

# PHOTOLYSIS OF DIAZOCYCLOPENTADIENE

## REACTIVITY OF CYCLOPENTADIENYLIDENE IN SULFIDES AND ETHERS

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**Abstract**—Photolysis of diazocyclopentadiene in the presence of dimethyl, diethyl and tetramethylene sulfides gave the corresponding sulfonium cyclopentadienylide. But the ylides from diisopropyl and di-*t*-butyl sulfides were unstable, and the reaction mixture gave the C—H and C—S insertion products of cyclopentadienylidene and olefin elimination products. Reaction of diazocyclopentadiene in ethers gave the C—H insertion and some C—O insertion products. For diethyl ether, the insertion ratio into secondary and primary C—H bonds was 19:1. For tetrahydrofuran, both  $\alpha$  and  $\beta$ -C—H insertion products were observed in ratio of 3:0. Photolysis of diazocyclopentadiene in allylic ethers gave the addition product of the carbene to the double bond, but in allylic sulfides gave both C—S insertion and addition products of the carbene.

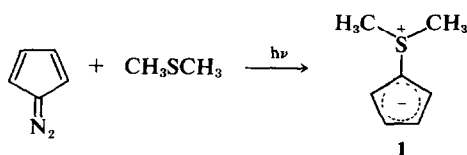
Reactions of diazocyclopentadiene (DCPD) have been extensively developed,<sup>1-8</sup> but relatively few studies have been reported in which onium cyclopentadienylide are produced.<sup>9-13</sup> Carbenes are known to react with hetero atom containing molecules to produce ylides, which generally at once undergo Stevens rearrangement, Hoffmann elimination or allylic inversion. A number of reactions of carbenes with hetero atoms have been explained by this mechanism.<sup>6</sup> No ylide had hitherto been isolated from such reactions of cyclopentadienylidene itself, although when diazotetraphenylcyclopentadiene was heated in pyridine, or in triphenyl-phosphine, -arsine, -bismuth, or in diphenyl sulfide,<sup>10-11</sup> tetraphenylcyclopentadienylides were obtained as stable forms. The photolysis of dimethyl diazomalonate in sulfur compounds gave the stable sulfonium ylides,<sup>14,15</sup> which produce thermally the Stevens or Hoffmann elimination products.<sup>16,17</sup> Most of these reactions have been proposed to proceed through the attack of the electrophilic singlet carbene on a lone pair of a S atom, and the interaction of carbene on S atom was found to be several times faster than attack on the  $\pi$ -bond of olefin.<sup>18</sup>

The study was extended to the photochemical reaction of diazocyclopentadiene, expecting that the electrophilic carbene formed by the photolysis will react with S compounds to form stable sulfonium cyclopentadienylides, and the reactivity toward a S atom is larger than that toward double bond. The results are also compared with the reaction in alkyl and allylic ethers.

### RESULTS AND DISCUSSION

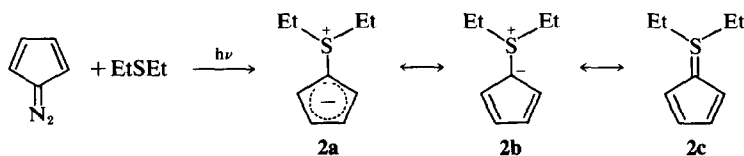
*Formation of sulfonium cyclopentadienylides in the reaction of diazocyclopentadiene with sulfides.*<sup>19</sup> Photolysis of DCPD in various alkyl sulfides was

carried out in Pyrex tubes with a high pressure mercury lamp. Nitrogen was evolved and the solution gradually become brown. The reaction could be monitored readily by withdrawing samples at intervals and noting the disappearance of the characteristic IR absorption at 2082  $\text{cm}^{-1}$ . Thus, the reaction of DCPD in dimethyl sulfide was complete in several hours, and addition of light petroleum ether to the cooled solution precipitated high yield of light purple solid, which was recrystallized from benzene to give colorless needles. This crystalline product was found to be a dimethyl sulfonium cyclopentadienylide **1** by comparison of its spectra



with those of authentic sample.<sup>20</sup> The previous preparation of compound **1** involved the reaction of dibromocyclopentene with dimethyl sulfide followed by treatment with alkali, which afforded **1** in only 15–20% yield. However, the carbene method improved the yield to 40%.

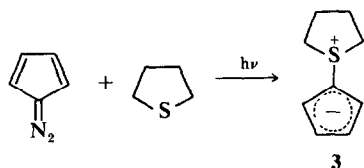
Photolysis of DCPD in other sulfides was also studied. When DCPD in diethyl sulfide was irradiated in Pyrex tubes, no precipitation could be observed in reaction mixture. After cold light petroleum ether was added to the reaction mixture and kept in refrigerator for several hours, brown crystalline of diethylsulfonium cyclopentadienylide appeared as a pure needle solid in 20% yield by decanting the solution and washing the remaining solid with light petroleum, m.p. 85–86° decomposition. (Found: C, 69.83; H, 9.30; S, 20.90. Calcd for



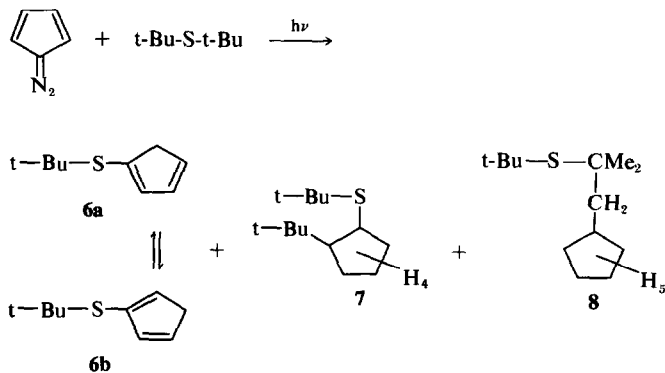
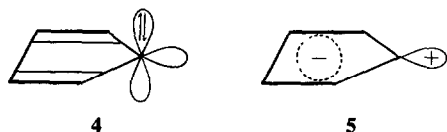
$C_5H_4S$ : C, 70.07; H, 9.15; S, 20.79%). The NMR spectrum in  $CDCl_3$  showed equivalent Et groups as triplet ( $J=7$  c/s) at 1.24 ppm and a quartet ( $J=7$  c/s) at 3.05 ppm, and four equivalent protons as singlet at 6.23 ppm. The freshly prepared crystalline diethylsulfonium cyclopentadienylide **2** slowly became brownish black on exposure to light and air, or on attempted recrystallisation. The results on cyclopentadienylide **2** indicate that the chemical shift of the ring protons is very much the same as that of other cyclopentadienylides reported.<sup>21,22</sup>

Then the ylide **2** may be represented by resonance contributing forms **2a** more than **2b** and **2c** types.

Photolysis of DCPD in tetramethylene sulfide gave tetramethylene-sulfonium cyclopentadienylide **3** in moderate yield.



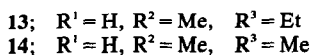
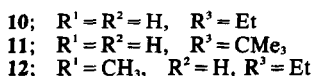
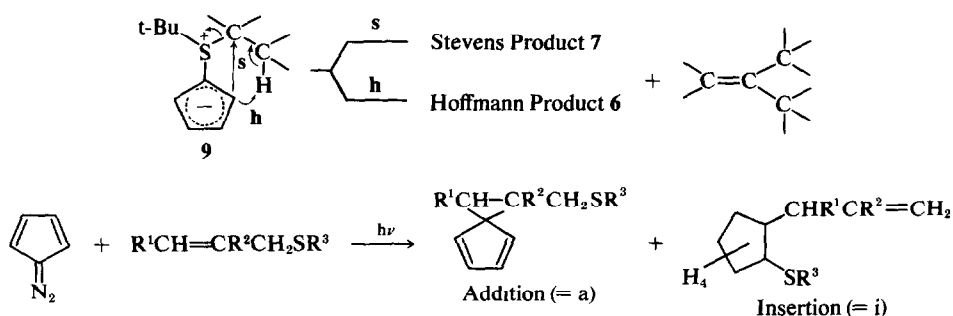
The reaction of DCPD with sulfides may be envisaged as involving a singlet state of the carbene, which may be represented as **4**; the vacant  $\sigma$ -orbital in the plane of the ring can react with the lone pair of electrons on the S atom to form a covalent bond. This singlet configuration is stabilized since the carbenic electrons interact with the remaining  $\pi$ -electrons in the ring to form an aromatic sextet as depicted alternatively by **5**.



Similar reactions were attempted in diisopropyl and di-*t*-butyl sulfides. When DCPD was irradiated in diisopropyl sulfide, the reaction mixture became black tarry solution although the IR spectrum of a withdrawing sample of the solution showed the rapid disappearance of the characteristic diazo absorption. No ylide could be isolated from the solution after addition of cold light petroleum ether, but several peaks were observed by gas chromatography.  $\alpha$ -Cyclopentadienyl diisopropyl sulfide, one of them, was found in 10% yield, but other components could not be identified. In photolysis of DCPD in di-*t*-butyl sulfide, although di-*t*-butylsulfonium cyclopentadienylide was not isolated, gas chromatographical analysis indicated the formation of three products, **6**, **7** and **8** in moderate yield, respectively. Actually, their NMR spectra were clearly not that expected for single product, but rather in keeping with a mixture of 2 isomers. For example, **6** showed NMR integral area of vinyl, allyl and alkyl protons in the ratio 3:2:9. These products were 97% homogeneous on SF-96 VPC.

These products, however, became tarry black materials on standing at room temperature. The products, **6** and **7** from di-*t*-butyl sulfide are considered to be produced by further Hoffmann  $\beta$ -elimination (process h) and Stevens reaction (process s) of the corresponding cyclopentadienylide **9**.

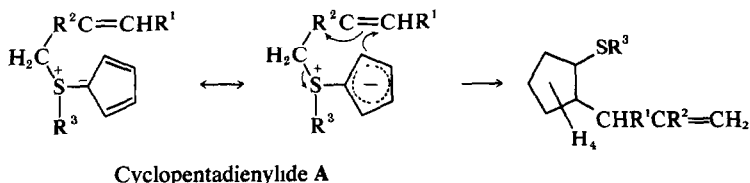
*Photolysis of diazocyclopentadiene in allylic sulfides.* The photolysis of DCPD in allylic sulfides solution led to the formation of spiro[2,4]heptadienes, and the insertion product of the carbene into the C—S bond. Irradiation of DCPD in allyl ethyl sulfide afforded a mixture of two products (VPC). One of them was identified as 1-allyl-2-ethylthiocyclopentadiene, **10-i** which showed the evidence of alkenyl hydrogens, C—C



diene band ( $1595$  and  $1638\text{ cm}^{-1}$ ) and terminal vinyl band ( $914$  and  $992\text{ cm}^{-1}$ ) in IR spectrum. Its NMR spectrum, however, was keeping with a mixture of three isomers.

These results were to be expected, it having been demonstrated that cyclopentadienylidene attacks on a S atom to form intermediate sulfonium cyclopentadienylide followed by 3,3-sigmatropic rearrangement. It is of interest that relative to the other ylides from the carbene reactions, the sulfonium cyclopentadienylide has an aromatic character; that is, the structure A predominantly contributes to the resonance hybrid of the cyclopentadienylide, and the rearrangement would be expected to occur preferentially at 2(5)-position since the transition stage for this reaction is allowed in a supra-supra manner.

duct **12-i** and 8% of spiro product. The insertion product was identified as 1-(1-methyl-2-propenyl)-2-ethylthiocyclopentadiene by spectral analysis. No trace of any isomer such as 1-(2-butenyl)-2-ethylthiocyclopentadiene or 5-(1-methyl-2-propenyl)-5-ethylthiocyclopentadiene. Table 1 gives the yields of insertion and addition products in the photolysis of DCPD in various allylic sulfides. An interesting feature was the ratio of insertion and addition. In allyl ethyl sulfide, the insertion reaction appeared to be about 2.4 times faster than the addition. This fact indicates that cyclopentadienylidene is electrophilic species and reacts with a S atom more favourably than with olefin. The insertion and addition ratio in allyl ethyl sulfide also showed that this carbene has somewhat less selectivity toward a S atom than bis(carbometh-

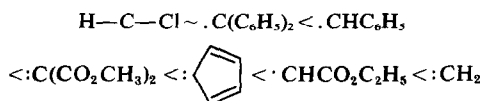


The second product isolated from photolysis of DCPD in allyl ethyl sulfide was addition product **10-a** of cyclopentadienylidene to the double bond; its structure was established by NMR and IR and elemental analyses. Photolysis of DCPD in  $\gamma$ -methylallyl ethyl sulfide gave 35% of insertion pro-

oxy)carbene ( $5.1$ )<sup>18</sup> and phenylcarbene ( $8.0$ )<sup>23</sup> or diphenylcarbene ( $>26$ ),<sup>23</sup> but more selectivity than carboethoxycarbene ( $1.5$  in *n*-butyl allyl sulfide).<sup>18</sup> If relative ratio of the insertion and addition is assumed to be a measure of electrophilicity of carbene, the series of increasing reactivity of carbenes suggested by Closs<sup>24</sup> and Moss<sup>2</sup> will be expanded as follows.

Table 1. Photolysis of diazocyclopentadiene in allylic sulfides

Sulfide	Addition	Insertion	i/a
$\text{CH}_2=\text{CHCH}_2\text{SEt}$	13%	31%	2.4
$\text{CH}_2=\text{CHCH}_2\text{S-t-Bu}$	24%	37%	1.6
$\text{CH}_3\text{CH}=\text{CHCH}_2\text{SEt}$	8%	35%	4.3
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{SEt}$	17%	40%	2.4
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{SMe}$	18%	28%	1.5

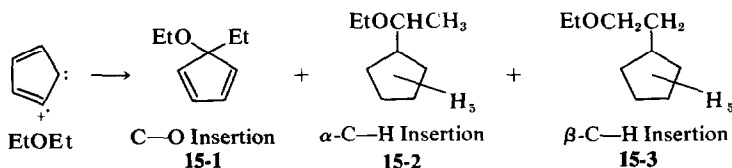


In the reaction with allyl *t*-butyl sulfide, however, the ratio of insertion and addition appeared to be 1:6. This effect is a presumable consequence of

steric effect of t-Bu group on the S atom, which prevents the attack of the carbene on the S atom. On the other hand, in the reaction with  $\gamma$ -methylallyl ethyl sulfide, the insertion reaction predominantly occurs in the factor of 4.3, probably because of steric effect on addition to the double bond.

**Photolysis of diazocyclopentadiene in alkyl ethers.** The second most frequently studied property cyclopentadienylidene is the insertion into C—H bond of an ether. These reactions appear to be very attractive for comparison with the reaction in a S compound. Analogous reaction of cyclopentadienylidene was developed by Basinski,<sup>9</sup> but no detailed studies have been reported.

Photolysis of DCPD in diethyl ether afforded the insertion products into the C—O,  $\alpha$ -C—H and  $\beta$ -C—H bonds. The structures of these products were assigned on the basis of IR, NMR and elemental analyses. The C—O insertion product was found to be 5-ethoxy(5-ethyl)cyclopentadiene in 9% yield, and its NMR spectrum showed signals of cyclopentadiene protons as two broad singlet at 6.11 and 6.15 ppm, and protons of OEt and Et groups. No allylic protons were observed.



The formation of C—O insertion product is of interest and is in marked contrast to the reactions of diazomalonnate and diazoacetate in linear alkyl ether, which gave no C—O insertion product or a trace if any in liquid phase reactions.<sup>25</sup>

The results of Jones<sup>26</sup> and our previous reports<sup>18,27</sup> with bis(carbomethoxy)carbene had suggested that carbene probably attacks an O atom to form the oxonium ylide which rearranges rapidly to C—O bond insertion product. However, it should be noted that there is no 1-ethyl-2-ethoxycyclopentadiene.

Cyclopentadienylidene inserts into both  $\alpha$ -C—H

and  $\beta$ -C—H bonds of diethyl ether, producing 15-2 and 15-3 in 27 and 2% yields, respectively. The correction by statistical factor shows that the reaction occurred 19 times faster at an  $\alpha$ -C—H bond than at  $\beta$ -C—H bond. These values were essentially independent of DCPD concentration over the range 1–10 mmoles, and it was unaltered under the reaction conditions.

These results might suggest that one of the factors controlling the insertion reaction is stabilization of a partial positive charge on the adjacent C atom.

This consideration led us to study the reaction of DCPD with various ethers (Table 2). The yields of products obtained in the reactions with DCPD did not vary markedly with the structure of ethers. However, with allyl ethyl ether, only spiro-[2.4]heptadiene was found to be formed, indicating that terminal double bond is much more reactive than an allylic C—H bond towards the carbene.

Competition experiments, in which mixtures of an ether and either cyclohexane or 2,3-dimethylbutane were allowed to react with cyc-

lopentadienylidene, gave some indication that both resonance and inductive effects of O atom influenced the rate of insertion reaction of the carbene. Relative reactivities of C—H bonds were calculated from the relative yields of C—H bond insertion products. The results of these competition experiments are shown in Table 3. These values remained constant within experimental error as the relative concentration of hydrocarbon and alkyl ether changed from 1:1 to 1:2.

As in the case of other carbene reaction,<sup>6</sup> cyclopentadienylidene inserts into C—H bonds most favourably when a partially positive charge on C

Table 2. Reactions of diazocyclopentadiene with ethers

Ether	C—O bond	Yield of insertion product		
		$\alpha$ -C—H bond	$\beta$ -C—H bond	$\gamma$ -C—H bond
Et <sub>2</sub> O	9%	27%	2%	
i-Pr <sub>2</sub> O	8%	31%	18%	
n-Pr <sub>2</sub> O	10%	44%	16%	9%
t-BuOMe	9% <sup>a</sup>	15%	9%	
	0%	32%	10%	
CH <sub>2</sub> =CHCH <sub>2</sub> OEt	32%	(addition product to the C=C bond)		

<sup>a</sup>Insertion product of cyclopentadienylidene into t-Bu and oxygen bond.

Table 3. Relative rates of C—H insertion reaction in the photolysis of DCPD in ethers (*ca* 20°)

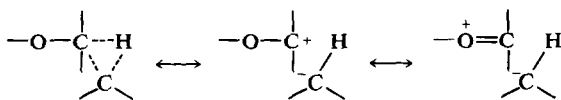
Ether	$\alpha$ -C—H	$\beta$ -C—H	$\gamma$ -C—H
Diethyl ether	5.9 ± 0.2	0.32 ± 0.02	
i-Propyl ether	6.2 ± 0.1	0.55 ± 0.01	
n-Propyl ether	6.2 ± 0.1	2.3 ± 0.2	0.9 ± 0.1
t-Butyl methyl ether	2.7 ± 0.2	0.58 ± 0.06	
Tetrahydrofuran	4.2 ± 0.4	1.3 ± 0.1	
2,3-Dimethylbutane	1.00 <sup>a</sup>	Standard	
Cyclohexane	3.9 ± 0.3 <sup>b</sup>		

<sup>a</sup>Insertion into primary C—H bond. Relative rate into tertiary C—H bond was 6.6 ± 0.2 (lit.<sup>2</sup> 7.32).

<sup>b</sup>Secondary C—H bond insertion reaction.

atom involved could be stabilized. For instance, in the case of 2,3-dimethylbutane, cyclopentadienyldiene reacts with tertiary C—H bond 6.6 times more than with primary C—H bond, and its selectivity has been explained in terms of either inductive and resonance effects of alkyl substituent. Similarly, the inductive and resonance effects of alkoxy group can be seen in the results shown in Table 3. With t-butyl methyl ether, the insertion of cyclopentadienyldiene into the primary  $\alpha$ -C—H bond is favourably over insertion into the primary C—H bond of 2,3-dimethylbutane by factor of 2.7.

With diethyl ether, the secondary  $\alpha$ -C—H bond is somewhat more reactive than the secondary C—H bond of cyclohexane. These results were rationalized in terms of polar resonance structures of the transition state as suggested by Doering.<sup>28</sup>



However, tertiary  $\alpha$ -C—H bond of isopropyl ether is only 6.2 times more reactive than the primary C—H bond of 2,3-dimethylbutane. This is essentially same as the tertiary C—H bond of 2,3-dimethylbutane. Apparent effect of  $\alpha$ -oxygen was not observed on the tertiary  $\alpha$ -C—H bond of ether. These data are summarized in Table 4.

In contrast to accelerating effect of alkoxy group on insertion into  $\alpha$ -C—H bond, a  $\beta$ -C—H bond of ether was found to be less reactive than C—H bonds of 2,3-dimethylbutane or cyclohexane. Since it is clear that there is no extra resonance effect to stabilize a partial positive charge on  $\beta$ -carbon, the inductive effect of O atom probably reduced the reactivity of the  $\beta$ -C—H bond towards attack of the electron seeking carbene. There is no essential difference in reactivity between  $\gamma$ -C—H bond and corresponding alkyl C—H bond. Inductive effects of oxygen seem not to appear on the remote  $\gamma$ -position.

Table 4. Relative rates of cyclopentadienyldiene insertion into C—H bond of ethers

	$\alpha$ -C—H	$\beta$ -C—H	$\gamma$ -C—H	C—H
Primary	2.7	0.3–0.6	0.9	1.00 <sup>a</sup>
Secondary	4.2–6.2	1.3–2.3		3.9 <sup>b</sup>
Tertiary	6.2			6.6 <sup>c</sup>

<sup>a</sup>Primary C—H of 2,3-dimethylbutane; <sup>b</sup>Secondary C—H of cyclohexane; <sup>c</sup>Tertiary C—H of 2,3-dimethylbutane.

#### EXPERIMENTAL

**General.** Photolysis was carried out with the system previously described.<sup>14</sup> IR spectra were recorded using a Hitachi Infracord EPI-G3. NMR spectra were obtained using a Varian A-60D spectrometer. Chemical shifts are given in  $\delta$ -units, ppm downfield from internal TMS. Gas chromatography was used extensively for the separation and purification of products and for yield determinations. The GLPC column used included (A); 10% SF-96, 1.3 m  $\times$  6 mm, on Celite 545, and (B); 10% Carbowax 20M, 1.6 m  $\times$  6 mm, on Celite 545. Diazocyclopentadiene (DCPD) was prepared by method of Weil,<sup>29</sup> and collected at 30–34° (20 mm). IR properties were in agreement with those reported by Doering,<sup>30</sup> and its NMR spectrum was in agreement with that reported by Ledwith.<sup>31</sup> DCPD was stored over Dry Ice. The sulfides and ethers used were either commercial products whose purity was checked before use or prepared in a straight forward manner by the method reported previously.<sup>17, 18</sup>

**Dimethylsulfonium cyclopentadienyldiene (1).** A soln of DCPD 1.09 mmole in 39.9 mmole Me<sub>2</sub>S was photolyzed with a high pressure mercury lamp for 2 h. The colour of the soln became brown and the IR spectrum of a withdrawn sample showed the absence of diazo absorption at 2082 cm<sup>-1</sup>, indicating that reaction was complete. The light petroleum ether (b.p. 30–45°) was added to the soln and the precipitated light pink solid was filtered off, washed well with light petroleum, and dried, to yield 50.8 mg, 37% yield; m.p. 127–128° (lit.<sup>20</sup> 129–130°). The IR and NMR spectra were in good agreement with those given in the literature.<sup>20</sup>

**Diethylsulfonium cyclopentadienyldiene (2).** Low temp (*ca* 0°) irradiations for a soln of DCPD (1.25 mmole) and Et<sub>2</sub>S (22.1 mmole) carried out in a small vessel immersed in a half-silvered Dewar flask, irradiated externally by a water-cooled Rikosha high pressure mercury lamp. This ylide (39.8 mg, 21% yield) had m.p. 85–86° at decomp, and unstable on standing at room temp and on attempted recrystallization: IR (KBr); 3050 (w), 2940 (m), 2900 (m), 1650 (w), 1440 (w), 1426 (m), 1412 (m), 1370 (m), 1330 (w), 1227 (m), 1245 (w), 1195 (m), 1183 (m), 1038 (s), 1013 (v s), 784 (m), 702 (v.s.), and 661(s) cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>); 1.24, 6H), 3.05 (q, 4H) and 6.23 ppm (s, 4H). Furthermore, its NMR spectrum in DMSO-d<sub>6</sub> showed a multiplet centered at 5.97 ppm (4H, cyclopentadienyl). The multiplet for the ring protons appears as an AA'BB' type (Fig 1) (Found: C, 69.83; H, 9.30; S, 20.90. Calcd for C<sub>8</sub>H<sub>14</sub>S: C, 70.07; H, 9.15; S, 20.79%).

**Tetramethylenesulfonium cyclopentadienyldiene (3).** A soln of DCPD (2.09 mmole) and tetramethylene sulfide (48.5 mmole) was irradiated in a Pyrex vessel with the high pressure mercury lamp as described previously. Addition of cooled light petroleum into the mixture precipi-

tated a light brown needle crystal, 88.8 mg, 28% yield. It decomposed approximately above 150° without melting; IR (KBr): 3030 (m), 2950 (m), 2890 (m), 2825 (m), 1420 (m), 1405 (s), 1325 (m), 1255 (m), 1245 (m), 1190 (m), 1178 (s), 1040 (m), 1005 (s), 860 (m), 698 (s), and 688 cm<sup>-1</sup> (s); (these IR absorption bands are characteristic of the derivative of cyclopentadienylide); NMR (CDCl<sub>3</sub>): 2.32 (m, 4H), 3.33 (m, 4H), and 6.23 ppm (s, 4H). In DMSO-d<sub>6</sub>, NMR spectrum showed the characteristic multiplet ring protons as AA'BB' type centered at 5.92 ppm (Fig 2). (Found: C, 70.45; H, 8.18; S, 20.85. Calcd for C<sub>5</sub>H<sub>12</sub>S: C, 70.99; H, 7.95; S, 21.06%).

**Attempted reaction of DCPD with isopropyl sulfide.** When an intimate mixture of DCPD and di-isopropyl sulfide was irradiated in a cooled Pyrex vessel with the high pressure mercury lamp as described before. After addition of light petroleum, a tarry brown solid was isolated, which was not soluble in solvent such as chloroform, acetone, and DMSO. The corresponding sulfonium ylide probably polymerized under the reaction conditions. Although gas chromatographic analysis of the mixture indicated the formation of a number of products, only one product was identified as the insertion product of cyclopentadienylidene into tertiary C—H bond. The NMR spectra showed the peaks at 1.10 (d, 6H), 1.50 (s, 3H), 1.54 (s, 3H), 2.48 (m, 1H), 2.98 (m, 2H), and 5.8–6.7 ppm (m, 3H).

**Reaction of DCPD with di-*t*-butyl sulfide.** An intimate mixture of DCPD (1.28 mmole) with di-*t*-butyl sulfide (15.8 mmole) was irradiated in a cooled Pyrex vessel as described before until evolution of N<sub>2</sub> ceased. The addition of a cooled light petroleum could not separate the precipitation. The mixture was analyzed directly by gas chromatography with column (A), and showed three main products, **6**, **7** and **8**, in 23, 29 and 14% yields, respectively. The product **6** showed an IR (neat) spectrum at 3080 (w), 2950 (s), 2930 (s), 2915 (s), 2890 (m), 2860 (m), 1600 (w), 1470 (w), 1455 (m), 1363 (s), 1352 (m), 1340 (m), 1260 (w), 1167 (s), 950 (m), 890 (s) and 868 (m) cm<sup>-1</sup>; NMR (CCl<sub>4</sub>): 1.30 (s, 9H), 3.06 (d, 2H) and 6.3–6.6 ppm (m, 3H). The

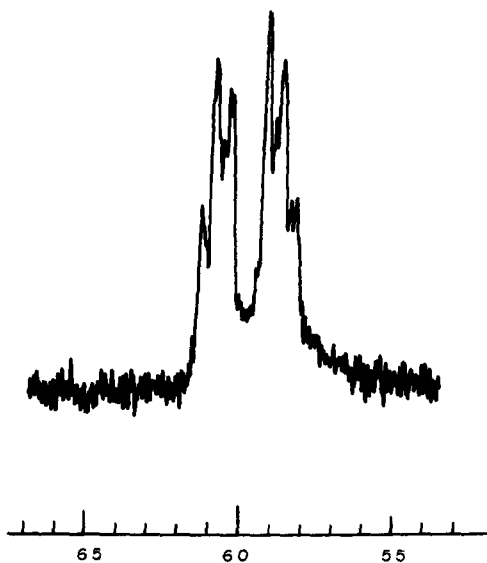


Fig 1. NMR spectrum of the ring protons in diethylsulfonium cyclopentadienylide **2** (DMSO-d<sub>6</sub>).

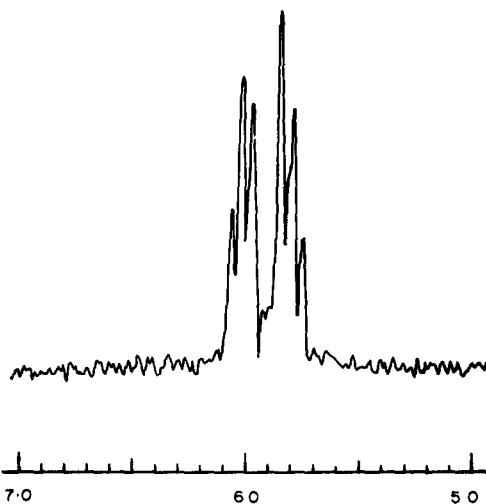


Fig 2. NMR spectrum of the ring protons in tetramethylenesulfonium cyclopentadienylide **3** (DMSO-d<sub>6</sub>).

compound **7** was identified as an insertion product of cyclopentadienylidene into C—S bond by NMR spectrum, which had peaks at 1.18 (s, 9H), 1.32 (s, 9H), 2.9–3.1 (m, 2H) and 5.9–6.7 ppm (m, 2H). The IR spectrum had prominent peaks at 3075 (w), 2970 (s), 2925 (s), 2905 (s), 2870 (s), 1600 (w), 1590 (w), 1475 (m), 1460 (m), 1367 (s), 1280 (m), 1193 (m), 1183 (m), 1170 (m), 911 (m), and 902 cm<sup>-1</sup> (m). (Found: C, 73.98; H, 10.81; S, 15.65. Calcd for C<sub>13</sub>H<sub>22</sub>S: C, 74.21; H, 10.54; S, 15.24%). The compound **8** was identified as an insertion product of cyclopentadienylidene into C—H bond by NMR spectrum, which had peaks at 1.37 (s, 6H), 1.42 (s, 9H), 2.6–2.7 (m, 2H), 3.1 (broad d, 2H), and 5.8–6.5 ppm (m, 3H). The IR spectrum had a prominent peak at 3050 (w), 2960 (s), 2920 (s), 2895 (s), 1600 (w), 1461 (m), 1377 (m), 1360 (s), 1190 (m), 1180 (m), 1165 (m), 1125 (s), 902 (m), 790 (s) and 767 (m).

**Photolysis of DCPD in allyl ethyl sulfide (10).** Irradiation of a cooled soln of 1.35 mmole DCPD in 22.2 mmole allyl ethyl sulfide contained in a Pyrex vessel resulted in the evolution of N<sub>2</sub> gas. After the IR spectrum of the mixture showed no diazo band, the products were isolated by GLPC method. IR spectrum of the compound **10-a**, spiro[2.4]heptadiene showed peaks at 3050 (w), 2950 (s), 2910 (s), 2850 (w), 1620 (w), 1478 (s), 1441 (m), 1420 (w), 1372 (w), 1268 (m), 1240 (m), 1120 (w), 1085 (w), 1048 (m), 973 (s, cyclopropyl group), 890 (m) cm<sup>-1</sup>; NMR: 1.22 (t, 3H), 1.4–2.0 (m, 3H), 2.48 (q, 2H), 2.67 (d, 2H), 6.0 (m, 2H) and 6.4 ppm (m, 2H). (Found: S, 18.86. Calcd for C<sub>10</sub>H<sub>14</sub>S: S, 19.28%) Compound (**10-i**) had IR peaks at 3050 (w), 2945 (s), 2900 (s), 1638 (m), 1595 (w), 1447 (w), 1426 (m), 1370 (m), 1262 (m), 992 (m) and 914 cm<sup>-1</sup> (s, vinyl olefin). The NMR spectrum had peaks at 1.23 (t, 3H), 2.65 (q, 2H), 2.9–3.1 (m, 4H), 4.83 (m, 2H), 5.1–5.3 (m, 1H), 6.5 ppm (m, 2H). (Found: S, 19.15. Calcd for C<sub>10</sub>H<sub>14</sub>S: S, 19.28%).

**Photolysis of DCPD in allyl *t*-butyl sulfide (11).** A soln of 1.17 mmole DCPD in 19.8 mmole of **11** was irradiated. The mixture was analysed directly by gas chromatography. Two main products were collected and identified as **11-a** and **11-i**. The IR spectrum of product **11-a** had prominent peaks at 3040 (w), 2930 (s), 2920 (s), 2890 (s), 2870 (s), 2840 (w), 1640 (w), 1610 (w), 1456 (m), 1450 (m), 1360 (s), 1165 (s), 1040 (m), 968 (s, cyclopropyl) and 822 cm<sup>-1</sup>

(m); NMR: 1.29 (s, 9H), 1.5–2.1 (m, 2H), 2.1–2.5 (m, 2H), 2.70 (d, 2H), 6.1 (m, 2H) and 6.4 ppm (m, 2H). (Found: C, 74.05; H, 9.48. Calcd for  $C_{12}H_{18}S$ : C, 74.16; H, 9.34%). The compound **11-i** had prominent IR (neat) peaks at 3080 (w), 2970 (s), 2950 (m), 2925 (m), 2900 (m), 2870 (m), 1640 (m), 1595 (w), 1475 (m), 1460 (m), 1368 (s, shoulder at 1377), 1170 (s), 997 (m), 917 (s), and 890 (m)  $cm^{-1}$ , NMR (CCl<sub>4</sub>): 1.28 (s, 9H), 2.97 (m, 2H), 3.18 (m, 2H), 4.87 (m, 2H), 5.08 (m, 1H) and 5.3–6.6 ppm (m, 2H). Its NMR spectrum was clearly not that expected for **11-i**, but more in keeping with a mixture of the two isomers.

**Photolysis of DCPD in  $\gamma$ -methylallyl ethyl sulfide (12)**  
Photolysis of a soln of 1.31 mmole DCPD in 22.4 mmole of **12** gave two products, **12-i** and **12-a**. The product **12-i** showed IR (neat) peaks at 3050 (w), 2940 (s), 2900 (s), 2845 (m), 1635 (w), 1600 (w), 1450 (m), 1370 (m), 1260 (m), 911 (s, vinyl) and 880  $cm^{-1}$  (m); NMR spectrum at 1.27 (t, 3H), 1.30 (d, 3H), 2.76 (q, 2H), 3.00 (m, 2H), 3.16 (m, 1H), 4.90 (m, 2H), 5.11 (m, 1H) and 6.45 ppm (m, 2H). (Found: C, 73.56; H, 9.07; S, 17.69. Calcd for  $C_{11}H_{16}S$ : C, 73.27; H, 8.94; S, 17.78%). The product **12-a** showed an IR (neat) band at 3065 (w), 2955 (s), 2910 (s), 2870 (m), 1638 (w), 1602 (w), 1477 (m), 1453 (m), 1374 (m), 1190 (m), 1179 (s), 1176 (m), 1042 (s), 1007 (m), and 920 (m)  $cm^{-1}$ ; NMR peaks at 1.23 (t, 3H), 1.36 (d, 3H), 1.5–2.9 (m, 6H), 6.12 (m, 2H), 6.40 (m, 2H). (Found: C, 73.15; H, 8.65; S, 17.68. Calcd for  $C_{11}H_{16}S$ : C, 73.27; H, 8.94; S, 17.78%).

**Photolysis of DCPD in  $\beta$ -methylallyl ethyl sulfide (13)**  
A soln of 1.14 mmole DCPD and 18.7 mmole of **13** was irradiated as described previously. GLPC analysis with column (A) gave two main products, **13-i** and **13-a** in 40.2 and 16.6% yields, respectively. The product **13-i** had prominent IR (neat) peaks at 3080 (w), 2970 (s), 2925 (s, shoulder at 2870), 1650 (m), 1600 (w), 1450 (s), 1375 (s), 1360 (m), 1337 (m), 1265 (m), 1191 (m), 1180 (m), 1055 (m), 1023 (m), 895 (s), 790 (m) and 768 (m)  $cm^{-1}$ ; NMR peaks at 1.23 (t, 3H), 1.68 (broad s, 3H), 2.4–3.2 (m, 6H), 4.68 (m, 2H), and 5.7–6.5 ppm (m, 2H). The product **13-a** was found to be spiro[2.4]heptadiene by NMR spectrum, which had peaks at 1.21 (t, 3H), 1.48 (s, 3H), 1.72 (s, 2H), 2.48 (q, 2H), 2.80 (s, 2H), 6.15 (m, 2H) and 6.39 ppm (m, 2H); IR spectrum (neat): 3050 (w), 2950 (s), 2910 (s), 2855 (m), 1650 (w), 1595 (w), 1474 (m), 1440 (m), 1370 (m), 1240 (s), 1182 (m), 1170 (s), 1085 (w), 1063 (m), 1020 (w), 967 (s), 925 (w), 867  $cm^{-1}$  (m).

**Photolysis of DCPD in  $\beta$ -methylallyl methyl sulfide (14)**  
A soln of 1.13 mmole DCPD in 25.7 mmole  $\beta$ -methylallyl methyl sulfide was irradiated in a Pyrex vessel at room temp for 2 h. After irradiation, the mixture was injected directly into the gas chromatograph. The insertion product (**14-i**) of cyclopentadienylidene into allyl C—S bond was isolated together with the addition product (**14-a**). The product **14-i** showed IR (neat) peaks at 3050 (w), 2950 (m), 2890 (s), 1645 (w), 1595 (w), 1430 (m), 1370 (m), and 890  $cm^{-1}$  (s, terminal methylene); NMR spectrum at 1.67 (broad s, 3H), 2.27 (s, 3H), 2.95 (broad s, 2H), 3.08 (broad s, 2H), 4.70 (m, 2H), and 5.6–6.5 ppm (m, 2H). (Found: S, 18.94. Calcd for  $C_{10}H_{14}S$ : S, 19.28%).

The product **14-a** showed the IR (neat) bands at 3040 (w), 2940 (m), 2920 (m), 2890 (s), 1640 (w), 1615 (w), 1475 (m), 1435 (s), 1376 (m), 1245 (m), 1064 (m), 957 (s, cyclopropane group), and 877  $cm^{-1}$  (m); NMR peaks at 1.45 (s, 3H), 1.72 (s, 2H), 2.00 (s, 3H), 2.76 (s, 2H), 6.15 (m, 2H) and 6.38 ppm (m, 2H). (Found: S, 18.94. Calcd for  $C_{10}H_{14}S$ : S, 19.28%).

**Photolysis of DCPD in diethyl ether.** In 69.6 mmole

diethyl ether was dissolved 3.90 mmole DCPD. The soln was then irradiated for 2 h using high pressure mercury lamp as described before. From the analysis by gas chromatography with column (B), three main products were found: one of them was identified as **15-1** [IR (neat): 3140 (w), 2950 (s), 2920 (s), 2862 (s), 1650 (w), 1620 (w), 1460 (m), 1390 (m), 1364 (m), 1300 (m), 1108 (s), 1080 (s), 1066 (s) and 769  $cm^{-1}$  (m); NMR: 0.94 (t, 3H), 1.06 (t, 3H), 1.65 (q, 2H), 3.30 (q, 2H), 6.11 (m, 2H) and 6.15 (m, 2H). (Found: C, 77.92, H, 10.50. Calcd for  $C_8H_{14}O$ : C, 78.21, H, 10.21%)]. The compound **15-2** was also found as the insertion product of cyclopentadienylidene into  $\alpha$ -C—H bond. This showed the IR (neat) peaks at 3050 (w), 2960 (s), 2920 (m), 2855 (s), 1605 (w), 1445 (m), 1371 (s), 1320 (m), 1185 (m), 1100 (s), 946 (w), 901 (s) and 760  $cm^{-1}$  (w). The mass spectrum showed a parent peak at  $m/e$  138 (as expected) and some peaks at 123 ( $M^+ - CH_3$ ), 93 ( $M^+ - OEt$ ), 92 ( $M^+ - EtOH$ ) and 65, corresponding to  $Et^+$ . Third product **15-3** was found the insertion product of the carbene into  $\beta$ -C—H bond. It showed the IR (neat) bands at 3020 (w), 2940 (s), 2890 (m), 2820 (s), 1610 (w), 1600 (w), 1440 (w), 1370 (m), 1358 (m), 1345 (m), 1107 (s, shoulder at 1123), 890 (m), and 880  $cm^{-1}$  (m); NMR: 1.15 (t, 3H), 2.60 (broad t, 2H,  $J = 7$  c/s), 2.85 (m, 2H), 3.42 (q, 2H), 3.48 (t, 2H,  $J = 7$  c/s), and 5.7–6.5 ppm (m, 3H);  $m/e = 138$  (as expected). Compound **15-3** was also prepared independently by adding 2-chlorodiethylether to cyclopentadienylsodium in THF, standing overnight and then adding water of decompose sodium salt.

**Photolysis of DCPD in tetrahydrofuran.** In a typical run, 1.34 mmole DCPD in 36.1 mmole THF was irradiated in a cooled Pyrex tube with high pressure mercury lamp as described before. After 2 h irradiation, no starting diazo compound remained. Two products, **17-1** and **17-2** were isolated by gas chromatograph column (A). **17-1** was found to be the insertion product of cyclopentadienylidene into  $\alpha$ -C—H bond, which showed IR (neat) bands at 3020 (w), 2920 (s), 2850 (s), 1640 (w), 1455 (w), 1435 (m), 1340 (m), 1175 (m), 1050–1060 (s) and 915  $cm^{-1}$  (m); NMR spectrum at 1.67–2.3 (m, 4H), 2.93 (broad s, 2H), 3.5–4.1 (m, 2H), 4.4–4.75 (m, 1H) and 6.0–6.6 (m, 3H). (Found: C, 78.95, H, 9.07. Calcd for  $C_8H_{12}O$ : C, 79.37; H, 8.88%). **17-2** was the insertion product of the carbene into  $\beta$ -C—H bond, which had NMR peaks at 1.5–2.4 (m, 2H), 2.9 (m, 2H), 3.0–4.0 (m, 5H) and 5.9–6.5 ppm (m, 3H).

**Photolysis of DCPD in diisopropyl ether.** Photolysis of 1.26 mmole DCPD in 18.9 mmole diisopropyl ether gave three products. 5-isopropyl-5-isopropoxycyclopentadiene as C—O insertion product of the carbene showed the prominent IR peaks (neat) at 3040 (w), 2940 (s), 2890 (m), 2830 (m), 1635 (w), 1450 (m), 1373 (m), 1355 (s), 1110 (s), and 1050  $cm^{-1}$  (s); NMR peaks at 0.93 (d, 6H), 1.03 (d, 6H), 1.77 (m, 1H), 3.12 (m, 1H) and 6.12 ppm (broad s, 4H). The insertion product of cyclopentadienylidene into  $\alpha$ -C—H bond as second product showed the IR (neat) peaks at 3030 (w), 2940 (s), 2900 (m), 1615 (w), 1460 (m), 1375 (s), 1365 (s), 1162 (m), 1108 (s), 1005 (s), 990 (m) and 900  $cm^{-1}$  (m); NMR spectrum at 0.98 (d, 6H), 1.33 (s, 3H), 1.37 (s, 3H), 2.95 (m, 2H), 3.5 (m, 1H), 6.0–6.7 (m, 3H). (Found: C, 79.74; H, 11.01. Calcd for  $C_{11}H_{18}O$ : C, 79.46; H, 10.92%). Third product was found to be the insertion product of cyclopentadienylidene into  $\beta$ -C—H bond, which had the IR (neat) peaks at 3050 (w), 2960 (s), 2910 (m), 1615–1590 (w), 1460 (m), 1375 (s), 1370 (s), 1428 (m), 1122 (s), 1080 (m), 1055 (m), 995 (m) and 895  $cm^{-1}$  (m); NMR spectrum at 1.05 (d, 6H), 1.08 (d, 3H), 2.45

(m, 2H), 2.88 (m, 2H), 3.58 (m, 2H) and 5.8–6.5 ppm (m, 3H). (Found: C, 78.99; H, 11.22. Calcd for  $C_{11}H_{18}O$ : C, 79.46; H, 10.92%);  $m/e = 166$ .

**Photolysis of DCPD in di-n-propyl ether (20).** Photolysis of 1.09 mmole of DCPD in 24.9 mmole di-n-propyl ether gave four products, 20-1, 20-2, 20-3 and 20-4. The product 20-1 was found to be the insertion product of the carbene into C—O bond. The IR spectrum of 20-1 had prominent peaks at 3020 (w), 2925 (s), 2900 (s), 2845 (s), 1610 (w), 1460 (m), 1318 (m), 1257 (s), 1080 (s), 1015 (s) and 800  $cm^{-1}$ . The NMR spectrum had peaks at 0.6–1.0 (m, 6H), 1.0–1.7 (m, 6H), 3.10 (t, 2H) and 6.1 ppm (broad s, 4H). (Found: C, 79.32; H, 10.68. Calcd for  $C_{11}H_{18}O$ : C, 79.46; H, 10.92%). The products 20-2, 3 and 4 were found to be the insertion products of cyclopentadienyliene into  $\alpha$ -C—H,  $\beta$ -C—H and  $\gamma$ -C—H bonds, respectively. The IR spectrum (neat) of 20-2 had prominent peaks at 3020 (w), 2920 (s), 2895 (s), 2845 (s), 1600 (w), 1456 (m), 1368 (m), 1327 (w), 1085 (s), and 898  $cm^{-1}$  (m). Its NMR spectrum showed the peaks at 0.85 (t, 3H), 0.88 (t, 3H), 1.1–2.0 (m, 4H), 2.90 (d, 2H), 3.2 (m, 2H), 3.90 (t, 1H) and 6.0–6.6 ppm (m, 3H). (Found: C, 79.19; H, 10.71. Calcd for  $C_{11}H_{18}O$ : C, 79.46; H, 10.92%). Product 20-3 showed the IR (neat) spectrum peaks at 3020 (w), 2920 (s), 2895 (s), 2845 (s), 1595 (w), 1455 (m), 1365 (m), 1104 (s) and 894 (m)  $cm^{-1}$ ; NMR: 0.90 (t, 3H), 1.15 (d, 3H), 1.52 (sextet, 2H), 2.3 (m, 1H), 2.87 (s, 2H), 3.3 (m, 4H) and 5.7–6.5 ppm (m, 3H). (Found: C, 79.67; H, 11.21. Calcd for  $C_{11}H_{18}O$ : C, 79.46; H, 10.92%). Product 20-4 showed the IR (neat) bands at 3020 (w), 2920 (s), 2890 (s), 2810 (s), 1608 (w), 1455 (m), 1360 (m), 1010 (s), and 893  $cm^{-1}$  (m); NMR: 0.92 (t, 3H), 1.6 (m, 4H), 2.45 (m, 2H), 2.85 (m, 2H), 3.30 (t, 2H), 3.37 (t, 2H) and 5.8–6.5 ppm (m, 3H). (Found: C, 79.75; H, 10.81. Calcd for  $C_{11}H_{18}O$ : C, 79.46; H, 10.92%).

**Photolysis of DCPD in t-butyl methyl ether.** A soln of 1.25 mmole DCPD and 25.9 mmole t-butyl methyl ether was irradiated at 25–30° for 2 h and worked up as the described previously. Three major products, 21-1, 21-2 and 21-3 were isolated by GLPC. Compound 21-1 was found to be the insertion product of cyclopentadiene into t-butyl and oxygen bond. The IR spectrum had prominent peaks at 3040 (w), 2935 (s), 2900 (s), 2850 (m), 2795 (m), 1650 (w), 1602 (w), 1457 (m), 1388 (m), 1355 (s), 1186 (m), 1175 (m), 1140 (m), 1080 (s), 1003 (m), 973 (m), 950 (m), 813 (m) and 720  $cm^{-1}$  (s); NMR: 0.97 (s, 9H), 3.10 (s, 3H), 6.07 (m, 2H) and 6.20 (m, 2H). (Found: C, 79.03; H, 10.56. Calcd for  $C_{10}H_{16}O$ : C, 78.89; H, 10.59%). Products 21-2 and 3 were found to be the insertion products of cyclopentadienyliene into methyl C—H bond and t-butyl C—H bond, respectively. 21-2 showed the IR (neat) bands at 3025 (w), 2945 (s), 2900 (s), 2875 (m), 2845 (m), 1625 (w), 1460 (w), 1388 (m), 1362 (s), 1258 (m), 1225 (m), 1195 (s), 1078 (s), 1020 (m), and 900  $cm^{-1}$  (w); NMR: 1.22 (s, 9H), 2.92 (m, 2H), 4.20 (m, 2H), and 5.7–6.6 ppm (m, 3H). (Found: C, 78.69; H, 10.69. Calcd for  $C_{10}H_{16}O$ : C, 78.89; H, 10.59%). Product 21-3 showed the IR (neat) peaks at 3030 (w), 2950 (s), 2920 (s), 2890 (m), 2815 (m), 1615 (m), 1462 (m), 1362 (s), 1220 (m), 1187 (s), 1177 (s), 1075 (s), and 900 (m); NMR (CCl<sub>4</sub>): 1.10 (s, 6H), 2.60 (m, 2H), 2.93 (m, 2H), 3.20 (s, 3H), and 5.7–6.5 ppm (m, 3H). (Found: C, 78.62; H, 10.81. Calcd  $C_{10}H_{16}O$ : C, 78.89; H, 10.59%).

**Reaction of DCPD with cyclohexane.** DCPD (0.5 g) was dissolved in 10 ml cyclohexane and irradiated for 3 h with the high pressure mercury lamp. Excess cyclohexane was stripped, and the residue was analysed directly by gas chromatography with column (A). The product was 97% homogeneous on column (A) and (B) VPC. It was iden-

tified as C—H insertion product (16) of cyclopentadienyliene in comparison with authentic sample.<sup>32</sup> It showed the IR (neat) 3060 (w), 2910 (s), 2840 (s), 1605 (w), 1448 (a), 1370 (m, shoulder at 1360 and 1350), 897 (s), and 887  $cm^{-1}$ ; NMR (CCl<sub>4</sub>): 0.75–2.6 (m, 11H), 2.85 (m, 2H) and 5.7–6.5 ppm (m, 3H).

**Reaction of DCPD with 2,3-dimethylbutane (18).** DCPD (0.5 g) was dissolved in 10 ml of 2,3-dimethylbutane. Irradiation and work-up as above gave two products, 18-1 and 2. They were identified as the insertion products of cyclopentadienyliene into tertiary and primary hydrogen bonds by comparison of their spectra with authentic samples.<sup>2</sup>

**Competition experiments.** In typical run, cyclohexane (10 mmole) was weighed and mixed with diethyl ether (10–20 mmole). 1.10 mmole of DCPD was added to the soln. The mixture, in a Pyrex test tube, was immersed in water bath (maintained at ca 20°) and irradiated for 2 h with the high pressure mercury lamp. After the reaction, the relative rates were derived directly by analysis of expected components appeared in VPC. Then, the relative values of  $k_\alpha$  or  $k_\beta$  can be obtained from the ratio of  $\alpha$ - or  $\beta$ -C—H insertion product to cyclohexane C—H insertion product, corrected for the initial concentration ratio of the reactants.

$$\alpha\text{-C—H} \quad \text{Relative rate} = k_\alpha/k_c \\ = [\text{cyclohexane}][\alpha\text{-C—H}]/[\text{Et}_2\text{O}][A]$$

$$\beta\text{-C—H} \quad \text{Relative rate} = k_\beta/k_c \\ = [\text{cyclohexane}][\beta\text{-C—H}]/[\text{Et}_2\text{O}][A]$$

A = Insertion product of cyclohexane.

**Reaction of DCPD with allyl ethyl ether.** Photolysis of 1.37 mmole of DCPD in 16.8 mmole of allyl ethyl ether gave the only addition product of cyclopentadienyliene on the double bond in 35% yield. The NMR spectrum had peaks at 1.15 (t, 3H), 1.67 (m, 2H), 2.22 (m, 1H), 3.40 (q, 2H), 3.53 (d, 2H), 6.0 (m, 2H) and 6.4 (m, 2H). The IR (neat) had prominent peaks at 3050 (w), 2950 (s), 2910 (m), 2845 (s), 1708 (w), 1677 (w), 1640 (w), 1620 (m), 1480 (m), 1152 (m), 1105 (s), 1050 (m), 813 (m), and 743  $cm^{-1}$  (s). (Found: C, 80.41; H, 9.67. Calcd for  $C_{10}H_{14}O$ : C, 79.95; H, 9.39%);  $m/e = 150$  (as expected).

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