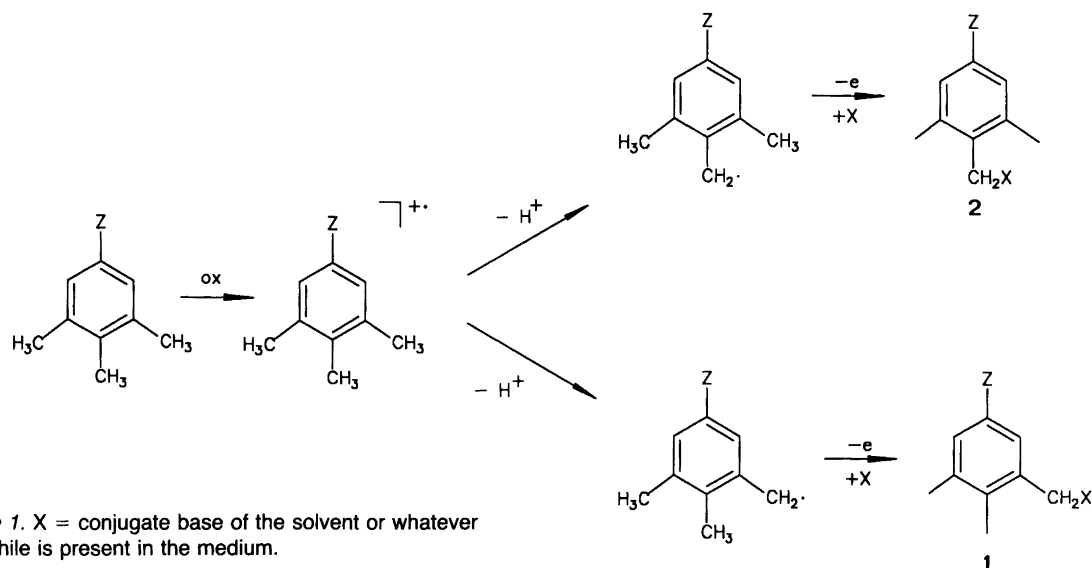
Information in this respect comes from a product study on the CAN-promoted and electrochemical oxidation of 5-substituted 1,2,3-trimethylbenzenes.⁵ Since the deprotonation step is irreversible,⁶ the 2:1 product ratio (statisti-

Table 1. Rate constants for the deprotonation reaction of some methylbenzene radical cations in water.^a

Radical cation	k/s^{-1}
Toluene	1×10^7
<i>p</i> -Xylene	1.4×10^6
Mesitylene	1.5×10^6
Isodurene	1×10^5
Pentamethylbenzene	1.6×10^4

^aData from Ref. 4.

* Presented as a main section lecture at the 32nd IUPAC Congress in Stockholm, Sweden, August 2–7, 1989.



Scheme 1. X = conjugate base of the solvent or whatever nucleophile is present in the medium.

cally corrected) is a measure of the relative deprotonation rate of the intermediate radical cation, from the methyl groups *para* and *meta* to the substituent R (Scheme 1).

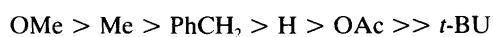
The 2:1 product ratios for the anodic oxidation of several 5-substituted hemimellitenes are reported in Table 2. These data clearly show that the effect of a ring substituent on the deprotonation rate strongly depends on whether the substituent is *para* or *meta* relative to the side-chain. Thus, when Z = OCH₃ deprotonation takes place nearly exclusively from the *para*-CH₃ group. A preference for deprotonation from the *meta*-CH₃ group can be inferred from the data for Z = CO₂CH₃ but, in this case, the effect is very small.

Interestingly, the largest effects favoring *para* deprotonation are observed for +R substituents, independently of their overall electronic effect. Accordingly, both CH₃ and Br direct deprotonation at the *para* CH₃ group to a similar extent, even if the former is an electron-donating and the latter an electron-withdrawing substituent.

Certainly, these effects are too large to be rationalized on the basis of the different stabilities of the isomeric benzyl radicals formed in the deprotonation reactions and

furthermore a product-like transition state would be in line with neither the aforementioned mentioned exergonicity of the reaction nor with experimental evidence.³ Presumably, the effects displayed in Table 2 have their origin in the electron density distribution in the radical cation, even if it is not yet known which factor (positive charge density, LUMO electron density, spin density) plays the major role in this respect.⁵ The role of spin density appears to be questioned by the finding that the greatest value is at the *para* position with ethyl benzoate radical cation⁷ whereas no preference for *para*-CH₃ deprotonation when R = CO₂Et is observed in Table 2.

The side-chain deprotonation rate should also be significantly influenced by α -substitution. Since no information in this respect is available, a study has been undertaken of the product distribution in the anodic and CAN-promoted oxidations of α -substituted *p*-xylenes. As shown in Scheme 2, the product distribution can again be related to the relative rate of deprotonation from the CH₂R and CH₃ groups in the radical cation. Preliminary data⁸ have shown that the effect of the α -substituent R on the rate of proton loss decreases in the following order:

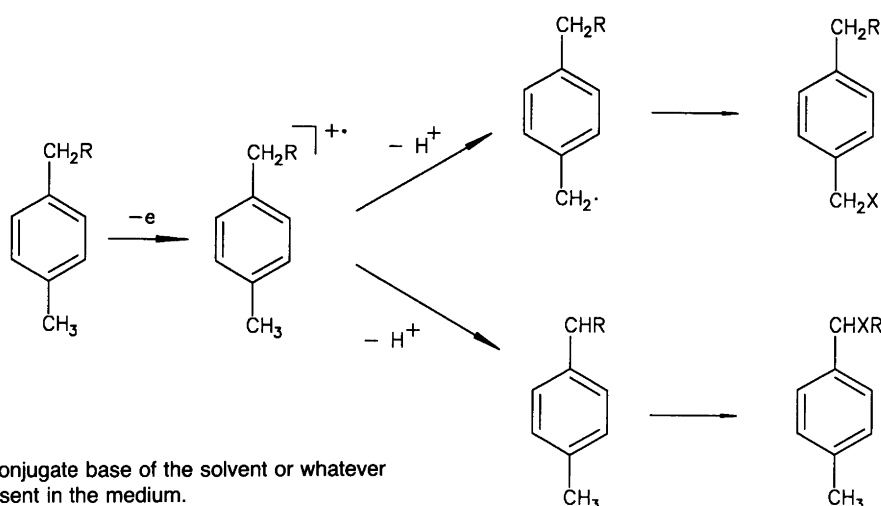


The role of steric effects is clearly shown by the finding that when R = *t*-Bu the deprotonation rate from the CH₂R group becomes negligible compared with when R = H. The observed effect should mainly be determined by the stereoelectronic requirements of the deprotonation reaction. For the breaking of the C-H bond an intramolecular electron transfer is necessary between the σ C-H bond and the half-empty b₁ molecular orbital of the aromatic system, and this requires that the C-N bond be collinear with the π -system (conformation 3 in Scheme 3). However, when the bulky *t*-Bu group is present (Scheme 3, R = *t*-Bu) confor-

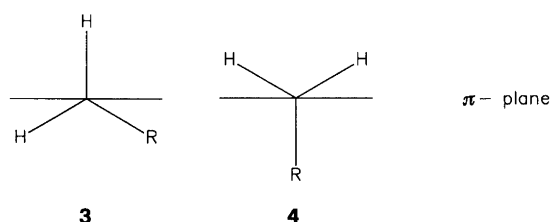
Table 2. Relative rate of oxidation at 2- and 1-CH₃ groups (k_2/k_1) in the anodic oxidation of 5-Z-1,2,3-trimethylbenzenes in AcOH.^a

Z	k_2/k_1
CO ₂ Me	2.0
H	3.4
<i>t</i> -Bu	24
Br	42
Me	55
OMe	>200

^aData from Ref. 5. Bu₄NBF₄ is the supporting electrolyte. The data are statistically corrected.



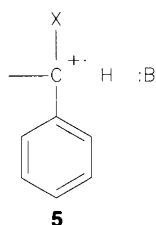
Scheme 2. X = conjugate base of the solvent or whatever nucleophile is present in the medium.



Scheme 3.

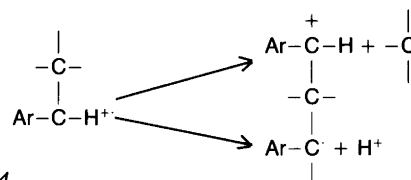
mation **3** is made unstable by the steric interaction of this group with the *ortho* hydrogens and the equilibrium is completely shifted toward conformation **4** where the C-N bonds can no longer interact with the π -system.

Electronic effects should be responsible for the difference in reactivity observed for the other groups, which exhibit quite similar steric requirements. The reported reactivity order seems to indicate that α -substituents increase the deprotonation rate according to their ability to stabilize an adjacent positive charge. It might be suggested that the transition state for the deprotonation reaction is similar to **5**



(B = base) where most of the positive charge resides in the region of the α -carbon. This suggestion is only tentative and the investigation of a wider series of substituents is required to reach more firm conclusions.

C-H vs. C-C bond cleavage. When an α -carbon is bonded to both a hydrogen atom and a saturated carbon, two



Scheme 4.

reaction pathways become available to the radical cation as illustrated in Scheme 4.

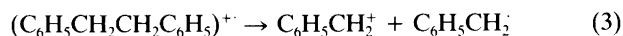
The possible competition between these two reaction channels has been studied in many systems. One of the cases which has attracted much attention is that of bibenzyl radical cation. This is because bibenzyl is a simple coal model compound⁹ and there is interest in the possibility of breaking down coal macromolecules by electron transfer reactions, under mild conditions.

Mass spectrometric studies have clearly shown that in the gas phase, the breakage of the C-C bond, with formation of a benzyl radical and a benzyl cation, is a very important decomposition mode of the bibenzyl radical cation.¹⁰ By simple thermochemical calculations^{2,11} the ΔH° value for this process can be estimated to be ca. 27 kcal mol⁻¹, which compares with a ΔH° value of ca. 200 kcal mol⁻¹ for the competing cleavage of the C-H bond (to give a carbon radical and H⁺).

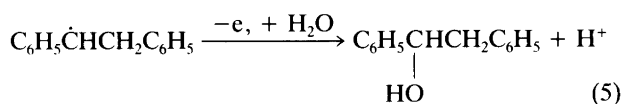
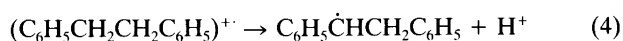
In solution, however, the situation is drastically modified. In MeCN as the solvent, the deprotonation reaction is exergonic ($\Delta G^\circ = -15$ kcal mol⁻¹)^{12a,13} whereas the ΔH° value for the cleavage of the C-C bond should not significantly change with respect to the gas phase^{12b} value since solvent stabilization of the benzyl cation is not expected to be much different from that of bibenzyl radical cation. Thus, in solution the process thermodynamically favoured is that involving the cleavage of the C-H bond and this is certainly due to the very high solvation energy of the proton, much higher than that of the benzyl cation.

Kinetics however, might produce a different outcome

and; currently there is a quite widespread belief that bibenzyl radical cation should also undergo the rupture of the C–C bond rather than of the C–H bond. This belief originated from the observation that when bibenzyl is oxidized by CAN in MeCN/H₂O, C–C bond cleavage products (benzyl alcohol, benzyl nitrate and benzaldehyde), indeed form, which indicated the scission shown in eqn. (3).

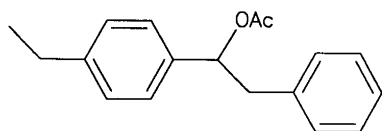
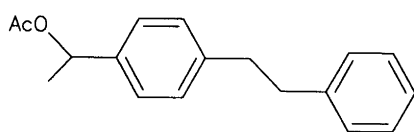


However, a subsequent, more detailed investigation, using *p*-ethylbibenzyl as the substrate, has clearly demonstrated that reaction (3) does not occur, deprotonation eqn. (4) being the exclusive reaction of the bibenzyl radical cation,¹⁵ in line with thermodynamic predictions.



The C–C cleavage products, observed in the reaction of bibenzyl with CAN, in MeCN/H₂O, are formed by the fast oxidation, under the reaction conditions, of the side-chain substitution product formed as shown in eqn. (5) (*vide infra*).¹ Accordingly, when side-chain substituted products are formed which resist further oxidation, no C–C bond cleavage is observed. This is the case for the anodic and CAN-promoted oxidations of *p*-ethylbibenzyl in AcOH, which lead exclusively to the formation of the side-chain acetoxyated products **6** and **7**.¹⁵ Interestingly, it was also shown that under the same reaction conditions no C–C bond cleavage occurs with 4,4'-dimethoxybibenzyl radical cation.

Similar conclusions have been reached in studies of bibenzyl oxidation promoted by peroxydisulfate¹⁶ and light in the presence of oxygen¹⁷ and, moreover, no evidence for the occurrence of C–C cleavage to the state of the intermediate radical cation has been found in the CAN-promoted oxidation of acenaphthene.¹⁸

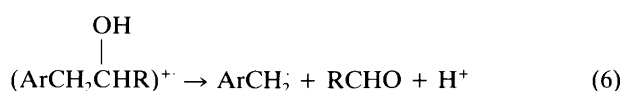
**6****7**

Of course, the C–C bond cleavage pathway can compete more favourably with the C–H bond rupture in systems where the former reaction leads to species more stable than the benzyl radical and the benzyl cation formed by the cleavage of bibenzyl radical cation.

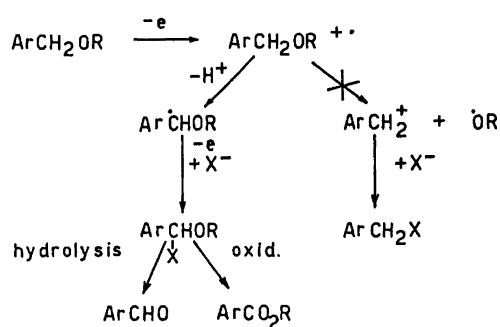
Thus, Arnold and coworkers have shown that in the photosensitized oxidation of 1,1,2,2-tetraphenylethane (**8**) in MeOH products are formed (diphenylmethane and diphenylmethyl methyl ether) which can be reasonably ascribed to C–C bond cleavage in **8**⁺.¹⁹ By this cleavage a diphenylmethyl radical and a diphenylmethyl cation are produced, which are significantly more stable than benzyl radical and benzyl cation, respectively. Likewise, C–C bond cleavage to the state of the radical cation takes place in the photosensitized oxidation of 2-methyl-1,1,2-triphenylpropane.¹⁹

The absence of C–H bond breakage products is, however, remarkable as also in these cases thermochemical calculations¹⁹ indicate that these process should still be favored thermodynamically. A possible reason is that the stereoelectronic requirements discussed above operate against the C–H bond cleavage. For example, in **8** two large groups are bonded to the α -carbon and this can prevent the alignment of the β C–H bond with the π -system. The C–C bond should instead be collinear with the π -system, thus further favoring the cleavage of this bond. In this respect, it is useful to point out that whereas the stereoelectronic requirements should hold for the breakage of whatever β -bond in an aromatic radical cation, they always disfavor the C–H bond breaking process when in competition with the cleavage of other bonds. This is because the H atom has the least steric interaction with *ortho*-hydrogens of the aromatic ring.

The presence of α and/or β OH and OCH₃ groups in the side-chain of the radical cation favors the C–C bond cleavage channel, since highly stabilized α -hydroxy or α -alkoxy carbocations can be formed. As an example, breaking of the C–C bond occurs to some extent in the radical cation of methyl 2-phenylethyl ether,²⁰ and is the main pathway in the radical cations of methyl 2,2-diphenylethyl methyl ether¹⁹ and 2-phenylacetaldehyde dimethylacetal.²¹ Likewise, facile C–C bond breakage is also observed in arylpinacols and arylpinacol ethers.²² When a hydroxy group is present, the possibility should be considered that C–C bond cleavage may be assisted by proton loss, as shown in eqn. (6). Evidence for a concerted C–C bond cleavage and proton loss has recently been presented for the photoreactions of β -amino alcohols.²³



It should be mentioned that the basicity of the medium might play an important role in the competition between the C _{α} –H and C _{α} –C bond breaking reaction pathways of a radical cation, the former presumably being favored in

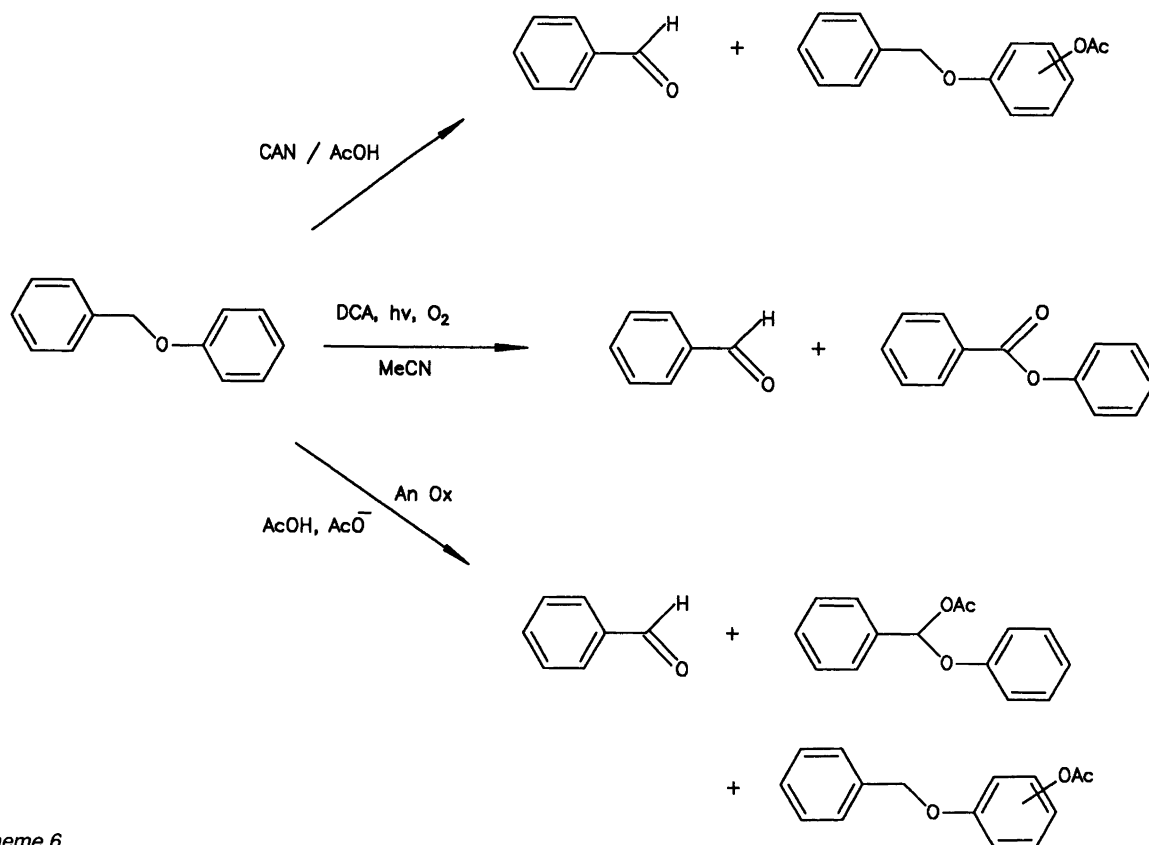
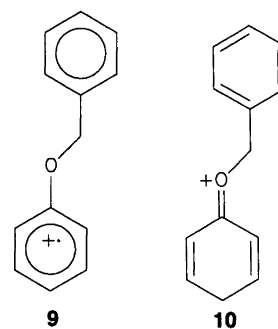


Scheme 5. X = conjugate base of the solvent or whatever nucleophile is present in the medium.

C-H vs. C-O bond cleavage. In the one-electron oxidation of benzyl ethers no benzylic reaction products are observed, only benzaldehyde and, in some case, alkyl benzoate.²⁴ As illustrated in Scheme 5, this clearly shows that the intermediate radical cation has exclusively undergone C-H bond cleavage.

The same conclusion holds for the dibenzyl ether radical cation²⁵ in spite of a claim to the contrary.²⁶ These results are in line with the very large thermodynamic advantage in solution for the C-H bond cleavage pathway with respect to the process involving C-O bond rupture.²⁷

more basic solvents. Even though no systematic study in this respect is available, it appears that for the dibenzyl radical cation deprotonation also prevails in solvents of basicity as low as that of AcOH. Thus, the nature of the solvent should not have a significant influence on the C-H vs. C-C bond cleavage competition in this system. However, this possibility exists in the other cases where the breaking of the C-C bond is the main process. Further study in this respect is certainly welcomed.



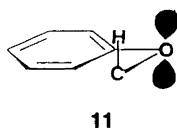
Scheme 6.

A different situation might pertain to the benzyl phenyl ether radical cation (**9**). In **9** the positive charge should exclusively be localized on the oxygen-carrying ring (anisole is much more easily oxidizable than toluene), and consequently, *only* the O–C bond can interact with the positively charged π -system. Thus, in **9** the breakage of this bond, which also leads to the formation of the stable phenoxyl radical, might be observed.

However, no evidence in this respect has been obtained in a study of one-electron oxidations of benzyl phenyl ether.²⁸ As shown in Scheme 6 (DCA = 9,10-dicyanoanthracene) in no case were benzylic derivatives formed. In addition to the ring substituted products, products were obtained the formation of which can easily be rationalized by the sequence shown in Scheme 5 (R = C₆H₅) if the radical cation **9** undergoes proton loss.

That deprotonation can successfully compete with ring attack is remarkable since, as already observed, the C–H bond cannot interact directly with the positively charged benzene ring. It is probable that a significant part of the positive charge also resides on the oxygen atom, as illustrated by the resonance structure **10**, and this could significantly enhance the kinetic acidity of the adjacent C–H bonds. Evidence in this respect is provided by ESR studies that show that in methoxybenzene radical cations the hydrogen atoms of the methoxy group exhibit a significant hyperfine coupling constant.²⁹

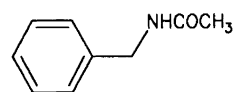
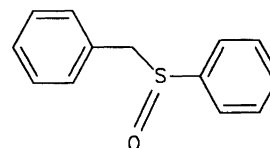
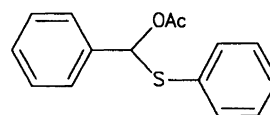
It should also be mentioned that photo electron spectroscopy measurements suggest **11** to be the preferred confor-



mation of a phenyl ether radical cation.³⁰ In this conformation the O–C bond is in the plane of the ring and the interactions between the oxygen *p*-electrons and the b_1 molecular orbital of the benzene ring are maximized. In this conformation, no interaction between the C–O bond and the π -system is possible, whereas the β -C–H bond can overlap with the mixed p - π molecular orbital. Thus, in **9** breakage of the C–H bond is a much easier process than breakage of the C–O bond.

In this respect, however, the benzylic nature of the C–H bond must play a fundamental role. Accordingly, only ring substitution products have been observed in the anodic oxidation of phenyl 2-phenylethyl ether.²⁸ Clearly, the deprotonation reaction, which would involve a non-benzylic C–H bond, cannot compete with ring attack in the intermediate phenyl 2-phenylethyl ether radical cation.

C–H vs. C–S bond cleavage. A more complex situation exists with benzyl sulfide radical cations which, besides C–H and C–S bond cleavage, can also undergo a nucle-



ophilic attack at sulfur, eventually leading to sulfoxides and/or sulfones.

The properties of benzyl phenyl sulfide radical cation are under study and the information available so far indicates that all the above processes actually occur, their relative weight being strongly influenced by the reaction conditions and the substrate structure.³¹

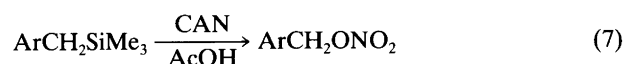
Thus, the anodic oxidation of benzyl phenyl sulfide in AcOH/AcO⁻ leads nearly exclusively to the formation of **12**, indicating that in this medium the intermediate radical cation is predominantly deprotonated. However, it has been reported that the sulfoxide **13** and the benzyl derivative **14** are the main products in MeCN, suggesting the predominance of the pathways involving attack at sulfur and C–S bond cleavage.³² presumably, in AcOH/AcO⁻ the presence of a strong base favors deprotonation over the other reaction modes.

The structure of the substrate, however, seems to play an important role in this regard, since in the anodic oxidation of benzyl 4-methoxyphenyl sulfide in AcOH/AcO⁻, the corresponding sulfoxide and benzyl acetate are formed.³¹ Thus, the presence of a 4-methoxy substituent on the sulfur-containing ring profoundly modifies the reactivity of the radical cation, the deprotonation reaction being replaced by attack at sulfur and C–S bond cleavage.

Clearly, further systematic work is necessary before conclusions can be drawn concerning the competition between the different pathways available to a benzylsulfide radical cation. In such cations most of the positive charge is probably located on the sulfur atom, even though there is considerable mixing between the sulfur *p*-type orbital and the π -molecular orbital.³³ This might play a role in making C–S bond cleavage in benzyl sulfide radical cations easier than the scission of the C–O bond in the radical cations of the corresponding ethers. From a thermodynamic point of view, the breakage of the two bonds in the corresponding radical cations is characterized by similar ΔH° values.

C-H vs. C-Si bond cleavage. For the radical cations examined so far, C-H bond cleavage either is the exclusive reaction pathway or, at least, it can compete with the other types of bond rupture.

A completely different situation exists for benzyltrimethylsilane radical cation which exclusively undergoes C-Si bond cleavage. Accordingly, formation of benzyl derivatives is the general outcome for one-electron oxidation of benzyltrimethylsilane under a variety of conditions: CAN-promoted oxidation in AcOH,³⁴ anodic oxidation in MeOH,³⁵ sensitized photooxidation,³⁶ and reaction with triarylaminium radical ions.³⁷ The CAN-promoted reaction eqn. (7) is characterized by a very high and negative ρ value (-5.5), which is in line with the slow formation of a radical cation intermediate undergoing fast C-Si bond breaking.



In addition, 4-methoxybenzyltrimethylsilane radical cation has recently been detected in laser flash photolysis experiments in MeCN and the fast decay of this radical cation to 4-methoxybenzyl radical has been demonstrated.³⁸

It might be possible that the exclusive occurrence of C-Si bond breaking in benzyltrimethylsilane radical cation is again due to stereoelectronic requirements governing the breaking of β -bonds in aromatic radical cations. Trimethylsilyl is a bulky group and even though the C-Si bond is longer than the C-C bond, the situation should be similar to that previously discussed when dealing with the effect of an α -*t*-Bu group in the deprotonation reactions. In other words, in benzyltrimethylsilane radical cation only the C-Si bond should have the required geometry to undergo cleavage. However, this cannot be the only explanation since 4-methylbenzyltrimethylsilane is also oxidized by CAN to give exclusively products of C-Si bond cleavage.³⁴ In the intermediate radical cation there is no stereoelectronic constraint for deprotonation from the *para*-methyl group; therefore the rate of C-Si bond breakage has to be intrinsically much higher than that of C-H bond cleavage.

Quantitative information in this respect has been obtained by laser flash photolysis experiments. In MeCN the first-order rate constant for the desilylation of 4-methoxybenzyltrimethylsilane radical cation at 25 °C is $1.2 \times 10^6 \text{ s}^{-1}$.³⁸ This compares with a value of $2 \times 10^4 \text{ s}^{-1}$ measured for the deprotonation of 4-methoxytoluene radical cation in the same solvent.^{39,40} Taking into account the statistical factor, the cleavage of the C-Si bond is ca. 200 times faster than that of the C-H bond. It is probable that the intrinsic difference is still higher since the stability of 4-methoxybenzyltrimethylsilane radical cation is higher than that of 4-methoxytoluene radical cation.

At least two factors contribute to make the rate of C_α -Si bond cleavage in an aromatic radical cation so fast. First, there is a strong hyperconjugative interaction between the

σ C-Si bond and the π -system,⁴¹ which should favour the intramolecular electron transfer from the former to the latter. Secondly, silicon forms very strong bonds, still stronger than those formed by hydrogen, with atoms (i.e., N and O) which are the reactive centers in many nucleophiles.⁴² The latter actor can therefore play a major role in making the C-Si bond cleavage pathway the most favoured for the benzyltrimethylsilane radical cation.

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