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Reactions of Triplet Carbenes with Sulfides and Disulfides: Ylide vs. Radical Formation[1]

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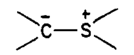
Abstract: The reactions between triplet diphenylcarbene and fluorenylidene with a variety of sulfides and disulfides were investigated with use of electron paramagnetic resonance (EPR) spectroscopy, laser flash photolysis, and product studies. Diphenylcarbene reacted with these substrates by a radical-like displacement mechanism. Rate constants were ca. 10^6 M^{-1} s^{-1}, and the resulting thio-substituted diphenylmethyl radicals were identified by their EPR and optical spectra. By contrast, the analogous reactions of fluorenylidene had rate constants of 10^8–10^9 M^{-1} s^{-1} and proceeded by an ylide mechanism. Product studies were consistent with these results but were not sufficient in themselves to reveal these mechanistic differences.

The chemistry of sulfur ylides, I,[3] has been the subject of extensive investigation, largely because of the synthetic challenge of making stable molecules of this kind and because of the interesting rearrangements which they often undergo.[4,5]



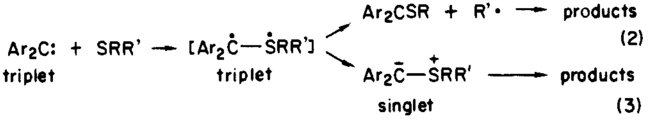
I

The most common method for ylide generation involves the removal of a proton from a sulfonium salt.[5,6] However, a more direct but less commonly employed method makes use of the reaction between a carbene and a sulfide, eq 1.[5,7]

$$R_2C: + R'_2S \rightarrow \mathrm{I} \tag{1}$$

The carbene approach to ylide formation has been extensively explored by Ando and his co-workers,[5] who generally used carbenes with strongly electron withdrawing substituents. These had the effect of stabilizing the resulting ylides, so that they were often isolable and could be thoroughly characterized. In addition, the carbenes themselves had *singlet* ground states, so that reaction with sulfides led to directly to ground-state ylides, without any requirement for spin inversion. The reactions between carbenes with *triplet* ground states and sulfur-containing compounds have, by contrast, received little attention.[7] Obviously, the fact that triplet carbenes generally do not contain electron withdrawing groups and their spin multiplicities are factors which militate against facile ylide formation.[8]

One can envisage two possible pathways for the reactions between triplet carbenes and substrates containing divalent sulfur (eq 2 and 3). Reaction 2 is akin to the familiar homolytic substitution, S_H2, process. This would lead initially to a triplet pair of radicals whose immediate recombination would be spin forbidden. The radical pairs would therefore diffuse apart and would ultimately react with other radicals in the system to give the final products.[9]



R = alkyl, Ph
R' = alkyl, Ph, thioalkyl

Reaction 3 represents a process in which triplet carbene and sulfur compound combine and during the course of this combination access the singlet manifold to form an ylide in its singlet state. This kind of mechanistic proposal has been the subject of some controversy because the reaction is formally spin forbidden.[8] Nevertheless, it has been advanced to account for the anomalous reactions of triplet diphenylcarbene with alcohols[10] and amines[11] and for the reaction of triplet fluorenylidene with thioketones.[12]

An alternative description of singlet ylide formation is that the triplet carbene undergoes intersystem crossing to its singlet state which, in a second and discrete step, reacts with the substrate of interest. However, this description has not always survived the test of kinetic scrutiny.[8,10–12]

Irrespective of the precise mechanistic details, there exists the broad distinction between the possibilities of ylide and radical-like chemistry in the reactions between triplet carbenes and sulfur-containing substrates. Interestingly, product studies (vide infra) do not provide a means of differentiating between the two pathways since both may lead to similar compounds.

In an attempt to bring new evidence to bear on the triplet carbene chemistry, we have investigated the reactions of diphenylcarbene and fluorenylidene with sulfides and disulfides. In addition to product studies, laser flash photolysis was used to search for ylide formation (eq 3) while EPR spectroscopy was used to probe the homolytic pathway (eq 2). The results provide a fairly comprehensive picture of the relative importance of the two possible mechanism.

Experimental Section

Materials. Diphenyldiazomethane[13] and diazofluorene[14] were synthesized following literature methods. The former was purified by sublimation at room temperature and the latter by recrystallization from hexane. Acetonitrile (spectroscopic grade) was distilled from calcium hydride. Benzene was washed with concentrated sulfuric acid and then with water. It was dried over magnesium sulfate and was finally distilled from calcium hydride. Diphenyl disulfide was recrystallized from methanol. Di-*tert*-butyl disulfide was fractionally distilled to remove

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[1] National Research Council of Canada. Issued as NRCC No. 25529.

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[3] A biradical structure or one in which the dipole is the opposite sense may also be valid descriptions.

[4] Trost, B. M.; Melvin, L. S., Jr. *Sulfur Ylides*; Academic Press: New York, 1975.

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[7] Ando, W.; Yamada, J.; Matsuzaki, E.; Migita, T. *J. Org. Chem.* **1972**, *37*, 3791.

[8] For a review of spin multiplicity effects on carbene reactions see; Griller, D.; Nazran, A. S.; Scaiano, J. C. *Tetrahedron* **1985**, *41*, 1525.

[9] A small proportion of radicals would undergo more complex behavior related to the CIDNP phenomenon.

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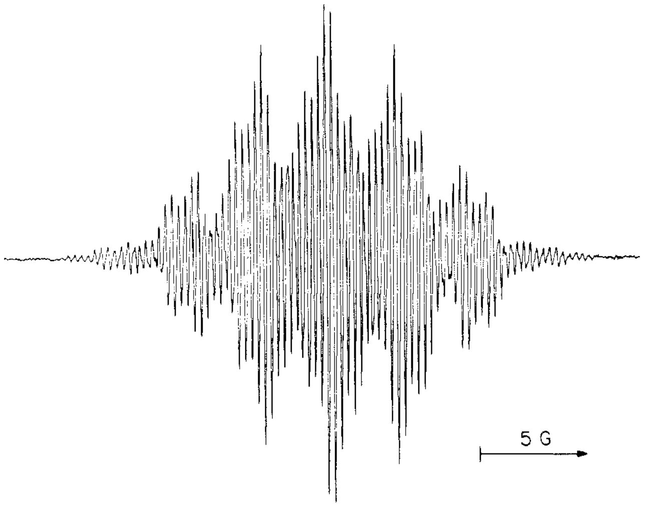

Figure 1. EPR spectrum of $Ph_2\dot{C}SPh$ at 298 K obtained by photolysis of a benzene solution containing diphenyldiazomethane and diphenyl disulfide.

impurities of the trisulfide and was found to be >99% pure (g.c. analysis). Other materials were commercially available in high purity and were used as received.

Product Studies. Product distributions were investigated for the reactions of the two diazo compounds with all of the sulfur-containing compounds which were used in this work. In a typical experiment, the diazo compound (0.025 M) was dissolved in a benzene solution of sulfide or disulfide (0.2 M). The mixture was thoroughly purged with nitrogen and was then photolyzed with a tungsten lamp until the characteristic pink color of the diazo compound had disappeared. The solutions were then concentrated to at least half of their original volume by distillation of the solvent at reduced pressure. The product distributions were characterized by GC/MS (Hewlett Packard 5995) and were quantified by GC (Hewlett Packard 5890 A) with use of 10 m, 0.2 mm diameter, cross-linked methyl silicon columns.

Apparatus. The laser flash photolysis system has been described in detail elsewhere.[15] Briefly, samples purged with nitrogen were photolyzed at 308 nm with an excimer laser (pulse width ca. 4 ns, up to 80 mJ/pulse) or at 337 nm with a nitrogen laser (pulse width ca. 8 ns, up to 10 mJ/pulse). The detection system consisted of a monitoring lamp, monochromator, and photomultiplier tube. The output of the photomultiplier was fed to a transient digitizer, and the digitized signals were stored and averaged into a computer which was also used to analyze the data.

EPR spectra were recorded with a Varian E104 spectrometer. Radicals were generated by photolysis or thermolysis of nitrogen purged, benzene, or *tert*-butylbenzene solutions containing diphenyldiazomethane or diazofluorene (ca. 0.2–0.3 M) and an appropriate sulfide or disulfide (ca. 0.1–0.5 M). The light source was a 1000-W high-pressure mercury arc lamp, and the light was filtered through an aqueous solution of $CoSO_4$ (0.21 M) and $NiSO_4$ (1.14 M) which removed much of the visible and most of the infrared radiation.

Results and Discussion

Do triplet carbenes react with compounds containing divalent sulfur via a radical mechanism, an ylide mechanism, or by a mixture of both? The answer to this seemingly simple question cannot be gleaned from product studies alone, since the formation of a given product is often consistent with ylide and radical mechanisms (vide infra). We therefore used EPR spectroscopy to investigate the reactions of triplet diphenylcarbene and fluorenylidene with a variety of sulfur-containing compounds, to see if radicals were actually generated in these reactions. This approach was supported by laser flash photolysis experiments, which were designed to provide information of the reaction kinetics and on the identities of the transient intermediates.

EPR Studies. Photolysis, in the cavity of an EPR spectrometer, of benzene or *tert*-butylbenzene solutions containing diphenyldiazomethane[16] and a variety of disulfides led to the formation of thio-substituted diphenylmethyl radicals (eq 2, Figure 1). Thermolysis of diphenyldiazomethane in the presence of diphenyl- or di-*tert*-butyl disulfide at 333 and 353 K, respectively, led to the same radicals as were produced by photolysis. Similarly, a seleno-substituted diphenylmethyl radical was formed when diphenyl diselenide was used as substrate.

Table I. EPR Parameters of Substituted Diphenylmethyl Radicals $Ph_2\dot{C}$–XR at 298 K

XR	g	a_o, G	a_m, G	a_p, G	a (other), G
SMe	2.0035	2.85	1.16	3.14	1.16 (CH_3)
SEt	2.0035	2.84	1.21	3.14	1.64 (CH_2), 0.29 (CH_3)
SCH_2Ph	2.0033	2.82	1.21	3.14	1.57 (CH_2)
S-*i*-Pr	2.0035	2.87	1.20	3.16	0.28 ($2CH_3$), <0.08 (CH)
S-*t*-Bu	2.0031	2.89	1.22	3.23	0.34 ($3CH_3$)
SC(O)Pr	2.0028	3.02	1.25	3.31	0.15 ($2CH_3$), 0.15 (CH)
SPh	2.0032	2.92	1.22	3.23	0.30 (5H)
a	2.0032	2.91	1.21	3.21	0.28 (3H)
b	2.0029	3.03	1.29	3.39	0.26 (1N)
SePh	2.0048	3.05	1.40	3.05	unresolved structure

[a] 3,5-Di(methylthio)phenylthiyl. [b] 1,3-Benzothiazol-2-ylthiyl.

Thio-substituted diphenylmethyl radicals were also formed by photochemical reaction of diphenyldiazomethane with several sulfides (eq 2), although the spectral intensities were much lower than those obtained with disulfides.

EPR parameters for all of the radicals produced by these methods are reported in Table I and were in excellent agreement with literature data[17] in the three cases (R = Me, Et, *t*-Bu) where comparison was possible, with the exception that for $Ph_2\dot{C}SEt$, $a^H(CH_2) = 1.64$ G provided a far better computer simulated fit to the experimental spectrum than the value of 1.22 G previously reported.[17] In general the spectra of the thio-substituted diphenylmethyl radicals were quite intense, suggesting that these radicals were relatively persistent.

As further confirmation of the assignments, several of the radicals investigated were generated by other routes. For example, $Ph_2\dot{C}$–SPh was obtained by the route shown in eq 4 and 5; $Ph_2\dot{C}$–S-*t*-Bu was obtained by addition of *tert*-butyl to thiobenzophenone (eq 6 and 7).

$$Ph_2CO \xrightarrow{h\nu} Ph_2CO^* \tag{4}$$

$$Ph_2CO^* + Ph_2CHSPh \rightarrow Ph_2\dot{C}OH + Ph_2\dot{C}SPh \tag{5}$$

This method proved to be unsatisfactory for the isopropyl analogue since *i*-Pr$\dot{C}$O was scavenged by the thioketone and the resulting spectrum of $Ph_2\dot{C}$–SC(O)-*i*-Pr

$$(t\text{-Bu})_2CO \rightarrow 2\,t\text{-Bu}\cdot + CO \tag{6}$$

$$t\text{-Bu}\cdot + Ph_2C{=}S \rightarrow Ph_2\dot{C}\text{–S-}t\text{-Bu} \tag{7}$$

interfered with that of the desired radical.[2] However, the latter was successfully generated by the method described in eq 8–10.

$$Re_2(CO)_{10} \xrightarrow{h\nu} 2\dot{R}e(CO)_5 \tag{8}$$

$$\dot{R}e(CO)_5 + i\text{-PrBr} \rightarrow Re(CO)_5Br + i\text{-Pr}\cdot \tag{9}$$

$$i\text{-Pr}\cdot + Ph_2C{=}S \rightarrow Ph_2\dot{C}\text{-SPr-}i \tag{10}$$

In all cases generation of thio-substituted diphenylmethyl radicals by independent routes confirmed the original assignments.

The EPR results immediately demonstrate that the reactions between diphenylcarbene and a variety of sulfides and disulfides

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(15) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

(16) Direct photolysis of diphenyldiazomethane leads initially to the singlet state of the carbene. However, intersystem crossing to the triplet ground state is a very rapid process which occurs in ca. 0.2 ns, see: Sitzmann, E. V.; Langan, J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1984**, *106*, 1868.

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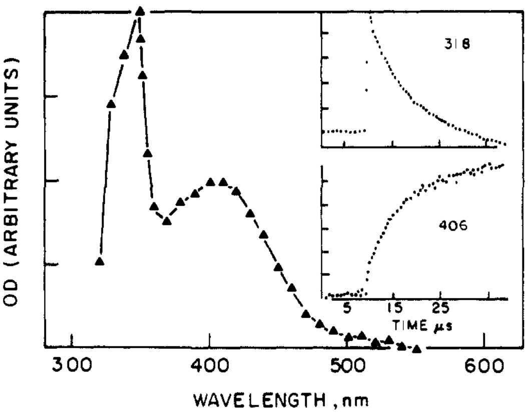
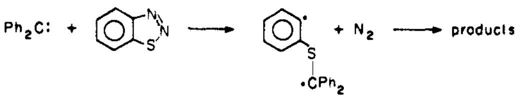


Figure 2. Transient absorption spectrum of $Ph_2\dot{C}SCH_3$ obtained by laser flash photolysis of diphenyldiazomethane in the presence of dimethyl disulfide. Inset: Decay of signal due to triplet Ph_2C: at 318 nm; concurrent growth of signal at 406 nm due to $Ph_2\dot{C}SCH_3$.

proceed partially or totally by a radical-like mechanism (eq 2). So far as we are aware, the only other instance where unequivocal evidence of this kind has been advanced was in the reaction of diphenylcarbene with 1,2,3-benzothiadiazole (eq 11).[18]



(11)

Similar experiments with diazofluorene did not give rise to any detectable EPR spectra. This was unlikely to have been due to the spectroscopic properties of 9-fluorenyl radicals since they show no particularly unusual properties when generated by other routes.[19] Moreover, even if attack at sulfur were unusually slow for this carbene, the 9-fluorenyl radical should have been detected since triplet fluorenylidene is known to be a particularly powerful hydrogen abstracting reagent[20] and would have attacked C–H bonds in the substrates or solvent. The absence of spectra suggest that an ylide mechanism (eq 3) may be dominant for fluorenylidene. To probe this possibility, we used laser flash photolysis to investigate the reactions of fluorenylidene and diphenylcarbene in an attempt to detect sulfur ylides and free radicals via their optical absorption spectra.

Laser Flash Photolysis. Laser flash photolysis (308 or 337 nm) of diphenyldiazomethane (10^{-3}–10^{-5} M) in benzene gave the optical absorption spectrum of triplet diphenylcarbene[21-23] (λ_{max} = 314 nm) within the time resolution (10 ns) of the instrument.[16] Under these conditions, the carbene had a lifetime of ca. 10 μs. Addition of sulfides or disulfides led to a more rapid decay of the triplet carbene and to the concurrent growth of new transients all of which had similar absorption spectra. These had sharp maxima at ca. 345 nm with broader and weaker absorptions at 390–450 nm (Figure 2). The spectra were therefore similar to that of diphenylmethyl itself[23] with the exception that the longer wavelength bands were more intense.

The bands detected in the longer wavelength range were not due to additional transients, since measurements of the lifetimes for decay were the same at all wavelengths. We therefore presume that the spectra were indeed due to diphenylmethyl radicals (eq 2) and that the relative strength of the longer wavelength bands was due to the fact that they were thio-substituted. To confirm this hypothesis, we generated a benzylic radical with a thio-substituent by photolyzing di-*tert*-butyl peroxide in the presence of dibenzyl sulfide (eq 12 and 13). As expected, the absorption spectrum of the benzylic radical[24] had an additional broad band with λ_{max} = 490 nm.

Table II. Rate Constants, k_t, for the Reactions of Triplet Diphenylcarbene with Sulfides and Disulfides at 298 K in Benzene as Solvent[a]

substrate	λ_{max} ($Ph_2\dot{C}SR$)	k_t, M^{-1} s^{-1}
MeSMe	345, 375	$(4.62 \pm 0.28) \times 10^6$
PhSPh	345, 425	$(1.66 \pm 0.48) \times 10^6$
t-BuSCH$_3$	348, 410	$(3.48 \pm 0.20) \times 10^5$
MeSSMe[b]	348, 406	$(6.81 \pm 1.08) \times 10^6$
MeSSMe	348, 406	$(7.27 \pm 0.50) \times 10^6$
EtSSEt	345, 420	$(6.71 \pm 1.22) \times 10^6$
i-PrSS-*i*-Pr	347, 427	$(2.92 \pm 0.14) \times 10^6$
t-BuSS-*t*-Bu[b]	343, 386	$(2.07 \pm 0.10) \times 10^6$
t-BuSS-*t*-Bu	343, 386	$(4.18 \pm 0.62) \times 10^6$

[a] Using 337-nm excitation. [b] Using 308-nm excitation.

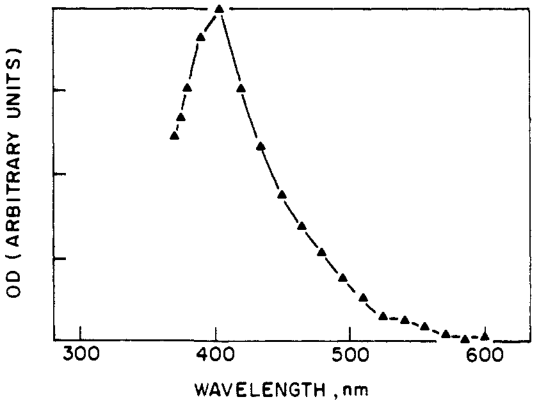


Figure 3. Transient absorption spectrum of Fl^--S^+(*t*-Bu)S-*t*-Bu obtained by laser flash photolysis of diazofluorene in the presence of di-*tert*-butyl disulfide.

$$t\text{-BuO–O-}t\text{-Bu} \xrightarrow{h\nu} 2\,t\text{-BuO}\cdot \qquad (12)$$

$$t\text{-BuO}\cdot + (PhCH_2)_2S \rightarrow t\text{-BuOH} + Ph\dot{C}HSCH_2Ph \qquad (13)$$

Rate constants for the reactions of triplet diphenylcarbene with the substrates in question were measured by monitoring the pseudo-first-order decay of the carbene at 314 nm and/or those for the growth of the radicals at ca. 345 nm. These observed rate constants, k_{obsd}, were related to that of interest, k_2, through the equation

$$k_{obsd} = k_0 + k_2[\text{substrate}] \qquad (14)$$

where k_0 is the rate constant for the decay of the carbene in the absence of the sulfur containing compounds. The values of k_2, thus obtained, are given in Table II.

Rate constants for the reactions of diphenylcarbene with sulfides and disulfides showed little variation with the structures of the substrates and were all in the range 2–8 × 10^6 M^{-1} s^{-1}. It is therefore possible that the rate-limiting step was common to all substrates and was coordination of the carbene to sulfur.

The laser flash photolysis results obtained for the reactions of fluorenylidene with sulfur-containing compounds were quite different from those for diphenylcarbene. Photolysis of diazofluorene in acetonitrile solvent gave rise to the absorption spectrum of triplet fluorenylidene[20] (λ_{max} = 470 nm) which had a lifetime of ca. 22 ns. In the absence of sulfur-containing compounds, the carbene decayed by two pathways: first, by reaction with the solvent in a hydrogen abstraction mechanism which gave rise to the absorption spectrum of the 9-fluorenyl radical (λ_{max} = 500 nm); and second, by combination with the solvent to give the nitrile ylide (λ_{max} = 400 nm) (eq 15 and 16).

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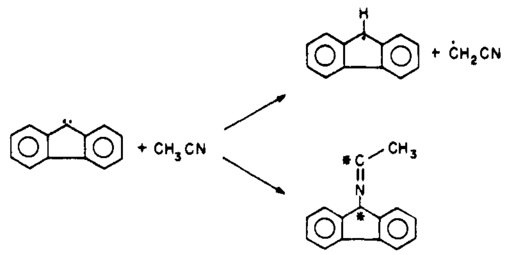


(15)

(16)

Addition of sulfur-containing compounds led to the growth of new transients with λ_{max} = 350–450 nm (Figure 3). Rate constants for the formation of these transients were analyzed with use of eq 14 and are reported in Table III. In all instances plots obtained by measuring the growth of the transients at ca. 400 nm gave values of k_0 which were within experimental error of those reported previously.[20] Since k_0 represents the lifetime of triplet fluorenylidene in acetonitrile, one can safely assume that the triplet carbene was indeed the precursor of the new transients and that the measured rate constants accurately describe the reactions of the carbene with the sulfur compounds employed.

Similar experiments were carried out with benzene as solvent. Again, in the presence of sulfur compounds, intense transient absorptions were detected between 350 and 400 nm. However, accurate kinetic analysis was not possible because of the particularly short lifetime of the carbene in this solvent. At concentrations of substrate which gave good signals due to the 400-nm transients, the lifetimes measured at this wavelength were similar to the response of the instrument.

By contrast with the reactions of diphenylcarbene, those of fluorenylidene with sulfur compounds almost certainly do not give rise to radical intermediates as major products. The 9-fluorenyl radical and its substituted analogues have absorption spectra at 500 nm consisting of two very sharp bands (width ca. 10 nm)[20] which are very similar to those of the triplet carbene. The spectra obtained by reaction of triplet fluorenylidene with sulfur-containing compounds are quite different, not only in terms of their absorption maxima (ca. 400 nm) but also in their spectral widths (50–100 nm). In fact, they are typical of the spectra of singlet state ylides which have been detected in the reactions of fluorenylidene with nitriles,[20] ketones,[25] oxygen, and thioketones.[12] We therefore conclude that fluorenylidene reacts rapidly with sulfur-containing compounds to give sulfur ylides in high yields (eq 3). This conclusion is quite consistent with the absence of spectra due to substituted fluorenyl radicals in the EPR experiments.

The mechanistic distinction between the reactions of diphenylcarbene and fluorenylidene with sulfur-containing compounds is typical of their respective chemistries. Triplet fluorenylidene is a highly reactive carbene and forms ylides with great rapidity.[12,20,25,26] By contrast, triplet diphenylcarbene only readily forms ylides with oxygen,[27] which is a spin-allowed process, there being a $^1/_9$th probability that the interaction of the two triplet molecules will lead directly to a singlet product.

Two mechanisms have been advanced to account for the reactions of the triplet carbenes with singlet substrates which, if they were to occur in a single step, are formally spin forbidden. The first involves an equilibrium step (eq 17) while in the second the triplet carbene combines with the substrate to give a complex

$$\underset{\text{(triplet)}}{Ar_2C:} \rightleftharpoons \underset{\text{(singlet)}}{Ar_2C:} \xrightarrow{\text{substrate}} \underset{\text{(singlet)}}{\text{ylide}} \qquad (17)$$

which undergoes intersystem crossing to the singlet manifold (eq 18). The latter mechanism evidently applies in the reactions of

$$\underset{\text{(triplet)}}{Ar_2:} + \text{substrate} \rightarrow \underset{\text{(singlet)}}{\rightarrow} \underset{\text{(singlet)}}{\text{ylide}} \qquad (18)$$

Table III. Rate Constants, k_2, for the Reactions of Triplet Fluorenylidene with Sulfides and Disulfides at 298 K

substrate	λ_{max}, nm	k_2, $M^{-1}\ s^{-1}$
MeSSMe[a]	443	$(2.0 \pm 0.1) \times 10^8$
t-BuSS-*t*-Bu[a]	404	$(4.0 \pm 0.2) \times 10^8$
PhSPh[a]	384	$(3.1 \pm 0.3) \times 10^8$
MeSSMe[b]	450	ca. 10^9
EtSSEt[b]	449	ca. 8×10^8
i-PrSS-*i*-Pr[b]	449	ca. 4×10^8
MeSMe[b]	ca. 357	ca. 10^9

[a] Acetonitrile as solvent. [b] Benzene as solvent.

Table IV. Yields of Major Products Formed in the Reactions of Diphenylcarbene with Sulfides and Disulfides at 298 K

	products, %		
substrate	II	III	other
MeSSMe	61	16	9 (IV)
EtSSEt	52	20	17 (IV)
i-PrSS-*i*-Pr	48	31	12 (IV)
t-BuSS-*t*-Bu	46	29	
MeSMe	24		44 (VII)
PhSPh	55	10	

[a] Ph_3CSPh.

fluorenylidene with thioketones.[12] The relative merits of these mechanisms are currently the subject of intensive investigation and debate.[8,10–12] Nevertheless, it is generally agreed that ylide formation, by either mechanism, should become more facile as the triplet–singlet energy gap becomes smaller and therefore that this gap must be significantly smaller for fluorenylidene than for diphenylcarbene.

Product Studies. Product studies were carried out on the reactions of fluorenylidene and diphenylcarbene with the sulfur-containing compounds used in laser flash photolysis and EPR studies.

Reaction of diphenylcarbene with disulfides gave three major products containing the carbene moiety II–IV. Their yields are given in Table IV. In general, they do not amount to 100% on

$$\underset{\text{II}}{Ph_2CHSR} \qquad \underset{\text{III}}{Ph_2C(SR)_2} \qquad \underset{\text{IV}}{Ph_2CR(\text{-}H)}$$

the basis of the starting diphenyldiazomethane. A number of minor products were detected and included benzophenone, benzophenone azine, tetraphenylethylene, and tetraphenylethane, which arise via reactions 19–23 and which were characterized by comparison with authentic samples.

$$Ph_2C: + O_2 \rightarrow Ph_2CO \qquad (19)$$

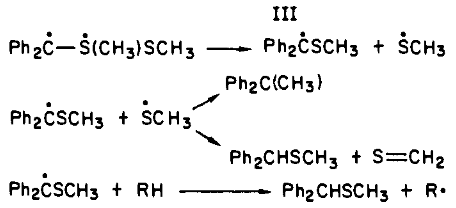
$$Ph_2C: + Ph_2CN_2 \rightarrow Ph_2C{=}N{-}N{=}CPh_2 \qquad (20)$$

$$2Ph_2C: \rightarrow Ph_2C{=}CPh_2 \qquad (21)$$

$$Ph_2C: + RH \rightarrow Ph_2\dot{C}H + R\cdot \qquad (22)$$

$$2Ph_2\dot{C}H \rightarrow Ph_2CHCHPh_2 \qquad (23)$$

The mechanisms for formation of II–IV cannot be determined from product studies alone. In principle, II and III could be formed via intramolecular reactions of the sulfonium ylides or in the reactions of free radicals. These possibilities are illustrated for dimethyl disulfide in eq 3, 24, 25 and eq 2 and 26–29, respectively.



$$Ph_2\bar{C}{-}\overset{+}{S}(CH_3)SCH_3 \rightarrow \underset{\text{II}}{Ph_2CHSCH_3} + S{=}CH_2 \qquad (24)$$

$$Ph_2\bar{C}{-}\overset{+}{S}(CH_3)SCH_3 \rightarrow \underset{\text{III}}{Ph_2C(SCH_3)_2} \qquad (25)$$

$$Ph_2\dot{C}{-}\dot{S}(CH_3)SCH_3 \longrightarrow Ph_2\dot{C}SCH_3 + \dot{S}CH_3 \qquad (26)$$

$$Ph_2\dot{C}SCH_3 + \dot{S}CH_3 \rightarrow Ph_2C(CH_3) \qquad (27)$$

$$Ph_2\dot{C}SCH_3 + \dot{S}CH_3 \rightarrow Ph_2CHSCH_3 + S{=}CH_2 \qquad (28)$$

$$Ph_2\dot{C}SCH_3 + RH \longrightarrow Ph_2CHSCH_3 + R\cdot \qquad (29)$$

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[27] Werstiuk, N. H.; Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, 2391. Casal, H. L.; Sugamori, S. E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7623.

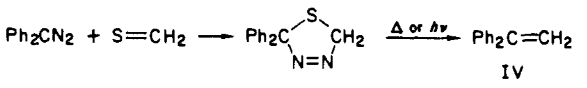
Table V. Yields of Major Products Formed in the Reactions of Fluorenylidene with Sulfides[a] and Disulfides at 298 K

	products, %		
substrate	IX	X	other
MeSSMe	69	4	14 (X)
EtSSEt	59	11	18 (X)
i-PrSS-*i*-Pr	62	5	30 (X)
t-BuSS-*t*-Bu	20	70	
MeSMe			69 (XI); 18 (XII)[b]

[a] PhSPh gave a large number of products which could not be satisfactorily analyzed. [b] XI = Fl(CH_3)SCH_3; XII = Fl(H)CH_2SCH_3.

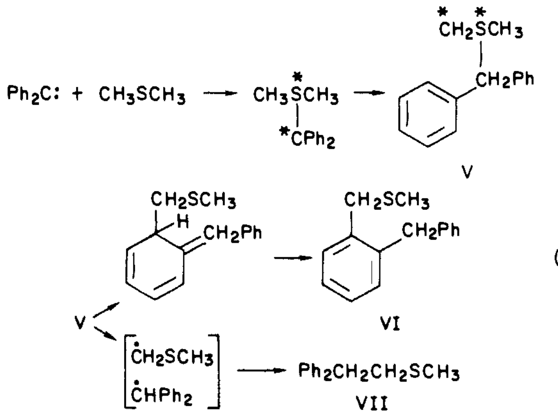
However, the EPR and laser flash photolysis experiments clearly show that the radical pathways (eq 26–29) are the routes which largely or totally give rise to the reaction products.

The formation of IV is somewhat unusual. We suggest that thioketones which are formed in reaction 28 react with the diazo compound itself to give a 1,3,4-thiadiazolines which are then thermolyzed or photolyzed to give the olefinic product. This reaction is illustrated for dimethyl disulfide in eq 30. Indeed, this approach has been used in the past for the synthesis of sterically crowded olefins.[28] The absence of this kind of product in the reaction of diphenylcarbene with di-*tert*-butyl disulfide supports the proposed mechanism.



(30)

Reaction of diphenylcarbene with dimethyl sulfide led to II and to two new products VI (3%) and VII (44%). The latter are presumably formed via the Sommelet–Hauser (eq 31 and 32) and Stevens (eq 33) mechanisms[7] (eq 31–33). As with the disulfides, the product studies do not lead to unambiguous conclusions about the reaction mechanism. Product II could have been formed via an intramolecular reaction of the sulfur ylide or by a free radical route. However, the fact that optical and EPR spectra of thiosubstituted diphenylmethyl radicals were detected implies that eq 2 must account for a significant part of the overall reaction and for the formation of II.

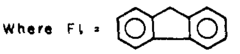


(31)
(32)
(33)

The formation of VII as the major reaction product in the sulfide case is more difficult to rationalize. It could be argued that homolytic cleavage of the S–S bond in dimethyl disulfide is more facile than C–S bond cleavage in the corresponding sulfide. This would make the carbene:substrate complex longer lived for the latter and would allow more time for rearrangement reactions to take place. However, thermochemical data barely support this hypothesis since the respective bond strengths are 75 ± 2 (CH_3S–SCH_3) and 77 ± 1.5 kcal mol^{-1} (CH_3S–CH_3).[29]

For diphenyl sulfide the products were consistent with a radical-like mechanism although it could be argued that III was formed partly via a Stevens rearrangement.

The reactions between fluorenylidene and sulfides or disulfides gave products which were not grossly dissimilar to those obtained in the reactions of diphenylcarbene (eq 34). However, the absence of EPR spectra due to free radicals and the observation of optical spectra which were consistent with ylide, rather than radical, formation suggest that the products were largely derived from intramolecular rearrangements of the ylides or, at the very least, of cage reactions of any radicals which might have arisen from their fragmentation.



Summary

Triplet diphenylcarbene reacted with sulfides and disulfides by a mechanism which is akin to the homolytic substitution (S_H2) process. Good yields of free radicals were obtained which were detected by both EPR and optical spectroscopy. For fluorenylidene, the chemistry was quite different. No EPR signals due to free radicals were detected and the optical absorption spectra were consistent with ylide rather than radical pathways. These results conform to the general observation that triplet fluorenylidene is readily able to access the singlet manifold, whereas diphenylcarbene generally displays chemistry characteristic of the triplet state.

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Registry No. II (R = Me), 15733-08-1; II (R = Et), 38793-64-5; II (R = Pr-*i*), 35906-28-6; II (R = Bu-*t*), 38793-70-3; II (R = Ph), 21122-20-3; III (R = Me), 101773-88-0; III (R = Et), 7282-09-9; III (R = Pr-*i*), 101773-89-1; III (R = Bu-*t*), 101773-90-4; III (R = Ph), 21122-23-6; VI, 35906-24-2; VII, 35906-23-1; VIII (R = Me), 59431-17-3; VIII (R = Et), 60147-53-7; VIII (R = Pr-*i*), 60147-54-8; VIII (R = Bu-*t*), 60147-55-9; IX (R = Et), 77415-27-1; IX (R = Pr-*i*), 101773-91-5; IX (R = Bu-*t*), 101773-92-6; XI, 84811-78-9; XII, 101773-93-7; •SMe, 7175-75-9; •SEt, 14836-22-7; •SCH_2Ph, 4985-63-1; •S-*i*-Pr, 25783-06-6; •S-*t*-Bu, 16812-19-4; •SC(O)Pr, 101773-86-8; •SPh, 4985-62-0; •SePh, 84065-55-4; MeSMe, 75-18-3; PhSPh, 139-66-2; *t*-$BuSCH_3$, 6163-64-0; MeSSMe, 624-92-0; EtSSEt, 110-81-6; *i*-PrSS-*i*-Pr, 4253-89-8; *t*-BuSS-*t*-Bu, 110-06-5; 3,5-di(methylthio)phenylthiyl, 101773-87-9; 1,3-benzothiazol-2-ylthiyl, 77001-64-0; diphenylcarbene, 3129-17-7; fluorenylidene, 2762-16-5; diphenyldiazomethane, 883-40-9; diazofluorene, 832-80-4.

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