oxide is a white solid and was recrystallized from $Cl_4C/MeOH$ (90:10): mp 180–186 °C; NMR δ (Cl_4C/Me_4Si) 5.3 (s, 1 H) 6.4–7.6 (m, 22 H); MS, m/e (relative intensity) 454 (23), 453 (13), 252 (15), 216 (100), 201 (51), 124 (23), 77 (52), 51 (15).

Photostimulated Reaction of Diphenylphosphide Ion with 9-Bromotriptycene in the Presence of Inhibitors. The procedure was similar to that for the previous reactions, except that in expt 4 (Table I) 20 mol % of *p*-dinitrobenzene was added and in expt 3 (Table I) 10 mol % of di-*tert*-butyl nitroxide was added.

Photostimulated Reaction of 9-Bromotriptycene with Diphenylarsenide ion. The procedure was similar to that for the previous reaction, except that the irradiation time was 60 min.

The residue of the ether extract was column chromatographed on silica gel and eluted with petroleum ether.

The product isolated was 9-triptycyldiphenylarsine, recrystallized from benzene: mp 242–246 °C; NMR (Cl_4C/Me_4Si) 5.4 (s, 1 H), 6.5–7.6 (m, 22 H); MS, m/e (relative intensity) 483 (10), 482 (80), 320 (28), 253.4 (100), 227 (43), 152 (20), 77 (5), 51 (5).

Photostimulated Reaction of 9,10-Dibromotriptycene with Diphenylphosphide Ion. The procedure was similar to that for the previous reaction. The reaction mixture was extracted as was described. The ethereal extract was oxidized with hydrogen peroxide, and the 9,10-bis(diphenylphosphinyl)triptycene produced was recrystallized from chloroform/petroleum ether (50:50): mp 325 °C; NMR δ 7–7.4 (m); MS, m/e (relative intensity) 655 (35), 454 (11), 453 (45), 252 (42), 202 (16), 201 (100), 185 (14).

Acknowledgment. Sara M. Palacios gratefully acknowledges receipt of a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina. INFIQC is jointly sponsored by the Consejo Nacional de Investigaciones Científicas y Técnicas and the Universidad Nacional de Córdoba. This work is partially supported by the SUBCYT. Professor James F. Wolfe is thanked for the gift of a sample of di-*tert*-butyl nitroxide.

Registry No. **1**, 768-90-1; **2**, 34676-89-6; **3**, 14971-22-3; **4** (M = As), 83135-27-7; **8**, 768-93-4; **10**, 15364-55-3; **11**, 92012-49-2; **13**, 92012-53-8; **15**, 92012-50-5; **16**, 795-42-6; **18**, 92012-51-6; 1-AdCl, 935-56-8; Na_2Te, 12034-41-2; Na_2Se, 1313-85-5; NH_2^-, 17655-31-1; $CH_3C(O)CH_2^-$, 71695-00-6; 1-AdTeTe-1-Ad, 92012-47-0; 1-AdSeSe-1-Ad, 92012-48-1; $CH_3C(O)\bar{C}HC(O)CH_2^-$, 54210-56-9; $O(CH_2CH_2)_2NC(O)CH_2^-$, 92012-52-7; $NCCH_2^-$, 21438-99-3; 2-picolyl anion, 18860-16-7.

Radical Intermediates in the Photoreaction between Disulfides and Acylsilanes

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Received May 14, 1984

Photolysis of cyclopropane solutions of a number of disulfides RSSR (R = Me, *n*-Bu, CF_3) in the presence of acylsilanes $R'C(O)SiMe_3$ led to radicals of general structure $R'\dot{C}(OSiMe_3)SR$ which have been detected by EPR spectroscopy. The structure of the observed paramagnetic species has been ascertained by producing $Ph\dot{C}(OSiMe_3)SMe$ via an alternative route, i.e., by reacting $Me_3\dot{S}i$ radicals with the thio ester PhC(O)SMe. The lifetime of these radicals varies considerably with the bulkiness of the substituents in the neighborhood of the radical center. The decay rates as a function of temperature, together with the corresponding activation parameters, have been determined for the hindered $t\text{-}Bu\dot{C}(OSiMe_3)SCF_3$ radical; it is suggested that the decay process involves an equilibrium with a dimeric species. A number of possible reaction sequences leading to these radicals have been examined, although the actual mechanism is as yet unclear.

Ethylenic and aromatic carbon–carbon double bonds readily undergo addition by a variety of organic and organometallic free radicals, including silicon, germanium, tin, phosphorus, and sulfur centered species;[1–3] in many cases the resulting spin adducts have been observed by EPR spectroscopy.[4–9] Group IVB organometallic and phosphorus centered radicals also add to the carbonylic and thiocarbonylic functions by attacking the more electronegative oxygen and sulfur atoms.[7,10–16] On the other hand, although detection of the radical derived from addition of MeS to thiocamphor has been reported[17] and formation of diadamant-2-yl disulfide upon photoreaction of adamantanethione with the corresponding thiol has been rationalized with the attack to C═S by adamantane-2-thiyl radical,[18] addition to thiocarbonyl compounds does not

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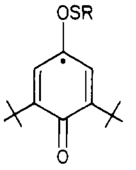
Table I. EPR Parameters (Splittings in Gauss) of Radicals 6 Obtained in Cyclopropane at 170 K by Photolysis of R′C(O)SiMe$_3$ (R′ = Ph, Me, *t*-Bu) in the Presence of RSSR (R = Me, *n*-Bu, CF$_3$). For Comparison the Splittings of Radicals 5 Obtained by Addition of Me$_3\dot{S}$i (from *t*-BuOOBu-*t* and Me$_3$SiH) to R′C(O)SiMe$_3$ (R′ = Ph, Me) Are Also Reported

radical	R = Me	R = *n*-Bu	R = CF$_3$
Ph$\dot{C}$(OSiMe$_3$)SR (**6a**)	$a_{SMe} = 0.35$ $a_m = a_{m'} = 1.45$ $a = 4.75$ $a_{o'} = 4.35$ $a_p = 4.90$ $g = 2.00312$	$a_{SCH_2} = 0.37$ $a_m = a_{m'} = 1.5$ $a_o = a_{o'} = 4.5$ $a_p = 5.0$ $g = 2.00307$	
Me$\dot{C}$(OSiMe$_3$)SR (**6b**)	$a_{SMe} = 0.75$ $a_{Me} = 17.8$	$a_{SCH_2} = 0.25$ $a_{Me} = 18.9$	$a_{3F} = 6.0$ $a_{Me} = 19.1$ $g = 2.00326^{a}$
t-Bu$\dot{C}$(OSiMe$_3$)SR (**6c**)	single line $\Delta H_{pp} = 3$ G $g = 2.00314$		$a_{3F} = 6.1$ $a_{9H} = 0.24$ $a_{Si^{29}} = 6.1$ $g = 2.00295$
Ph$\dot{C}$(OSiMe$_3$)SiR$_3$ (**5a**)	$a_m = a_{m'} = 1.5$ $a_o = a_{o'} = 4.25$ $a_p = 5.15$		
Me$\dot{C}$(OSiMe$_3$)SiR$_3$ (**5b**)	$a_{9H} = 0.3$ $a_{Me} = 22.1$		

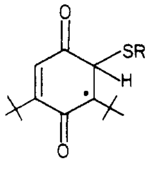
[a] A second radical is also observed, see ref 31.

appear to be a general feature of the reactivity of thiyl radicals. Even more unusual seems to be the addition of thiyl radicals to carbonyl derivatives. To the best of our knowledge only once has the EPR detection of radical adducts, apparently due to addition of thiyls to carbonyl compounds, been reported,[16] the species observed by reacting 2,6-di-*tert*-butyl-*p*-benzoquinone (DTBQ) with Me$\dot{S}$, Ph$\dot{S}$, and *t*-Bu$\dot{S}$ having been assigned structures **1a**, **1b** and **1c**, respectively.

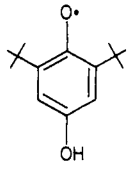


1a, R=Me
1b, R=Ph
1c, R=*t*-Bu

In the course of the present investigation of the photoreactions of acylsilanes with disulfides we also reexamined the behavior of DTBQ with a number of disulfides and obtained different results. Irradiation, within the EPR cavity, of solutions of DTBQ and CH$_3$SSCH$_3$ or CF$_3$SSCF$_3$ at temperatures lower than 250 K, led to the simultaneous formation of two radical species, which, on the basis of their EPR parameters, have been identified as the adducts resulting from addition of CH$_3\dot{S}$ or CF$_3\dot{S}$ to the quinone ring (**2a**, **2b**) and as the phenoxyl radical **3**, whose $a_H{}^{OH}$ splitting exhibits, as expected, a marked temperature dependence.



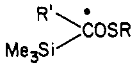
2a, R=CH$_3$ (a_H=12 G, a_{9H} =0.3 G)
2b, R=CF$_3$ (a_H=13.1 G)



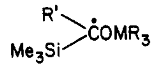
3, a_{2H}=0.91 G
$a_H{}^{OH}$=1.8 G (173 K)
$a_H{}^{OH}$=0.9 G (303 K)

Above 250 K radicals **2** disappear whereas **3** is observable up to 303 K. We have not been able to obtain evidences of the formation of other adducts containing the SMe or the SCF$_3$ fragments, while when diphenyl disulfide was used not even radicals **2** and **3** were detected. Only with *t*-Bu$\dot{S}$ (from *t*-BuSSBu-*t*) an EPR signal (a_{2H} = 0.95 G, g = 2.0043) consistent, in principle, with structure **1** was observed. However the absence of splittings other than from ring protons makes its identification questionable. In our opinion unambiguous evidence of radicals resulting from addition of thiyls to carbonyls is still lacking.

It is therefore quite interesting that photolysis of acylsilanes (R′C(O)SiMe$_3$) in the presence of disulfides (RSSR) does lead to radical species which can be detected by EPR. All these radicals contain the RS moiety, as indicated by the variation of the spectral multiplicity with the nature of the disulfide employed: a 1:3:3:1 quartet due to methyl with MeSSMe, a 1:2:1 triplet due to CH$_2$ with *n*-BuSSBu-*n*, and a wider 1:3:3:1 CF$_3$ quartet, due to a much larger fluorine splitting, with CF$_3$SSCF$_3$ (see radicals **6b**, R = Me, *n*-Bu, and CF$_3$, respectively, in Table I). In principle one could assume that these radicals have a structure (**4**) similar to that (**5**) of the intermediates resulting from addition of group IVB radicals to the same substrate (e.g., radicals **5a** and **5b** in Table I).



4



5, M=Si, Ge, Sn

Indeed the spectral parameters of such sulfur-containing radicals would be reasonably consistent with structure **4**, and one might thus advance the hypothesis that they are formed according to the following reaction sequence:

$$\mathrm{RSSR} \xrightarrow{h\nu} 2\mathrm{R\dot{S}} \qquad (1)$$

$$\mathrm{R\dot{S}} + \mathrm{R'C(O)SiMe_3} \rightarrow \mathrm{R'\dot{C}(OSR)SiMe_3} \qquad (2)$$

However, in the light of the aforementioned arguments on the reactivity of thiyl radicals toward carbonyl compounds, the above sequence appears somewhat unlikely and we believe that these radicals must be assigned a different structure. Actually their spectral parameters, in particular the g factors and the fluorine splittings in the SCF$_3$ adducts, are also consistent with those reported in the literature[19] for the spin adducts obtained by addition of $\dot{C}$F$_3$ and Me$_3\dot{C}$ radicals to some *O*-alkyl thio esters,

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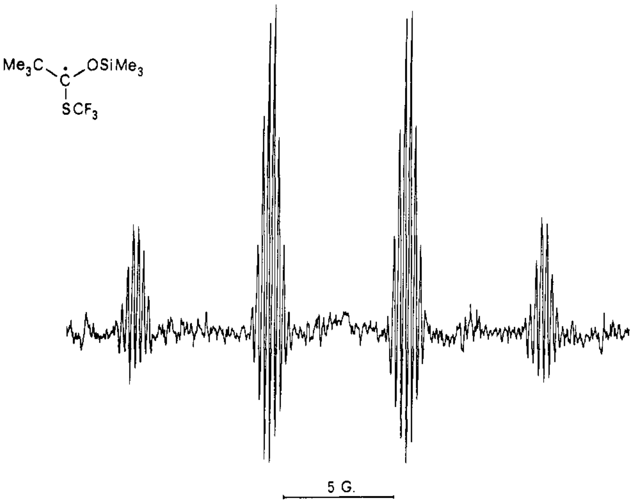
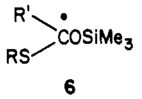


Figure 1. EPR spectrum (2nd derivative) of the radical t-Bu$\dot{C}$(OSiMe$_3$)SCF$_3$ (**6c**, R = CF$_3$) obtained by photolysis of CF$_3$SSCF$_3$ in a cyclopropane solution of t-BuC(O)SiMe at 260 K. On increasing the gain by a factor of 10, the Si^{29} satellites were observed.

namely, $CF_3S\dot{C}HOEt$ (a_F = 4.3 G, g = 2.0029), $CF_3S\dot{C}(Me)OEt$ (a_F = 6.8 G, g = 2.0031), $CF_3S\dot{C}HOBu$-t (a_F = 4.6 g, g = 2.0033), and t-$BuS\dot{C}HOEt$ (g = 2.0033). This suggests that the radicals we observed in the photoreaction of acylsilanes with disulfides may alternatively be assigned the general structure **6** rather than **4**.



6

If this is correct, then these species should also be obtainable by addition of trimethylsilyl radicals ($Me_3\dot{S}i$) to S-alkyl thio esters R′C(O)SR. We actually found that the EPR spectrum of the radical obtained by adding trimethylsilyl radical ($Me_3\dot{S}i$ produced by photolysis of t-BuOOBu-t with Me$_3$SiH) to the S-methyl thio ester of thiobenzoic acid (PhC(O)SMe), i.e., $Ph\dot{C}(OSiMe_3)SMe$, is superimposable with that obtained when reacting benzoylsilane (PhC(O)SiMe$_3$) with methylthiyl radical ($Me\dot{S}$). It would, therefore, appear that the spin adducts observed in the photoreaction of acetyl- and aroylsilanes with disulfides may be conceivably represented by structures **6** and also that thiyl radicals do not attack, in the present case, the carbonylic function. From the intensity of the EPR spectra it would however appear that radicals **6** are more efficiently generated by reacting disulfides with acylsilanes.

Radicals of general structure **6** turned out to be not-persistent species which decay with rates close to the diffusion-controlled limit once the UV irradiation is interrupted; the only exception is provided by the MeS and CF$_3$S adducts of t-Bu(CO)SiMe$_3$ (**6c**, R = Me and CF$_3$), possibly because of steric crowding in the surrounding of the radical center. The decay of t-Bu$\dot{C}$(OSiMe$_3$)SCF$_3$ (**6c**, R = CF$_3$), whose EPR spectrum is shown in Figure 1 was monitored at different temperatures. The process obeys a first-order kinetic law, but the radical concentration, under conditons of steady photolysis, depends upon the square root of the light intensity, thus indicating that we are not dealing with a simple unimolecular decay.[20-22] The kinetic process can be conceivably represented according to eq 3, where $\dot{X}$ = t-Bu$\dot{C}$(OSiMe$_3$)SCF$_3$. If the concentration of the dimer is larger than that of the radicals i.e., if $2k_1[\dot{X}]/k_{-1} > 1$, what is actually monitored is the first-order change in the dimer concentration.[20-22] Accordingly, the rate constants measured in this situation (k_{exp}) are not those corresponding to the radical decay (k_2) but are related to it via the relationship $k_{exp} = k_2k_1/2k_1$. A further indication that we are not dealing with a simple unimolecular process is provided by the anomalous value found for the frequency factor in the Arrhenius equation:

$$X_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\dot{X} \xrightarrow{k_2} \text{diamagnetic products} \qquad (3)$$

$$\log (k_{exp}/s^{-1}) = [(4.68 \pm 0.1) - (4.7 \pm 0.1)]/\vartheta$$

where ϑ = 2.3RT, kcal mol^{-1}. The very small values (4.68 ± 0.1) obtained for log A is indeed typical of decays involving equilibria with dimeric species.[20,21]

Although there is little doubt as to the fact that the radicals we observed can be correctly described by general structure **6**, the mechanism leading to their formation is as yet not clarified. Acyl- and aroylsilanes have been reported to display a peculiar photochemical behavior which varies with the nature of the reaction medium. Thus in halogenated solvents they undergo cleavage of the R′C(O)–SiMe$_3$ bond leading to silyl as well as to acyl or aroyl radicals,[23] whereas in alcoholic solutions and in presence of pyridine they give insertion reactions typical of carbenes.[24] In principle, three different reaction sequences, all leading to the observed radicals, can be written (eq 4–6).

$$R'C(O)SiMe_3 \xrightarrow{h\nu} R'C(O)SiMe_3{}^* \rightarrow R'\dot{C}O + \dot{S}iMe_3 \qquad (4)$$

$$RSSR \xrightarrow{h\nu} 2R\dot{S}$$

$$R'\dot{C}O + RSSR \rightarrow R'C(O)SR + R\dot{S}$$

$$R'\dot{C}O + RS \rightarrow R'C(O)SR$$

$$R'C(O)SR + \dot{S}iMe_3 \rightarrow \underset{\mathbf{6}}{R'\dot{C}(OSiMe_3)SR}$$

$$RSSR \xrightarrow{h\nu} 2R\dot{S} \qquad (5)$$

$$R'C(O)SiMe_3 + R\dot{S} \rightarrow R'C(O)SR + \dot{S}iMe_3$$

$$R'C(O)SR + \dot{S}iMe_3 \rightarrow \underset{\mathbf{6}}{R'\dot{C}(OSiMe_3)SR}$$

$$R'C(O)SiMe_3 \xrightarrow{h\nu} R'C(O)SiMe_3{}^* \rightarrow R'\ddot{C}OSiMe_3 \qquad (6)$$

$$R'\ddot{C}OSiMe_3 + RSSR \rightarrow R\dot{S} + \underset{\mathbf{6}}{R'\dot{C}(OSiMe_3)SR}$$

In a number of experiments involving PhC(O)SiMe$_3$, we detected an EPR signal attributable to benzoyl radical (a_{2H} = 1.18 G, g = 2.0006) whose presence would be consistent with the reaction sequence 4. Moreover, detection of $Ar\dot{C}(OSiAr_3)SiAr_3$ upon photolysis of solutions containing solely ArC(O)SiAr$_3$ has been reported:[25] a feature that is again in agreement with the homolytic cleavage of the PhC(O)–SiMe$_3$ bond. However, both reaction sequences 4 and 5 involve as a key step the addition of $Me_3\dot{S}i$ radicals

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to the thio ester R′C(O)SMe which is assumed to be formed in the photolytic process, while we have already mentioned that the direct addition of silyl radicals to this substrate is rather difficult and leads to weak EPR spectra.[26] Furthermore, reaction sequences 4 and 5 would take some time to build up a significant concentration of the byproduct R′C(O)SMe, hence one should expect that the EPR signal of radical **6** required an elapse of time to appear. This is contrary to the observation that the spectra are detectable almost immediately after irradiation of the samples begins.

It is also worthwhile noting that attempts of generating radical **6a** (R = Me) in the presence of *trans*-piperylene were unsuccessful; this, however, is far from constituting evidence of the occurrence of reaction sequence 6 as *trans*-piperylene, known[27] to be an effective "carbene trap", can also act as a scavenger for both silyl and thiyl radicals.

A choice between the different reaction sequences would thus be only speculative at this stage and it appears advisable to delay it until additional and more complete experimental data become available.

Experimental Section

The compounds used in the present work were commercially available, with the exception of benzoyltrimethylsilane,[28] acetyltrimethylsilane,[29] pivaloyltrimethylsilane,[29] and *S*-methyl thiobenzoate,[30] which were prepared according to the literature.

Samples for the EPR measurements were prepared under vacuum by the freeze-thaw technique in Suprasil quartz tubes. The spectra were run either on a Varian E-104 or on a Bruker ER-200 spectrometer equipped with a NMR gaussmeter (field calibration) and a frequency counter. A 500- or 1000-W high-pressure Hg lamp was used as UV light source.

Kinetic measurements were carried out with the rotating sector technique, and the decay curves were accumulated by means of an Aspect 2000 computer.

Acknowledgment. L.G. and L.L. thank the Ministry of Public Education (Rome) for financial assistance.

Registry No. **2a**, 92284-54-3; **2b**, 92284-55-4; **3**, 75195-55-0; **5a**, 92284-56-5; **5b**, 92284-57-6; **6a** (R = Me), 92284-58-7; **6a** (R = *n*-Bu), 92284-59-8; **6b** (R = Me), 92284-60-1; **6b** (R = *n*-Bu), 92284-61-2; **6b** (R = CF_3), 92284-62-3; **6c** (R = Me), 92284-63-4; **6c** (R = CF_3), 92284-64-5; **7**, 92284-65-6; DTBQ, 719-22-2; PhC(O)$SiMe_3$, 5908-41-8; MeC(O)$SiMe_3$, 13411-48-8; *t*-BuC(O)$SiMe_3$, 13411-49-9; MeSSMe, 624-92-0; *n*-BuSSBu-*n*, 629-45-8; CF_3SSCF_3, 372-64-5.

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[26] Addition to the C=O double bond of *S*-alkyl thio esters is actually a difficult process. For instance, we found that the radicals $Ph_3\dot{S}i$, $Ph_3\dot{G}e$, and $Ph_3\dot{S}n$ (produced by H-atom abstraction with *t*-BuOOBu-*t* from the corresponding hydrides) do not add to PhC(O)SMe to give the adducts $Ph\dot{C}(OMPh_3)SMe$ (M = Si, Ge, Sn, respectively) but rather yield adducts of structure[25] $Ph\dot{C}(OMPh_3)MPh_3$, where the SMe fragment has been replaced by MPh_3 (M = Si, Ge, Sn).

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[31] Upon prolonged irradiation a second signal becomes evident, superimposed on the original spectrum of **6b**, R = CF_3, and exhibiting couplings of the unpaired electron with two different sets of three fluorine atoms (a_{3F} = 3.0 G, a_{3F} = 4.08 G) and with a single hydrogen (a_H = 19.7 G); the *g* factor is 2.0028. We believe that this adventitious spectrum can be assigned to the radical $(CF_3S)_2\dot{C}HC(OSiR_3)SCF_3$ (**7**), where the SCF_3 group α to the radical center is responsible for the larger quartet splitting, and one of the two β-SCF_3 lies close to the nodal plane of the α-carbon and hence is characterized by a negligibly small splitting. Radical **7** may originate through a sequence of disproportionation and addition reactions undergone by the original adduct **6b**, R = CF_3.

Existence and Reactivity of Bicyclic Annulenones. 4-Phenylbicyclo[3.3.0]octa-1(5),3,6-triene-2,8-dione

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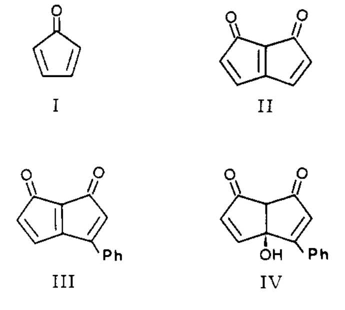
Received July 17, 1984

The elusive ketone 4-phenylbicyclo[3.3.0]octa-1(5),3,6-triene-2,8-dione has been generated from an insoluble polymeric precursor which was synthetized from chlorosulfonated macromolecular resin and 5-hydroxy-4-phenylbicyclo[3.3.0]octa-3,6-diene-2,8-dione. The liberated diketone can act as a diene but not as a dienophile in the assayed pericyclic reactions.

After studying the existence of cyclopentadienone (I) and its reactivity as a diene and dienophile,[1,2] we started the study of some related species, particularly the ones with fully unsaturated pentalenic structures as II. The presence of the second condensed ring of cyclopentadienone may remarkably affect the stability of such species and their reactivity in Diels-Alder processes. The study of such species has received no attention up to now, although partially saturated structures similar to II have shown to be very useful synthons for the synthesis of natural products and other compounds of theoretical interest.[3]

Chart I



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