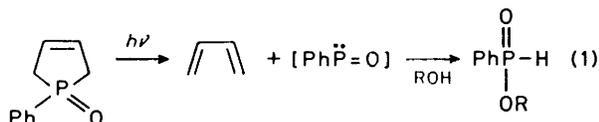


## Photochemistry of Phosholens. Part 7.<sup>1a</sup> Element Effects on the Photofragmentation of 3,4-Dimethyl-1-phenyl-3-phosphen. Phosphinothioylidene<sup>1b</sup>

By Hideo Tomioka,\* Shyoji Takata, Yoshio Kato, and Yasuji Izawa, Chemistry Department of Industry and Resources, Faculty of Engineering, Mie University, Tsu, Mie 514, Japan

Photolysis of 3,4-dimethyl-1-phenyl-3-phosphen 1-sulphide (1) in methanol afforded, in addition to the expected diene, *O*-methyl phenylphosphinothioate (3) and *OO*-dimethyl phenylphosphonothioate (4), whose composition was dependent on irradiation time. Compound (4) was shown to be a photolysis product of (3) in methanol. The rate and stereospecificities of the photo-extrusion of (2) are investigated and compared with that observed in the photofragmentation of the corresponding oxide. In proceeding from the oxide to the sulphide, the stereospecificities decreased in *cis*- $\alpha$ -methyl derivatives but increased in *trans*- $\alpha$ -methyl derivatives and the relative reactivities of the fragmentation decreased.

PREVIOUS studies<sup>2</sup> from this laboratory showed that 1-phenyl-3-phosphen 1-oxide, upon u.v. irradiation, efficiently cleaves to diene and phosphinidene oxide which is trapped by alcohol to give phenylphosphinate [equation (1)]. This photofragmentation was expected

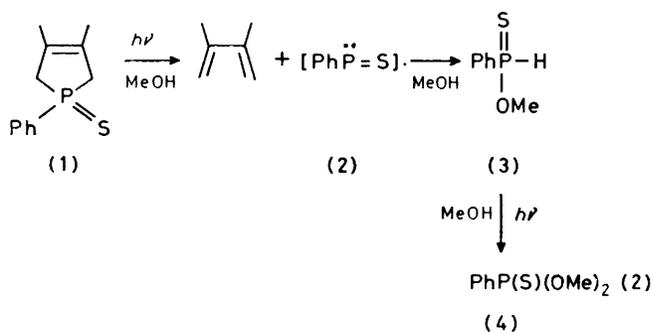


to be a convenient method to investigate the reactivity patterns of free phosphinidene oxide since most of other methods thus far reported<sup>3</sup> involve the use of high temperatures or a reactive metal which sometimes casts doubt on the strength of the evidence about the mode of the reactivity patterns of free phosphinidene oxide itself. In addition to the synthetic concerns described above, the reaction has attracted much attention as a member of a family of cheletropic reactions<sup>4</sup> because, in contrast to the other closely related five-membered cheletropic cycloreversions,<sup>5,6</sup> this system has an asymmetric leaving group and is expected to provide information on the relationship between the direction of ring opening and the stereochemical disposition of the leaving group. As expected, it has been shown<sup>7</sup> that the stereochemical disposition exerts a substantial effect not only on the direction of ring opening but on the rate of the fragmentation. As a continuing inquiry into the mechanistic details of the photofragmentation, as well as the scope and limitations of the method as a convenient route to the other important reactive phosphorus intermediates, *e.g.* metaphosphite and phosphinidenes, substituent effects on this new extrusion reaction were examined,<sup>8</sup> and showed that the presence of a phenyl group on phosphorus is required for the reaction to occur. As part of this study, we have examined the photolysis of 1-phenyl-3-phosphen 1-sulphide and found that the sulphide also undergoes cleavage to diene and phosphinothioylidene. In this paper we discuss the results of photo-extrusion and some reactions of phosphinothioylidene in terms of element effects on the stereochemical

course of the fragmentation and on the reactivity patterns of reactive phosphorus intermediates.

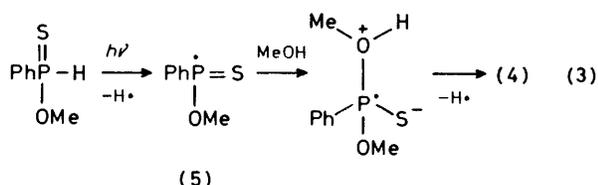
### RESULTS AND DISCUSSION

**Photoproducts.**—Photolysis of a methanol solution of 3,4-dimethyl-3-phosphen 1-sulphide (1) in a quartz tube was monitored by g.l.c., which revealed the gradual disappearance of starting material along with the formation of 2,3-dimethylbuta-1,3-diene. The presence of diene strongly indicates the transient existence of phenylphosphinothioylidene (2). After 14.5 h irradiation, the solution was evaporated and the resulting mixture was separated by silica gel chromatography. The only isolated phosphorus product was identified as *OO*-dimethyl phenylphosphonothioate (4) (27%), whose n.m.r. spectra showed a sharp 6-H doublet at  $\delta$  3.76 with  $J_{\text{PH}}$  12.0 Hz, characteristic of P-OCH<sub>3</sub>. The assignment was further supported by direct comparison of the thioate with a specimen prepared<sup>9</sup> independently by sulphurization of the corresponding phenylphosphonite.



The expected O-H insertion product (3) was not detected in this run. However, when irradiation was interrupted at low conversion (*ca.* 40%), the n.m.r. spectra of the reaction mixture showed a sharp doublet at  $\delta$  8.26 with a large coupling constant ( $J$  537 Hz), characteristic of the P-H group. Careful separation of the mixture by chromatography gave, in addition to the starting material and the phosphonothioate (4) (5.2%), a 6.0% yield of phosphinothioate (3), which was shown to be identical to

an authentic specimen prepared<sup>10</sup> from the phosphonite and H<sub>2</sub>S. The results suggest that the O-H insertion product (3), presumably an initial photoproduct, is quite photolabile and transformed to (4) upon u.v. irradiation [equation (2)]. This is further verified by controlled photolysis of (3) in methanol under identical conditions, which resulted in rapid formation of (4). The mechanism of this reaction must include the intermediacy of



the thiophosphino-radical (5) *via* initial photocleavage of the P-H bond since such cleavage has been frequently observed<sup>11</sup> in the photolysis of thiophosphino-compounds containing P-H bond(s). The next step in the reaction may be attack of the electron-deficient thiophosphino-radical on the oxygen atom of methanol rather than the abstraction of H from an O-H bond in view of the large dissociation energy of this bond [equation (3)]. The mechanism was originally introduced by Trippett<sup>12</sup> for the reaction of the phosphino-radical with methanol, and was also employed<sup>13</sup> to account for the formation of *O*-methyl diphenylphosphinothioate in the photolysis of diphosphine disulphide in methanol.

All attempts to trap phosphinothioylidene (2) with other reported trapping agents for a reactive phosphorus intermediate, *i.e.* diene,<sup>14</sup> ethers,<sup>15</sup> and amine<sup>16</sup> were unsuccessful. Thus, irradiation of (1) in acetonitrile resulted in gradual disappearance of the starting material accompanied by the formation of the diene. Examination of the n.m.r. spectrum of the reaction mixture, however, showed no proton signals attributable to the phosphorin structure. Although similar irradiations were carried out in the presence of diethyl ether or diethylamine, neither phosphorin nor the expected C-O or N-H insertion products were isolated.<sup>17</sup>

**Excited-state Multiplicity.**—Addition of 2,5-dimethylhexa-2,4-diene greatly reduced the formation of 2,3-dimethylbutadiene in the photolysis of (1). Stern-Volmer treatment of the quenching data gave linear plots whose slope was found to be 282 l mol<sup>-1</sup>. Fluorescence from (1) was also found to be quenched by the hexa-2,4-diene but its Stern-Volmer slope (6.8 l mol<sup>-1</sup>) was not identical with that for diene generation. The results clearly indicate that the photofragmentation of the sulphide occurs from the triplet excited state. This is in marked contrast to that observed<sup>7</sup> for the phospholen oxide, which undergoes photocleavage *via* the excited singlet state.

**Methyl Substituent Effect.**—For the purposes of evaluating how structural features affect the efficiency of the fragmentation, several methyl-substituted 3-phospholen sulphides were synthesized and the relative

apparent rate of diene generation from each sulphide was determined. Perusal of the results in Table I reveals similar but less drastic trends of methyl substituent effects on the rate compound with those observed<sup>7</sup> in the photofragmentation of the oxide. Thus, β- as well as *cis*-α-methylation enhances the rate, whereas *trans*-α-methylation reduces it. The trend is of special interest in connection with the fact that β-methylation has been shown<sup>5c</sup> to reduce the rate of thermal sulphur dioxide extrusion from sulpholen, presumably by stabilizing the starting material. It appears that product (diene) stabilities have some influence on the transition state in the present reaction. It should be noted that the replacement of the oxygen on phosphorus by sulphur also reduces the rate as well as the effectiveness of the methyl substituents on the rate. This, along with the marked dependence of the rate on the stereochemical disposition

TABLE I  
Relative rate of diene generation in the photolysis of  
3-phospholen 1-sulphide and 1-oxide

3-Phospholens	Relative rate <sup>a</sup>
<b>Sulphide</b>	
Parent <sup>b</sup>	1.0
3-Methyl-	1.1
3,4-Dimethyl- (1)	1.7
<i>trans</i> -2-Methyl- ( <i>t</i> -6a)	0.4
<i>cis</i> -2-Methyl- ( <i>c</i> -6a)	1.3
<i>cis,cis</i> -2,5-Dimethyl- ( <i>c,c</i> -7a)	4.5
<b>Oxide</b>	
Parent <sup>b</sup>	1.4
3-Methyl-	15.9
3,4-Dimethyl-	77.0
<i>trans</i> -2-Methyl- ( <i>t</i> -6b)	2.7
<i>cis</i> -2-Methyl- ( <i>c</i> -6b)	12.3
<i>trans,trans</i> -2,5-Dimethyl- ( <i>t,t</i> -7b)	1.8
<i>cis,cis</i> -2,5-Dimethyl- ( <i>c,c</i> -7b)	30.5

<sup>a</sup> Determined by g.l.c. analysis of total diene production upon simultaneous irradiation on a merry-go-round apparatus at room temperature. <sup>b</sup> Unsubstituted 1-phenyl-3-phospholen derivative.

of the α-methyl group, clearly suggests that the steric strain in the transition state is substantial.

**Stereochemistry.**—It is very interesting to explore the element effect, *i.e.* that of oxygen and sulphur, on the stereochemical course of the photofragmentation since such a study would be expected to provide additional insight into the nature of the ring opening. Therefore, 2-methyl- and 2,5-dimethyl-3-phospholen 1-sulphide were synthesized by treatment of the corresponding McCormack adduct with H<sub>2</sub>S and the resulting diastereoisomeric sulphides were separated into isomerically pure derivatives by repeated chromatography on silica gel. Configurational assignments as well as the purity (>99.9%) of each isomer are based on the n.m.r. spectra, showing that the methyl group *cis* (*c*) to phenyl always resonates at higher field compared to that of the *trans* (*t*) isomer\* (see Experimental section). All irradiations were interrupted at very low conversion (<2%) and yields of 1,3-diene were extrapolated to zero conversion

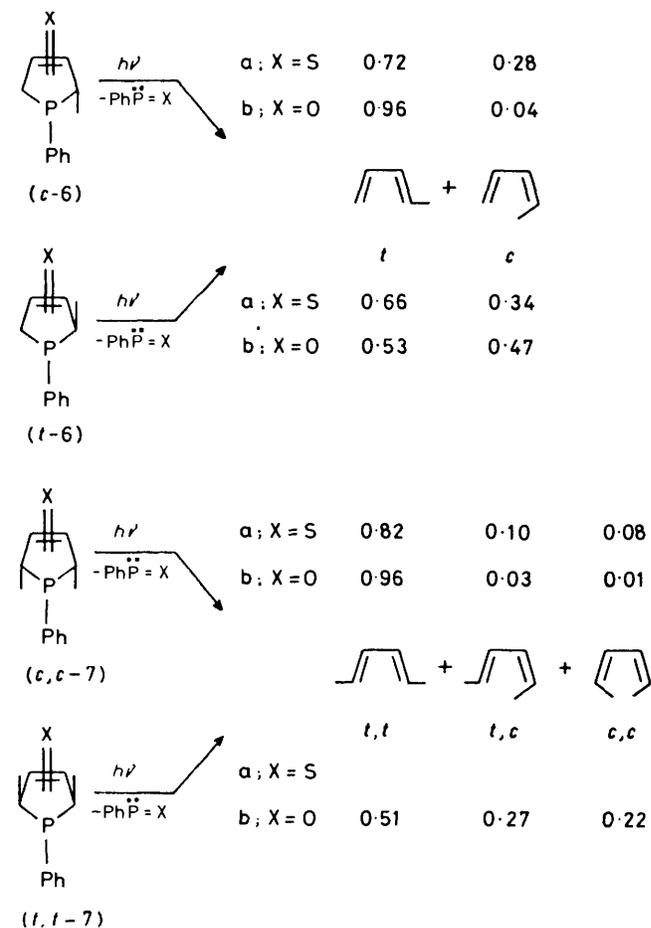
\* The symbols *c* and *t* refer to *cis*- and *trans*-orientation of phenyl with respects to the methyl(s).

as an appropriate correction for possible sensitized diene isomerization by the sulphide. The results are summarized in the Scheme along with those obtained <sup>7</sup> in the oxide photolysis for comparison. As is evident from the data, the complete lack of stereospecificity but marked dependence of diene composition upon the geometrical structure of the sulphide are noted also in this fragmentation. This is very reminiscent of other closely related photoextrusion reactions, *i.e.* photo-decarbonylation <sup>6b</sup> and -desulphonation, <sup>6a</sup> which also proceed with low stereospecificity to afford the mixture of stereoisomeric dienes, depending on the configuration of the starting material, whereas the related thermal processes have been shown <sup>5</sup> to be completely stereospecific. The apparent non-stereospecificity in the photodecarbonylation of cyclopent-3-enone has been interpreted, <sup>6b</sup> however, as a consequence of dual *linear and nonlinear concerted* pathways <sup>4</sup> without invoking two-step sequential mechanism leading to the loss of stereochemistry. Dependence of diene composition upon the geometrical configuration of the sulphide clearly eliminates a common triplet biradical intermediate capable of significant stereochemical loss in this reaction. Then, the present stereochemical results can also be explained in terms of steric forces operative during the *concerted* bond reorganization necessary for PhP=S extrusion, as has been employed <sup>7</sup> to explain similar stereochemical results of the PhP=O extrusion. As disrotatory bond rotation in (*c,c*-7) commences to give *c,c*-diene, for example, the two methyl groups are effectively brought into close proximity to the phenyl group. The conrotatory counterpart to give *t,c*-diene suffers from 1,2-phenyl-hydrogen and nonbonded methyl-hydrogen interactions occurring in the rotation. Such repulsive forces, which are absent when disrotation to *t,t*-diene is effected, are apparently sufficient to raise the energy of activation associated with rotation to *t,c*- and *c,c*-dienes to an extent which permits dominant formation of the *t,t*-diene.

One noteworthy feature of the results listed in the Scheme is that the replacement of oxygen by sulphur reduces the stereospecificity in the fragmentation of *cis*- $\alpha$ -methyl derivatives but, on the other hand, increases the stereospecificity in the reaction of the *trans*- $\alpha$ -methyl derivative. These effects also seem to reflect similar steric forces during the rotational process above and are explained in terms of the difference in van der Waals radius and/or lone-pair repulsions between the two elements.<sup>18</sup> Thus, in the *cis*- $\alpha$ -methyl derivative of the sulphide [(*c*-6a) and (*c,c*-7a)], the repulsion between a sulphur lone-pair and hydrogen on the  $\alpha$ -carbon during the disrotatory bond rotation is obviously substantially greater than in the corresponding oxides and hence would serve to destabilize the transition state for *t,t*-diene formation. Consequently, the substantial increase in the relative yield of *c,t*- and *c,c*-dienes is observed in the PhP=S extrusion. Similarly, inward, presumably disrotatory, methyl rotation to give *cis*-diene in the *trans*-sulphide should be more substantially hindered by methyl-sulphur lone-pair repulsion than that in the oxide.

An alternative explanation involves a consideration of conformational effects. Thus, with the all-*cis* oxide, the ground state is already distorted with all carbon substituents in the pseudo-equatorial position, owing to the methyl-phenyl non-bonded repulsion along with a pathway which could lead to *t,t*-diene.<sup>19</sup> In the all-*cis* sulphide, on the other hand, such distortion might induce sulphur-hydrogen repulsion and hence becomes less important.

One cannot exclude a two-step mechanism since such considerations can equally be applied to mechanisms involving phosphorus-centred biradicals or zwitterions which retain their configuration during the time scale of



SCHEME

the reaction. Moreover, the fact that even a rather long-lived intermediate can possess sufficient stereochemical integrity, as has been shown <sup>20</sup> in the SO-diene cycloaddition, might support the two step-mechanism. It has been shown,<sup>21</sup> however, that, while phosphoranyl and phosphoryl radicals are configurationally stable, a radical from optically active hydrogenphosphinothionate undergoes partial racemization. One would expect, then, a decrease in stereospecificity in proceeding from the oxide to the sulphide, if one assumes a stepwise mechanism involving a phosphorus centred radical. The reverse is true in the case of the *trans*-2-methyl deri-

vatives as noted above. Moreover, no photochemical *cis-trans* isomerization of the starting sulphide was observed even after prolonged irradiation.

The methyl substituent effect on the relative rate can also be explained in terms of the difference in steric strain in the transition state. The acceleration of the decomposition by *cis-α*-methylation, as well as its reduction by *trans-α*-methylation, apparently indicate the importance of the steric strain during bond reorganization. A similar configurational effect of an  $\alpha$ -methyl group on the rate of decomposition has been observed<sup>5e</sup> in the concerted SO<sub>2</sub> extrusion from sulpholen. The lowering of the reactivity in going from the oxide to the sulphide is also attributable to the increase in the steric strain. Thus, even the parent sulphide would suffer from hydrogen-sulphur repulsion in addition to the 1,2-hydrogen-phenyl interaction occurring in each mode of rotation, whereas hydrogen-oxygen repulsion should be less important in the corresponding oxide. Finally, it should be noted that the rate of  $\alpha$ -cleavage to give biradicals is enhanced only by  $\alpha$ -methylation in the photolysis<sup>22</sup> of cycloalkanone derivatives.

#### EXPERIMENTAL

**General.**—I.r spectra were determined on a JASCO IR-G recording spectrometer. <sup>1</sup>H N.m.r. spectra were determined on a JEOL JNM-MH-100 n.m.r. spectrometer: chemical shifts are reported in  $\delta$  downfield from Me<sub>4</sub>Si. U.v. and fluorescence spectra were measured with a Shimadzu UV 250 recording spectrometer and a Hitachi

prepared according to the procedure of Bartlett.<sup>24</sup> All other dienes were obtained from commercial sources. 1-Phenyl-3-phospholen 1-sulphides were prepared by cycloaddition of dienes and phenylphosphonous dibromide, followed by the treatment of the resulting adducts with H<sub>2</sub>S in benzene according to the procedure of Quin.<sup>25</sup> A mixture of the diastereoisomeric 2-methyl-3-phospholen 1-sulphides (6a) was obtained from the adduct between the phosphonous dibromide and isomeric mixture of penta-1,3-diene. The mixture was chromatographed on silica gel with ether-light petroleum (5:95) as eluant to give an isomerically pure sample [*c*- and *t*-6a] as a liquid. Likewise diastereoisomeric mixtures of 2,5-dimethyl derivatives (7a) was obtained from the adduct with hexa-2,4-dienes. Chromatography of the mixture gave only (*c,c*-7a) as a solid, m.p. 67–68 °C, along with 2-phospholen 1-sulphide. Further attempt to isolate the *t,t*-isomer was unsuccessful. <sup>1</sup>H N.m.r. data for the starting materials are collected in Table 2.

*O*-Methyl phenylphosphinothioate (3) was prepared<sup>10</sup> by the reaction of dimethyl phenylphosphonite<sup>26</sup> with H<sub>2</sub>S in benzene in the presence of *NN*-diethylaniline, followed by distillation, b.p. 101–102 °C at 1 mmHg (lit.,<sup>10</sup> b.p. 100° at 1 mmHg);  $\delta$  (CDCl<sub>3</sub>) 3.80 (3 H, d, *J* 12.0 Hz, P-OCH<sub>3</sub>), 8.26 (1 H, d, *J* 537 Hz, P-H), and 7.30–8.10 (5 H, m, C<sub>6</sub>H<sub>5</sub>).

*OO*-Dimethyl phenylphosphonothioate (4) was prepared<sup>9</sup> by the sulphurization of the phosphonite with atomic sulphur in dry benzene, b.p. 103–104 °C at 0.4–0.5 mmHg;  $\delta$  (CDCl<sub>3</sub>) 3.76 (6 H, d, *J* 12.0 Hz, P-OCH<sub>3</sub>) and 7.50–8.08 (5 H, m, C<sub>6</sub>H<sub>5</sub>).

**Irradiations.**—All irradiations were conducted using a Halos 300-W high-pressure mercury lamp and a water-cooled quartz immersion well. The solution was purged with nitrogen before and during the irradiation. The progress of the photochemical reactions was monitored by g.l.c. analysis of portions removed periodically. For product identification, the irradiation mixtures were concentrated on a rotary evaporator, and individual components were isolated by silica gel column chromatography and characterized by direct comparison with authentic specimens. The irradiations outlined in Tables 1 and 2 were conducted in a sealed quartz tube of 5.0-ml capacity strapped to an immersion well. Control runs showed that no reaction occurred in the absence of light.

**Irradiation of 3,4-Dimethyl-1-phenyl-3-Phospholen 1-Sulphide (1).**—(A) *In methanol.* In a typical run, irradiation of the sulphide (1) (2.0 g) in methanol (240 ml) under nitrogen for 15 h followed by isolation of the major product by column chromatography, eluted with ether-light petroleum (4:6), afforded (3) (93 mg, 6.0%) and (4) (95 mg, 5.2%), both of which were identical in all respects with the authentic specimens prepared above. When similar irradiation was conducted for 24 h, only (4) (491 mg, 27%) was isolated. No other volatile product except an intractable yellow oil was isolated.

(B) *In other solvents.* A solution of (1) (2.0 g) in appropriate solvents, e.g. acetonitrile, diethyl ether, tetrahydrofuran, and dioxan (200–250 ml) was irradiated for 50 h under nitrogen. Detection of the diene in each run indicated the intervention of (2). Chromatography of the resulting mixtures afforded only intractable polymeric material in addition to the starting material.

**Diene Compositions in the Photolysis of (6) and (7).**—A solution 20mm-sulphide in 5.0 ml of methanol was irradiated at room temperature. Portions were removed at intervals of

TABLE 2  
<sup>1</sup>H N.m.r. data of 3-phospholen 1-sulphides

Compounds	$\delta^a$		
	—CH	C—CH <sub>3</sub>	—CH <sub>2</sub>
Parent	0.03 (d, <i>J</i> 30.0 Hz)		3.03 (d, <i>J</i> 10.5 Hz)
3-Methyl-	5.63 (d, <i>J</i> 32.0 Hz)	1.92 (s)	2.75–3.10 (m)
3,4-Dimethyl-		1.77 (s)	2.76 (d, <i>J</i> 16.3 Hz)
<i>trans</i> -2-Methyl-	6.00 (d, <i>J</i> 28.3 Hz)	1.36 (d,d, <i>J</i> 8.0 and 19.2 Hz)	2.60–3.80 (m)
<i>cis</i> -2-Methyl-	5.56–6.28 (m)	0.88 (d,d, <i>J</i> 8.0 and 18.7 Hz)	2.76–3.52 (m)
<i>cis,cis</i> -2,5-Dimethyl- <sup>b</sup>	5.91 (d, <i>J</i> 25.0 Hz)	1.00 (d,d, <i>J</i> 7.0 and 18.2 Hz)	3.12–3.74 (m)

<sup>a</sup> Multiplet at  $\delta$  ca. 7.2–7.9 attributable to P-Ph appears in all compounds. <sup>b</sup> For the <sup>1</sup>H n.m.r. data of the corresponding phospholen and its oxide, see G. Scott, P. J. Hammond, and C. D. Hall, *J.C.S. Perkin II*, 1977, 882.

MPF-2A spectrofluorometer, respectively. G.l.c. analyses were performed on a Yanagimoto instrument model G-80 using a 2.0 m × 5.0 mm column packed with (a) 5% silicon OV-17 for high boiling products and (b) 10% ODPN on 60–80 mesh Diasolid L for diene analysis. Woelm silica gel (activity III) was always used for column chromatography.

**Materials.**—2,3-Dimethylbuta-1,3-diene was prepared<sup>23</sup> by dehydration of pinacol and hexa-2,4-dienes were

1 min and the diene compositions were determined by g.l.c. and plotted against the irradiation times. All irradiations were interrupted at very low conversion (<2%). Diene compositions at zero conversion were easily determined from linear plots against irradiation time. Reaction conditions, *i.e.* solvent, temperature, and wavelength of light, did not affect the diene compositions.

We thank Professor L. D. Quin for disclosure of his results prior to publication and Dr. R. Okazaki for sending us the spectra and samples of 3,5-dihydro-1,2-thiaphosporin derivatives.

[9/1371 Received, 29th August, 1979]

#### REFERENCES

- <sup>1</sup> (a) Part 6, H. Tomioka, K. Sugiura, S. Takata, Y. Hirano, and Y. Izawa, *J. Org. Chem.*, 1977, **42**, 3070; (b) presented in part at the 37th Annual Meeting of the Chemical Society of Japan, Yokohama, 1978, Abstract 3M43.
- <sup>2</sup> H. Tomioka, Y. Hirano, and Y. Izawa, *Tetrahedron Letters*, 1974, 1865.
- <sup>3</sup> For reviews, see U. Schmidt, *Angew. Chem. Internat. Edn.*, 1975, **14**, 523.
- <sup>4</sup> R. B. Woodward and R. Hoffman, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970.
- <sup>5</sup> For stereochemical studies of thermal five-membered ring cheletropic reactions, see (a) S. D. McGregor and D. M. Lemal, *J. Amer. Chem. Soc.*, 1966, **88**, 2858; (b) W. L. Mock, *ibid.*, p. 2857; (c) D. M. Lemal and S. D. McGregor, *ibid.*, p. 1335; (d) J. E. Baldwin, *Canad. J. Chem.*, 1966, **44**, 2051; (e) W. L. Mock, *J. Amer. Chem. Soc.*, 1975, **97**, 3666, 3673, and references cited therein.
- <sup>6</sup> For stereochemical studies of photochemical five-membered ring cheletropic reactions, see (a) J. Saltiel and L. Metts, *J. Amer. Chem. Soc.*, 1967, **89**, 2232; (b) T. R. Darling, J. Pouliquen, and N. J. Turro, *ibid.*, 1974, **96**, 1247.
- <sup>7</sup> H. Tomioka and Y. Izawa, *J. Org. Chem.*, 1977, **42**, 582.
- <sup>8</sup> (a) H. Tomioka, Y. Hirano, and Y. Izawa, *Tetrahedron Letters*, 1974, 4477; (b) H. Tomioka, S. Nakamura, T. Ohi, and Y. Izawa, *Bull. Chem. Soc. Japan*, 1976, **49**, 3707.
- <sup>9</sup> L. I. Mizrakh and V. P. Evdakov, *Zhur. obshchei Khim.*, 1966, **36**, 469.
- <sup>10</sup> R. Schliebs, *Z. Naturforsch.*, 1970, **25b**, 111.
- <sup>11</sup> For examples, K. Kumamoto, H. Yoshida, T. Ogata, and S. Inokawa, *Bull. Chem. Soc. Japan*, 1969, **42**, 3245.
- <sup>12</sup> R. S. Davidson, R. A. Sheldon, and S. Trippett, *J. Chem. Soc. (C)*, 1969, 722.
- <sup>13</sup> T. Emoto, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Japan*, 1973, **46**, 898.
- <sup>14</sup> S. Nakayama, M. Yoshifuji, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Japan*, 1975, **48**, 546.
- <sup>15</sup> S. Nakayama, M. Yoshifuji, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Japan*, 1975, **48**, 3733.
- <sup>16</sup> H. Tomioka, T. Fujii, and Y. Izawa, unpublished observations.
- <sup>17</sup> See for examples, (a) W. Lwowski, 'Nitrenes,' Interscience, New York, 1970; (b) W. Kirmse, 'Carbene Chemistry,' Academic Press, New York, 1971, 2nd edn.
- <sup>18</sup> P. E. Stevenson, G. Bhat, C. H. Bushweller, and W. G. Anderson, *J. Amer. Chem. Soc.*, 1974, **96**, 1607.
- <sup>19</sup> Treatments of a similar nature have been employed to account for the various processes observed when pyrazolines lose nitrogen; R. Daniel-Bougout and R. Garrié, *Bull. Soc. chim. France*, 1969, 313.
- <sup>20</sup> P. Chao and D. M. Lemal, *J. Amer. Chem. Soc.*, 1973, **95**, 920, 922.
- <sup>21</sup> (a) L. P. Reiff and H. S. Aaron, *J. Amer. Chem. Soc.*, 1970, **92**, 5275; (b) L. S. Szafraniec, L. P. Reiff, and H. S. Aaron, *ibid.*, p. 6392.
- <sup>22</sup> (a) J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Barltrop, and J. D. Coyle, *J. Amer. Chem. Soc.*, 1971, **93**, 7213; (b) P. S. Engle, M. A. Schexnayder, H. Ziffer, and J. I. Seeman, *ibid.*, 1974, **96**, 924.
- <sup>23</sup> C. F. H. Allen and A. Bell, *Org. Synth.*, 1955, Coll. Vol. 3, 312.
- <sup>24</sup> P. D. Bartlett, C. J. Dempster, L. K. Montgomery, K. E. Schueller, and G. E. H. Wallbillich, *J. Amer. Chem. Soc.*, 1969, **91**, 405.
- <sup>25</sup> C. Symmes, jun., and L. D. Quin, *J. Org. Chem.*, 1976, **41**, 1548.
- <sup>26</sup> A. E. Arbuzov and A. I. Razumov, *Doklady Akad. Nauk S.S.S.R.*, 1945, 167.