Reactions between Grignard Reagents and Thiocarbonyl Compounds: A Revisitation

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The radical anions from thiobenzophenone, thiobenzoyltriphenylsilane, and 3,5-di-*tert*-butylthiobenzoyltriphenylsilane were detected by EPR spectroscopy when these compounds were reacted with a number of Grignard reagents, RMgBr. The radical adducts resulting from addition of R• radicals to the thiones were also detected. The formation of the radical anions indicates unambiguously the occurrence of a SET process which might be the initial stage of these reactions. In the case of tris(trimethylsilyl)ethanethial only the radical adducts were detected. The first reduction potentials of these thiones have also been measured in order to verify the feasibility of the SET process. In agreement with the EPR experiments, the calculated standard free energy changes suggest that electron transfer is possible in the first three cases and disfavored with the thioaldehyde.

Introduction

Secondary and tertiary alcohols can be readily and conveniently synthesized through the reaction of suitable Grignard reagents with aldehydes or ketones, respectively, followed by hydrolysis of the intermediates formed. Although initially these reactions were seen as simple nucleophilic additions of the partially negative $R^{\delta-}$ residue of the Grignard reagent to the partially positive end of the carbonyl function,[1] by the mid 1980's the formation of different complexes and the occurrence of single electron transfer (SET) processes with formation of ketyl radical pairs had been reported.[2] A particularly detailed picture for aromatic ketones was provided by Ashby and Bowers, who suggested a mechanism involving the formation of a *radical anion-radical cation* pair that could either collapse to 1,2-addition products or fragment to a radical ion pair and a neutral radical. These new species may recombine to give 1,2- and 1,6-addition products or may exit the solvent cage affording mainly pinacols and alkanes, together with other products.[3] In the following years direct EPR evidence of the formation of radical species in the course of the reaction of methylmagnesium bromide with benzophenone and fluorenone was obtained, the observed spectra being attributed to the presence in solution of the radical anions of the ketones and to aggregates between two radical anions and two molecules of the Grignard reagent.[4] It should, however, be emphasized that the EPR spectra from the latter aggregates could only be observed in solid matrices owing to the severe line broadening in solution due to the strong interaction between the two unpaired electrons.

The analogous reactions between Grignard reagents and thiocarbonyl compounds have also received some attention. These reactions do not normally lead to the corresponding thiols but afford different products which depend very much on the nature of the individual thiocarbonyl derivative; thus, while the reactions with aromatic thioketones lead to sulfides Ar_2CHSR, those with aliphatic thioketones afford either the corresponding reduction products R_2CHSH or the higher mercaptans R_2CRSH.[5] It would also appear that in the reactions with aliphatic thioketones the nature of the R residue of the Grignard reagents as well as the nature of the solvent employed strongly influence the relative yields of the products resulting from reduction, thiophilic addition, and carbophilic addition.[6]

The various studies carried out in the course of the years have led to the formulation of at least three different reaction mechanisms to account for the observed reactivity. According to mechanism A (direct nucleophilic addition) originally proposed for thioketones containing aromatic substituents, a polarization of the bonding electrons of the thiocarbonyl function opposite to that occurring in the case of carbonyl compounds would make the carbon more negative than sulfur; the latter atom would therefore be more likely to undergo nucleophilic attack by the partially negative hydrocarbon moiety of the Grignard.[7] On the other hand, aliphatic thioketones, such as 2,2,4,4-tetramethylpentane-3-thione, do afford the carbophilic addition product along with that resulting from thiophilic addition.[8]

A second mechanism (B), similar to that proposed for the reactions with ketones,[2] implies a SET process with formation of different charge-transfer complexes, which

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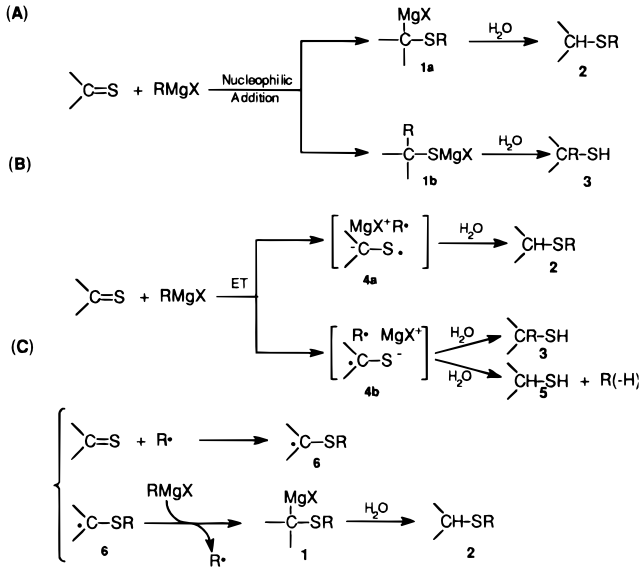
Scheme 1

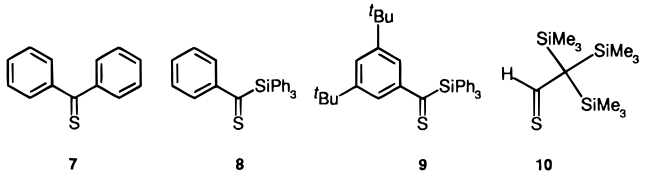


could subsequently collapse to the products.[9] The nature of the substituents linked to the thiocarbonylic function influences the electronic distribution in these charge transfer (CT)-complexes and therefore dictates the orientation of the addition. A third possibility (mechanism C) is that the radicals formed in the SET process escape from the cage and react homolytically with the starting thiocarbonyl.[9]

Addition to the sulfur atom via (A) should prevail for those thioketones having electron-withdrawing groups R^1 and R^2 bound to the C=S double bond and for aromatic thioketones where delocalization of the negative charge can lead to stabilization of the initially formed carbanion.[10] Although in an early work[11] it was found that the reaction of thiobenzophenone with enantiomerically pure (*Z*) or (*E*)-1-propenylmagnesium bromide resulted in the formation of the corresponding sulfides with substantial retention of configuration, it was not possible to discriminate between direct nucleophilic addition, A, and the intervention of caged radical species, B. EPR monitoring of several experiments involving thiobenzophenone,[12] thiopivalophenone, 2,2,5,5-tetramethylcyclopentane-1-thione, and thiofenchone[13] has proved that these processes do involve free radicals, but in all cases the detected species had the general structure **6** and were suggested to originate from cleavage of complexes **1a**.[12] However, in no case could the initial occurrence of an SET process be proved through direct EPR observation of the resulting radical ions. The detection of the radical adducts **6** would also be in line with the free radical chain mechanism (C) proposed by Ohno *et al.*[13]

In a recent EPR study of the reactivity of a few thiocarbonyl compounds having a phosphoryl group α to the C=S double bond, *i.e.* the diethoxyphosphoryl dithioformates $(EtO)_2P(O)C(S)SR$, some of us reported the detection of a weak spectrum attributed to the radical anion from the starting compound upon reaction of methylmagnesium bromide with the methyl dithioformate.[14] This finding prompted us to undertake a more detailed EPR study on the reactions of Grignard reagents with thiocarbonyl compounds, with the aim of obtaining definite evidence of the involvement of thioketyl radical anions or ion pairs in these processes. In this light, the choice of the substrates was addressed to species whose radical anions should be relatively persistent and exhibit simple EPR spectra in order to allow the identification of the several radicals which may be present simultaneously. We have therefore studied, besides thiobenzophenone **7**, whose radical anion gives a spectrum of some complexity, the two thiobenzoylsilanes thiobenzoyltriphenylsilane **8** and its 3,5-di-*tert*-butyl substituted derivative **9**, whose radical anions, owing to the presence of a silicon substituent α to the C=S double bond, are strongly stabilized[15] and give rise to EPR spectra characterized by a low number of lines.[16] 2,2,2-Tris(trimethylsilyl)ethanethial (**10**), given its unusually high stability, was used as prototype of aliphatic thiocarbonyl compounds.

We also carried out an electrochemical study of the four thiocarbonyls **7**−**10** to determine their reduction potentials and to check if the SET processes responsible for the formation of these radical anions are energetically feasible.



Results

EPR Studies. The reactions of thioketones **7**−**9** with excess methylmagnesium bromide, ethylmagnesium bromide, and phenylmagnesium bromide at ca. −40 °C in a 1:1 mixture of tetrahydrofuran (THF) and diethyl ether led in all cases to the observation of intense EPR spectra showing the simultaneous presence of two paramagnetic species. As a typical example, Figure 1 shows the EPR spectrum exhibited by the mixture of **7** and MeMgBr. The two species were characterized by similar couplings of the unpaired electron with the hydrogens of the aryl groups, but by very different *g*-factors. The spectrum with the lower *g*-factor also showed additional hyperfine structure originating from the hydrogens of the R residue of the Grignard (see Table 1).

The species responsible for the high-field signals were straightforwardly identified as the adducts XYC(•)−SR, **6**, of the R fragment of the Grignard with the thioketones XYC=S. Actually, their spectral parameters are identical to those previously reported for the authentic adducts obtained by addition of R• radicals to the appropriate thiones.[18] The signals at lower magnetic fields were instead assigned to the radical anions of the thioketones,

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(17) Bonini, B. F.; Maccagnani, G.; Masiero, S.; Mazzanti, G.; Zani, P. *Tetrahedron Lett.* **1989**, 2680.
(18) Alberti, A.; Benaglia, M.; Bonini, B. F.; Pedulli, G. F. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 3347.

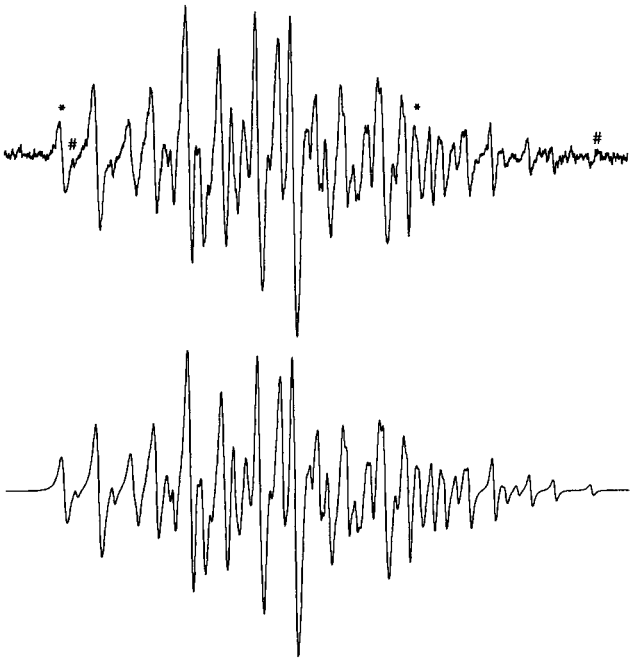
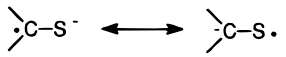


Figure 1. Experimental (above) and computer-simulated EPR spectrum observed when reacting thiobenzoyltriphenylsilane (**8**) with MeMgBr at ca. −20 °C. The first and last line of the spectrum of the radical anion from **8** are marked with ∗ while those of the spectrum of the methyl adduct to **8** are marked with #.

since their very high *g*-factor (ca. 2.006−2.007) suggested high spin delocalization at the sulfur atom. These values can be justified on the basis of the mesomeric structure **12**, implying a larger spin delocalization on sulfur.[19−21]



(11) **(12)**

While at low temperature the signals of the radical anions were largely dominant, by increasing the temperature their intensity decreased while that of radicals **6** increased, the latter adducts becoming the only detectable species near or above room temperature. This behavior was not reversible, and after their disappearance the spectra of the radical anions could not be observed again upon recooling the solution.

Thiobenzoyltriphenylsilane **8** was also reacted at low temperature with excess 5-hexenylmagnesium bromide: the reaction led to the detection of the radical anion of the thioketone and of the adduct **6** resulting from addition of the 5-hexenyl radical, with virtually no trace of the other possible adduct, *i.e.* that of cyclopentylmethyl radical resulting from the cyclization of 5-hexenyl. For the sake of comparison, the authentic adducts of **8** with 5-hexenyl and cyclopentylmethyl radicals were generated by photolyzing a solution of the thioketone containing some iodosobenzenediacetate (IBDA) and excess 6-heptenoic acid or cyclopentylacetic acid.[22] The spectra of the two adducts were slightly different (see Table 1), and each adduct could be readily identified.

When the thioaldehyde **10** was similarly reacted with methyl-, ethyl-, or phenylmagnesium bromide inside the cavity of the EPR spectrometer, the spectra of the rather persistent methyl-, ethyl-, or phenyl adducts were observed (see Table 1), but no signals from the thioaldehyde radical anion at temperatures as low as −70 °C.

In order to ascertain whether the observed radical anions were present as dissociated anions or radical ion pairs, thioketones **8** and **9** were also treated with alkali metals in THF at low temperature in order to generate their lithium, sodium, potassium, and magnesium radical ion pairs (see Table 2). Below −70 °C, and at very high dilution, the spectrum of the dissociated anions were also observed overimposed to those of the ion pairs.

The dissociated radical anions of compounds **7**−**9** were also obtained by electrolysis of DMF solutions of the thiocarbonyl compounds containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte, and their hyperfine spectral parameters are collected in Table 2. Similar attempts to generate the radical anion of **10** resulted in the observation of a strong doublet ($a_H = 16.90$ G) centered at $g = 2.0042_6$. This latter value is unexpectedly low for a thioketyl while is characteristic of a ketyl radical. The observation of ketyls during the electrolysis of thioketones is well known[23] and in the present case is consistent with the irreversibility of the first reduction wave in the voltammogram of compound **10** (see below).

Electrochemistry. Electrochemical investigations have been carried out in DMF at −55 °C with scrupulous exclusion of any trace of water and of other proton donors. In cyclic voltammetry all three thioketones **7**−**9** showed two reduction peaks; while in the case of thiobenzophenone **7** both peaks correspond even at low scan rate (0.05 V/s) to one electron diffusion controlled reversible processes, in the case of compounds **8** and **9** this is true only for the first peak, provided the direction of the scan is reversed before the second peaks start developing. This indicates that the radical anions formed from **7**−**9** through the first electron transfer are stable in the time scale of the voltammetric experiments. The values of the half-wave potentials, $E_{1/2}$, derived by adding 21 mV to the peak potentials, E_p, are −0.99, −1.12, and −1.04 V for thiones **7**−**9**, respectively.

As to the second peaks for **8** and **9**, their morphology and characteristics depended strongly on sweep rate and temperature, suggesting the occurrence of a complex electrode mechanism which is also dependent on the nature of the compound. Since the electrochemical side of his work was mainly devoted to the evaluation of the driving force relative to electron transfer reactions between the donors (Grignard reagents) and the acceptors (compounds **7**−**9**), the attention was focused on the characteristics of the first peaks. The overall electrochemical behavior of these compounds will be reported and discussed in a subsequent paper.

Differently to what found for **7**−**9**, compound **10** showed a single one-electron irreversible reduction peak in the available potential window, with a peak potential $E_p = -2.06$ V *vs* SCE at 0.2 V/s. The irreversibility remained the same up to the maximum sweep rate accessible without severe distortion of the curve (100 V/s). At low and moderate sweep rates (0.050−1 V/s), E_p varied linearly with the logarithm of the sweep rate by 45 mV

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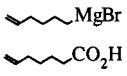
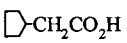
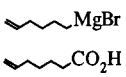
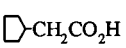
(21) Voss, J.; Bruhn, F.-R. *Annalen*, **1979**, 1931. Voss, J.; Schlapkohl, K. *Tetrahedron* **1975**, *31*, 2982. Klages, C. P.; Voss, J. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 726.
(22) Alberti, A.; Benaglia, M.; Vismara, E. *Res. Chem. Intermed.* **1989**, *11*, 117.
(23) Lunazzi, L.; Maccagnani, G.; Mazzanti, G.; Placucci, G. *J. Chem. Soc. (B)* **1971**, 162.

Table 1. EPR Spectral Parameters (hfs constants in Gauss = 10^{-4} T) for Radicals from 7-10 in Diethyl Ether

Comp.	Reactant	Radical	a_p	a_o	a_m	$a_{^{29}Si}$	a_{other}	g	T/K
7	RMgBr[a]	ion pair	3.05	2.74	1.10	----	----	2.0048_8	243
7	MeMgBr	adduct	3.15	2.86	1.17	----	1.17(3H)	2.0034_6	298
7	EtMgBr	adduct	3.17	2.82	1.27	----	1.29(2H), 0.33(3H)	2.0034_2	298
7	PhMgBr	adduct	3.20	2.93	1.21	----	0.31(5H)	2.0031_0	298
8	RMgBr[a]	ion pair	3.58	3.23	1.19	n.d.	----	2.0063_2	243
8	MeMgBr	adduct	3.06	2.95	1.24	n.d.	2.08(3H)	2.0044_3	298
8	EtMgBr	adduct	3.08	2.89	1.25	n.d.	1.17(2H), 0.35(3H)	2.0044_5	298
8	PhMgBr	adduct	3.70	3.23	1.25	n.d.	0.39(5H)	2.0039_8	298
8		adduct	3.16	3.01	1.26	n.d.	1.07(2H), 0.30(2H)	2.0044_5	298
8		adduct	3.13	3.05	1.27	n.d.	1.10(2H)	2.0044_5	298
9	RMgBr[a]	ion pair	3.54	3.20	----	10.76	----	2.0062_1	243
9	MeMgBr	adduct	3.38	3.23	----	n.d.	1.66(3H)	2.0048_8	298
9	PhMgBr	adduct	3.47	3.44	----	9.56	0.42(5H)	2.0039_3	298
9		adduct	3.38	3.20	----		0.93(2H), 0.34(2H)	2.0043_1	298
9		adduct	3.39	3.23	----	9.13	0.98(2H)	2.0042_5	298
10	MeMgBr	adduct	----	----	----	15.7	15.96(1H), 1.86(3H)	2.0041_6	243

a) R = Methyl, Ethyl, Phenyl, 5-hexenyl.

Table 2. EPR Spectral Parameters (hfs constants in Gauss = 10^{-4} T) for Radical Ions from 7-9 in THF

compd	reactant	radical	a_p	a_o, $a_{o'}$	a_m	$a_{^{29}Si}$	a_M	g	T/K
7	electrochem	anion[a,b]	2.75	2.35	0.95	–	–	–	298
7	Li	ion pair	2.86	2.47	0.99	–	2.01	2.0062_1	298
7	Na	ion pair[c]	2.85	2.41	0.94	–	3.62	2.0068_0	296
7	K	ion pair	2.82	2.39	0.92	–	0.78	2.0068_8	298
7	Mg	ion pair	3.01	2.70	1.08	–	n.d.	2.0048_7	298
8	electrochem	anion[a]	3.44	2.85	0.96	n.d.	–	2.0094_7	298
8	–	anion	3.45	3.12, 2.62	0.97	n.d.	–	2.0098_5	203
8	Li	ion pair	3.48	3.11, 2.97	1.04	n.d.	2.49	2.0083_9	233
8	Na	ion pair	3.50	3.10, 2.74	1.00	n.d.	3.18	2.0088_8	233
8	K	ion pair	3.48	2.95	1.00	n.d.	0.75	2.0088_2	273
8	Mg	ion pair	3.51	2.58	1.00	n.d.	n.d.	2.0068_9	298
9	electrochem	anion[a]	2.81	2.45	–	n.d.	–	2.0093_2	298
9	Li	ion pair	3.35	2.98	–	9.99	3.23	2.0080_4	273
9	Na	ion pair	3.37	3.10, 2.81	–	9.75	4.45	2.0084_7	233
9	K	ion pair	3.35	3.07	–	9.64	0.86	2.0085_1	273
9	Mg	ion pair	3.40	3.20	–	10.39	–	2.0064_0	273

[a] In DMF. [b] Reference 23. [c] Reference 24.

per unit in average with a peak width, $E_{p/2} - E_p = 65$ mV in average. These values are typical of an "EC" (E, electron transfer process with the formation of the anion radical; C, first order cleavage of the anion radical) mechanism with a mixed kinetic control by E and C steps.[25] Thus, the reductive cleavage of **10** would follow a stepwise mechanism involving the intermediacy of the anion radical. It may not be obvious why the radical anions from compounds **7**–**9** should be stable while that from compound **10** should not. For thiobenzophenone, delocalization of the unpaired electron over two aromatic rings may lead to stabilization of the corresponding anion. Although in the anions from thiones **8** and **9** delocalization is possible only on one aromatic ring, further stabilization originates from the presence of a silicon atom directly linked to the partially negative radical carbon.[15] We believe that the instability of the radical anion from thioaldehyde **10** should not be attributed to the lack of delocalization of the unpaired electron (di-*tert*-butyl thioketone, **14**, exhibits a fully reversible first reduction wave even at scan rates as low as 0.02 V/s), but rather to the presence of the three silicon atoms. In fact, fragmentation of the C–C bond in $\mathbf{10}^{\bullet-}$ would result in the formation of a transient thioacyl radical and of a tris(trimethylsilyl)methyl anion: the strong stabilization of this carbanion by the three α-silicon atoms can certainly provide the driving force for fragmentation and justify the instability of $\mathbf{10}^{\bullet-}$.

As to the reduction potentials reported above, the $E_{1/2}$ values for **7**–**9** can be considered equal to the standard potentials $E°$ within the usual assumptions, while the E_p for **10**, even after the 21 mV correction, does not represent the $E°$ value because of the irreversibility of the peak. However, since the cyclic voltammetric data

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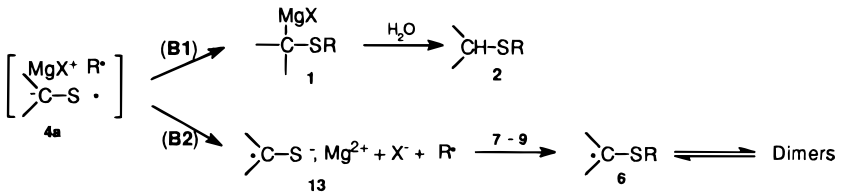
(25) Andrieux, C. P.; Le Gorande, A.; .Savèant, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 6892 and references therein cited.

Scheme 2



are consistent with an electrochemical reductive cleavage involving the intermediacy of the anion radical, it can be inferred that the standard potential of the **10**/**10**$^{\bullet-}$ couple must be more negative than the effective reduction potential. Thus, the E_p value represents an upper limit for $E°$.[25]

Discussion

The products obtained in the reaction of Grignard reagents and thiobenzophenone[7] or thiobenzoylsilanes[17] have been shown to be the sulfides XYCH−SR with yields spanning from 40 to 100%. As described above, their formation could be explained by any of the three mechanisms A, B, and C. The radical chain mechanism C might appear the more appropriate to account for the observation of the intermediate radical adducts **6**. Since, however, this mechanism implies the formation of free radicals R$^{\bullet}$ which are known to be planar, it is in conflict with the finding that the reaction proceeds primarily with retention of configuration of the R group.[11]

On the other hand, mechanism A should not lead to the observation of any radical species, unless the intermediate adduct **1** undergoes reversible homolytic cleavage of the carbon−magnesium bond to give **6**, as proposed by Dagonneau *et al.*[6]

However, neither of these mechanisms can explain the most relevant result of this work that is the direct detection of the radical anions from thioketones **7**−**9** during their reaction with the Grignards. The formation of these species, if admitting that they lie on the main reaction coordinate, can instead be accounted for by mechanism B involving initial electron transfer from the organomagnesium compound to the thioketones to give the radical pair **4a** or **4b**. This in turn can either collapse into adduct **1** (path B1), retaining the configuration of the R group, or evolve to the radical ion pairs **13** detected by EPR (path B2). Radicals R$^{\bullet}$ formed concomitantly to **13** may then attack another thioketone molecule to afford the adducts **6**, also observed by EPR.

Mechanism B2 seems to find some support in the dependence on temperature of the EPR spectra of radicals **6** and **13**. At low temperature the signals from the radical anions are largely dominant, this being expected in view of the well known greater solvating ability of ethers at low temperature[26] which would favor the cleavage of **4a** to give R$^{\bullet}$ and **13** over its collapse into **1**. An apparent discrepancy is the absence at low temperature of radicals **6**, resulting from addition of R$^{\bullet}$ to the thioketones.[27] This result can, however, be accounted for in terms of the equilibrium between thioketyl radicals and their diamagnetic dimers, which is known to be shifted toward the latter species at low temperature.[28] Indeed if the temperature is raised, the intensity of the signals from the radical anions become vanishingly small, while that of adducts **6** increases steadily, up to near the solvent boiling point.

In order to verify if adducts **6** really resulted from addition of radicals R$^{\bullet}$ to the thioketones, compounds **8** and **9** were reacted at room temperature with 5-hexenylmagnesium bromide. 5-Hexenyl radicals are known to readily undergo exocyclization to cyclopentylmethyl radicals with a rate constant $k_r^{298} = 2.3 \times 10^5$ M^{-1} s^{-1},[29] and are commonly used as indicators of radical reactions and also as radical clocks to time the rate of competing reactions. Thus, in reactions involving radical species, the use of 5-hexenyl radical leads to variable amounts of products containing either the 5-hexenyl or the cyclopentylmethyl moiety. In the present case, the reaction of **8** and **9** with $C_6H_{11}MgBr$ when performed inside the EPR cavity led to the observation of a spectrum showing coupling of the unpaired electron with the nuclei of the thioketone and with two additional pairs of equivalent protons (see Table 1). This spectrum can be attributed to the adduct of the unrearranged 5-hexenyl radical, since in the cyclopentylmethyl adduct coupling with a pair of protons and with a single proton is instead expected. For the sake of comparison, the authentic adducts to **8** and **9** were generated as described in the preceding section,[22] and the observed spectra confirmed the above assignment (see Table 1). During these experiments it was found that when the 5-hexenyl radical is reacted with a thioketone solution of the same concentration (ca. 0.1 M) used for the reactions with the Grignard, the adducts of the rearranged radical were not observed. This finding provides evidence that the rate of addition of the 5-hexenyl radical to the C=S double bond at room temperature is at least one order of magnitude faster than that of its rearrangement and is in line with previous results showing that alkyl radicals add to thiones with rate constants $\geq 10^6$ M^{-1} s^{-1}.[18,27] It is therefore concluded that the failure of detecting cyclopentylmethyl radical adducts to thioketones **8** and **9** by reaction with 5-hexenylmagnesium bromide does not represent a proof against a mechanism involving radical species such as mechanism B.

The radical ions detected by EPR in these reactions have spectral parameters typical of radical ion pairs between the radical anion of the starting thioketone and a magnesium counterion rather than of free radical anions. In order to prove this point, the authentic magnesium ion pairs of the radical anions from the thioketones were generated with a magnesium−mercury amalgam. In all cases the observed spectra were identical to those detected during the reactions between the thioketones and the Grignards and attributed to the ionic species. An examination of the data collected in Table 2 shows that the *g*-factors of the magnesium ion pairs are

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Table 3. Calculated $\Delta G°$/kcal·mol^{-1} for the Reactions between Grignard Reagents and Compounds 7-10

thione	MeMgBr	EtMgBr	PhMgBr
7	3.5	−6.0	9.3
8	0.5	−9.0	6.2
9	1.6	−7.8	7.4
10	25.16	15.7	30.9

in all cases much lower than those of the corresponding lithium, sodium, or potassium ion pairs. These low values indicate that the magnesium ion pairs are much tighter than those involving alkali counterions and can be rationalized by assuming that the ion pair involves a magnesium dication. This is in line with what was already suggested for the magnesium radical ion pairs with carbonyl compounds.[30]

The identification of these species as ion pairs is further supported by the much higher *g*-factors (see Table 2) exhibited by the dissociated radical anions of the thioketones observed either by electrochemical reduction in DMF at room temperature or by metal reduction in ether at very low temperature.

The detection of radical ions provides strong support to mechanism B involving an initial electron transfer from the Grignard to the thiocarbonyl compound. In this respect it is worth verifying the feasibility of this process on thermodynamic grounds.

The free energy change $\Delta G°$ for the electron transfer from an electron donor D to an electron acceptor A is given by eq 1, where $E°(D^{+\bullet}/D)$ and $E°(A/A^{-\bullet})$ are the standard reduction potentials of the appropriate redox couples, respectively, and ΔE_{coul} is the coulombic interaction energy for the two singly charged radical ions formed in the SET process.

$$\Delta G°/\text{kcal·mol}^{-1} = 23.06[E°(D^{+\bullet}/D) - E°(A/A^{-\bullet})] - \Delta E_{coul} \quad (1)$$

The last term can be calculated as

$$\Delta E_{coul}/\text{kcal·mol}^{-1} = 332.0244\frac{1}{r_{AD}\epsilon} \quad (2)$$

where r_{AD} is the distance between the reacting centers in the transition state expressed in Å (10^{-10} m), and ϵ is the dimensionless dielectric constant of the solvent.

The $\Delta G°$ value for the SET reaction can thus be calculated using the redox potentials of compounds **7**−**9** given above and those of the Grignard reagents available in the literature.[31] The coulombic energy was computed from eq 2[32] using the dielectric constant of diethyl ether (4.33) and assuming an interionic distance of 7 Å. As to the oxidation potentials of the Grignard reagents, it must be noted that they are not standard potentials. However, by taking into account the satisfactory Marcus plots for the reactions between alkylmagnesium bromides and some organic acceptors obtained utilizing these values and suitably correcting for the electrostatic term, qualitative information on the driving force of the reaction can be obtained. The $\Delta G°$ values calculated on this basis are reported in Table 3. It should be emphasized that the value relative to **10** must be considered a lower limit in view of the preceding considerations. Therefore, the actual $\Delta G°$ values for the electron transfer reactions with Grignard reagents should be larger than those reported in Table 3. From the $\Delta G°$ values collected in Table 3, it results that the reactions involving thiones **7**−**9** are slightly endoergonic or slightly exoergonic, while those of **10** are highly endoergonic. These results would indicate that the SET process is very unlikely in the case of **10**, while with thiones **7**−**9** the electron transfer is not thermodynamically disfavored.

In favor of such conclusion it should be mentioned that when reacting the thioaldehyde **10** with methylmagnesium bromide, only the corresponding radical adduct **6** could be detected even at low temperature (see Table 1). The failure of observing the radical anion from **10** seems to indicate that the reaction proceeds via nucleophilic addition rather than via an initial SET step and that the observed radical adduct might possibly originate from the cleavage of intermediate **1a**.[6]

As a final comment we wish to stress that while it is possible that the reactions between aromatic thiocarbonyl compounds and Grignard reagents do not actually proceed exclusively through the SET pathway, on the basis of the information provided by the present EPR and electrochemical data, SET should, however, be seriously taken into account and not regarded only as a side process of minor relevance.

Experimental Section

Materials. The thiocarbonyl compounds **7**-**10**[18,33,34] and **14**[26] were prepared as described in the literature. 5-Hexenylmagnesium bromide was prepared by reaction of the magnesium metal with 5-hexenylbromide in diethyl ether, while ethereal solutions of the other three Grignard reagents employed were commercially available, as were the 5-heptenoic acid, cyclopentylacetic acid, and iodosobenzene diacetate (IBDA).

EPR Experiments. EPR spectra were recorded on an upgraded Bruker ER200 D spectrometer equipped with a dedicated data system, a variable temperature kit, an NMR Gaussmeter for field calibration, and a frequency counter for the determination of the *g*-factors that were corrected with respect to that of the perylene radical cation in concd sulfuric acid. The UV light from a 1 kW high pressure mercury lamp focused on the EPR cavity was used when necessary.

In a typical experiment, a thoroughly argon-purged THF solution of a thioketone (ca. 0.1 M) was reacted inside the EPR cavity with a 2 to 4-fold excess of the appropriate Grignard reagent at the desired temperature. In all cases strong EPR spectra could be detected immediately after mixing the reactants.

The model 5-hexenyl and cyclopentylmethyl radical adducts to the two thiobenzoylsilanes were obtained by photolyzing inside the EPR cavity at room temperature argon-purged benzene solutions of **8** or **9** containing some IBDA and an at least two-fold excess of 5-heptenoic or cyclopentylacetic acid.[22]

In electrochemical EPR experiments, an electrolytic flat cell with a Pt-gauze as cathode was filled with argon-purged DMF solutions of thioketones **7**−**10** (ca. 10^{-3} M) containing tetrabutylammonium perchlorate (ca. 10^{-1} M) as supporting electrolyte. The current was supplied and controlled by an AMEL 2051 general-purpose potentiostat.

Electrochemistry. All the materials were reagent grade chemicals. Dry vacuum distilled *N*,*N*-dimethylformamide (DMF) was mixed under argon with sodium anthracenide and allowed to stand for five days in order to remove any traces of water and oxygen, according to the method of Aoyagui and co-workers.[34] The solvent was then distilled via a closed system into an electrochemical cell containing the supporting

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electrolyte and the species under examination. Before the distillation of the solvent, the cell containing the supporting electrolyte $(C_2H_5)_4NBF_4$ was dried under vacuum ($7-9 \times 10^{-5}$ mbar) at 140 °C for 48 h before each experiment. Successively, the species under study were introduced, under argon atmosphere, into the cell, which was then kept under the above vacuum conditions for 60 h at 90 °C.

The one-compartment electrochemical cell was of airtight design with high-vacuum glass stopcocks fitted with either Teflon or Kalrez (DuPont) O-rings in order to prevent contamination by grease. The connections to the high-vacuum line and to the Schlenck containing the solvent were obtained by spherical joints also fitted with Kalrez O-rings. The working electrode consisted of a 0.6 mm-diameter platinum wire (0.15 cm^2 approximately) sealed in glass. The counter electrode consisted of a platinum spiral, and the quasi-reference electrode was a silver spiral. The quasi-reference electrode drift was negligible for the time required by a single experiment. Both the counter and the reference electrode were separated from the working electrode by ~0.5 cm. Potentials were measured with the ferrocene standard[36] and are always referred to SCE.[37] The temperature-dependent ferrocinium/ferrocene couple standard potential was measured with respect to SCE by a nonisothermal arrangement according to the method outlined in ref 38. Ferrocene was also used as internal standard for checking the electrochemical reversibility of a redox couple.

Voltammograms were recorded with an AMEL Model 552 potentiostat controlled by an AMEL Model 568 programmable function generator, an AMEL Model 863 X-Y recorder, and a Nicolet Model 3091 digital oscilloscope. The minimization of the uncompensated resistance effect in the voltammetric measurements was achieved by the positive-feedback circuit of the potentiostat.

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