

19543-04-5; 16b, 19613-62-8; 16c, 19543-05-6; residue E, 19543-06-7; 17, 19543-07-8; 19, 19543-08-9; 20, 19543-09-0; 21a, 19543-10-3; 21b, 19543-11-4; 22, 19624-50-1; 24, 19543-12-5; 26, 19543-13-6; 28,

19543-14-7; 30, 19614-21-2; 31, 19614-22-3; 32, 19581-57-8; 33, 19553-07-2; 34b, 19581-58-9; 35, 19614-23-4; 37, 19581-59-0; 38, 19553-08-3; 39a, 19553-09-4; 39b, 19553-10-7; 40, 19553-11-8; 41, 19553-12-9.

## Studies on the Mechanism of Decomposition of Alkyl Diphenylphosphinates<sup>1</sup>

K. DARRELL BERLIN, JOHN G. MORGAN,<sup>2</sup> MELBERT E. PETERSON,<sup>3</sup> AND W. C. PIVONKA<sup>4</sup>

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074

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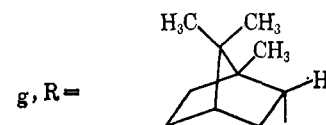
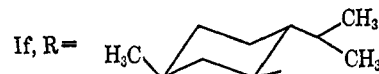
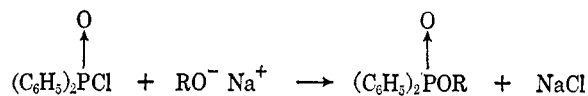
The following esters of diphenylphosphinic acid have been prepared and pyrolyzed: 3-phenylpropyl (Ia), 1,2-diphenylethyl (Ib), *trans*-2-methylcyclohexyl (Ic), *cis*-2-methylcyclohexyl (Id), 2-phenylethyl (Ie), menthyl (If), and bornyl (Ig). Pyrolysis was conducted in a static system under N<sub>2</sub> at atmospheric pressure or in a boiling solvent [dimethyl sulfoxide (DMSO) or diphenyl ether]. Although a concerted mechanism is used to explain most of the thermal pyrolyses, decomposition of Ia, If, and particularly Ig gives pyrolysates containing several alkenes which suggests an ionic process perhaps involving ion pairs. In boiling DMSO, Ic and Id appear to decompose by an E2 mechanism.

A recent report indicated the usefulness of the pyrolytic decomposition of alkyl diphenylphosphinates I in the preparation of olefins.<sup>5</sup> A mechanism was postulated to involve a cyclic transition state. Several new esters (see Table I) have been prepared and pyrolyzed with the intent of further elucidating this reaction mechanism. From the new results herein, it is apparent that a concerted cyclic mechanism cannot account for the product distribution.

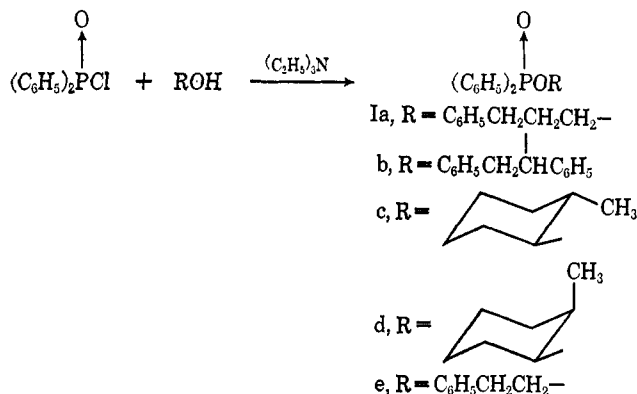
The selected esters used in this study were prepared by the reaction of the appropriate alcohol with diphenylphosphinic chloride in the presence of triethylamine<sup>6</sup> (method I), or by the reaction of diphenylphosphinic chloride with the sodium salt of the alcohol in toluene (method II). Pyrolysis was effected in a static system under a nitrogen atmosphere at atmospheric

reactions were, in all cases, apparently complete within 15 min.

### Method II



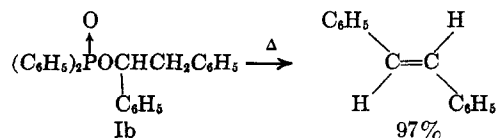
### Method I



pressure or in the presence of a boiling solvent [dimethyl sulfoxide (DMSO) or diphenyl ether]. Once the pyrolysis temperatures (Table II) were reached, the

When 3-phenylpropyl diphenylphosphinate (Ia) was pyrolyzed (Table II) at 185°, a mixture containing 78% allylbenzene and 22% 1-phenyl-1-propene was obtained. When the terminal alkene was heated to 200° (15° above the pyrolysis temperature) for 45 min in a sealed tube, both neat and in the presence of diphenylphosphinic acid, no detectable isomerization occurred. It appears then that the isomeric alkenes must arise directly as a consequence of the mechanism of the decomposition. However, one might anticipate formation of a greater amount of the more conjugated 1-phenyl-1-propene in the event of a carbonium ion involvement. Allylbenzene has been prepared in 76% yield by the pyrolysis of 3-phenyl-1-propyl acetate.<sup>7</sup>

Pyrolysis of 1,2-diphenylethyl diphenylphosphinate (Ib) resulted in essentially complete conversion into



*trans*-stilbene. In both a static pyrolysis (220–240°) and in DMSO (190°) the *trans* isomer was obtained in high yield. Examination of Newman projection formulas of the transition states leading to the two stilbenes

(1) We gratefully acknowledge partial support of this research by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-132-67. Partial support by the Research Foundation, Oklahoma State University, is also acknowledged.

(2) NDEA Fellow, Predoctoral Candidate, 1966–1969.

(3) Predoctoral Candidate 1964–1967; NSF Cooperative Fellow, 1965–1966.

(4) NSF College Teacher Research Participant, summer 1965.

(5) K. D. Berlin and T. H. Austin, *J. Org. Chem.*, **30**, 2745 (1965).

(6) K. D. Berlin, T. H. Austin, and M. Nagabhushanam, *ibid.*, **30**, 1267 (1965).

(7) A. W. Fort and J. D. Roberts, *J. Amer. Chem. Soc.*, **78**, 587 (1956).

TABLE I  
 PHOSPHINIC ESTERS, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(O)OR

Ester	Yield, %	Mp, °C	Ir, μ		Calcd. %			Found, %		
			P→O	P—O—C	C	H	P	C	H	P
Ia	91.0	69.5–70	8.22	9.95	74.99	6.29	9.51	74.82	6.31	9.35
Ib	82.5	142–143	8.22	10.0	78.38	5.82	7.77	78.73	5.94	7.29
Ic	68.0	73–74	8.13	9.90	72.59	7.38	9.85	72.63	7.40	10.04
Id	78.0	84–85	8.15	9.95	72.59	7.38	9.85	72.59	7.27	9.97
If <sup>a</sup>	51.2	72–73	8.17	9.87	74.13	8.20	8.69	74.17	8.15	8.69
Ig <sup>b</sup>	53.8	74–75	8.13	9.78	74.55	7.68	8.74	74.61	7.66	9.01

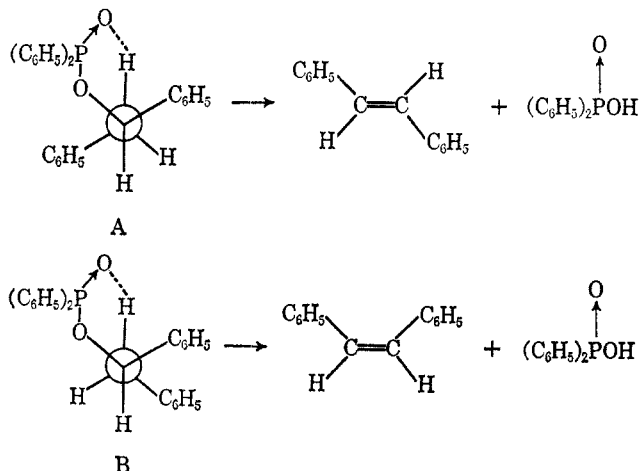
<sup>a</sup> [α]<sub>D</sub><sup>25</sup> -73.0° (8.280 g/100 ml of CHCl<sub>3</sub>). <sup>b</sup> [α]<sub>D</sub><sup>25</sup> -14.3° (5.892 g/100 ml of CHCl<sub>3</sub>).

 TABLE II  
 PYROLYSIS DATA OF PHOSPHINIC ESTERS<sup>a</sup>

Ester	Solvent	Pyrolysis temp, <sup>b</sup> °C	Yield, <sup>c</sup> %	Product distribution					
				Products	%				
Ia	Neat	185	Quant.	Allylbenzene	78.1				
				1-Phenyl-1-propene					
Ib	Neat	210–240	88	<i>trans</i> -Stilbene	18.70				
				<i>cis</i> -Stilbene	2.91				
	DMSO	184–190	65	<i>trans</i> -Stilbene	96.9				
				<i>cis</i> -Stilbene	3.1				
Ic <sup>d</sup>	Neat	200–220	93	Cyclohexenes, %					
				1-Methyl-	3-Methyl-				
				60.25	39.75				
				Ic	DMSO	185–192	48	1.0	99.0
				Ic	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> O	210–235	90	54.6	45.4
				Ic	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> O + hydroquinone	210–234	86	53.8	46.2
				Id <sup>d</sup>	Neat	190–210	75	91.80	9.20
				Id	DMSO	184–186	56	43.87	56.1
				Id	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> O	200–235	90	88.16	11.84
				If	Neat	220–260	88	Products	
<i>p</i> -Menth-2-ene (100% optically pure)	42								
<i>p</i> -Menth-3-ene (71% optically pure)	54								
Isomeric menthenes	4								
Ig	Neat	220–260	96	Bornylene	1.4				
				Tricyclene	21.2				
				Camphene (38% optically pure)	77.6				

<sup>a</sup> A minimum of two pyrolyses was examined with each ester. <sup>b</sup> After the indicated temperature is reached, completion of pyrolysis takes approximately 15 min or less. <sup>c</sup> Percentage yields were determined by glpc using standard solutions. <sup>d</sup> Only the 1- and 3-methyl cyclohexenes were observed in the pyrolysates.

reveals that steric interactions are at a minimum in conformation A, thus favoring the formation of the *trans* isomer. In transition state B *gauche* interactions between the bulky phenyl groups would be expected to reduce greatly the stability of this transition state.



The isomerization of *cis*- to *trans*-stilbene under reaction conditions is catalyzed by heat and acid (Table III). When *cis*-stilbene was heated (neat) under N<sub>2</sub> for 40 min (220–240°), glpc analysis of the mixture revealed a 75:25 ratio of *cis*- to *trans*-alkene. When an equivalent amount of diphenylphosphinic acid was added to *cis*-stilbene under identical conditions, the amount of *trans*-stilbene was markedly increased (55% *cis*, 45% *trans* isomer). Thus it is probable that not much *cis*-stilbene is formed in the pyrolysis of Ib.

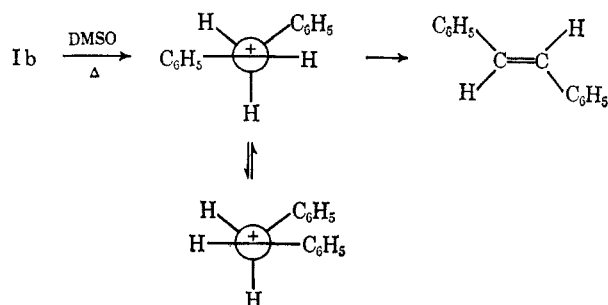


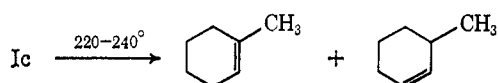
TABLE III  
 PRODUCT EQUILIBRATION STUDIES

Compd	Catalyst and solvent	Temp, °C	Time, hr	Products, %		
				Allylbenzene	<i>cis</i> -1-phenyl-1-propene	<i>trans</i> -1-Phenyl-1-propene
Allylbenzene <sup>a</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)OH	200	0.75	100	0	0
Cyclohexene derivative				1-Methylcyclohexene	3-Methylcyclohexene	
3-Methyl	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)OH	102-120	1.0		100	
1- and 3- <sup>b</sup> methyl	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)OH in diphenyl ether	90-105	3.0	46.5		54.4
1-Methyl	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)OH in DMSO	160-177	3.0	84.84		15.16
1-Methyl <sup>c</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)OH in DMSO, 0.5% water added	135	2.0	58.66		41.34
				<i>cis</i> -Stilbene	<i>trans</i> -Stilbene	
<i>cis</i> -Stilbene	Heat	220-245	1.0	75.3	24.7	
	Heat + acid	220-245	0.8	55.4	46.5	
<i>trans</i> -Stilbene	Heat + acid	210-240	1.0	2.2	97.8	
				Bornylene	Camphene	Tricyclene
Bornylene <sup>a</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)OH	220-260	0.75	4.7	64.1	31.2
Bornylene <sup>a</sup>	Neat	220-260	0.75	94.0	4.2	1.8

<sup>a</sup> Sealed tube. <sup>b</sup> The initial ratio of 1-:3-methylcyclohexene was 46.5:54.4. <sup>c</sup> Water was added to the above sample after 1 hr heating period. The mixture was then heated for an additional 2-hr period.

That an ionic E1 type of mechanism might be operative in DMSO with Ib must be considered in light of work reported by Nace.<sup>8</sup> DMSO was found to be effective in promoting the decomposition of sulfonic esters by an ionic pathway.<sup>8</sup> However, since pyrolysis of Ib proceeding through either an E1 or concerted elimination process would be expected to lead to a predominance of *trans*-stilbene, it is not possible to distinguish between the two processes in DMSO.

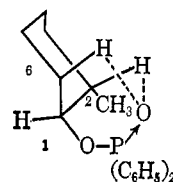
Pyrolysis of neat *trans*-2-methylcyclohexyl diphenylphosphinate (Ic) at 220-240° gave a mixture of 1- and 3-methylcyclohexene in a ratio of 60.25:39.75. The possibility does exist that after formation of the 3 isomer an isomerization (acid catalyzed) to the 1-alkene could occur. However, attempts to isomerize 3-methylcyclo-



hexene under these conditions (Table III) were unsuccessful.<sup>9</sup> Had an equilibrium been established, one would expect to find evidence of the 4 isomer as well as methylenecyclohexane; neither isomer was detected in any of the isomerization studies.

The nearly statistical ratio of 1- and 3-methylcyclohexene obtained from Ic suggests a *cis*-concerted process but does not rule out a mechanism involving ion pairs. Both the *cis* protons at C-2 and C-6 are readily accessible to the phosphoryl oxygen in a cyclic transition state. The predominance of the 1-methylcyclohexene is reminiscent of the higher ratio of Saytzeff to Hoffmann

alkene in the pyrolysate of such esters as menthyl<sup>10</sup> and *trans*-2-phenylcyclohexyl xanthate.<sup>11</sup>



The *cis*-2-methylcyclohexyl ester Id, when pyrolyzed, led to a 91.80:8.20 ratio of 1-:3-methylcyclohexene. This result is clearly inconsistent with a *cis*-concerted mechanism since no simple conformation of Id can be imagined from examination of models in which the tertiary proton at C-2 alone is available for abstraction. Indeed, there is some evidence from nmr data that the ground state of Id may be that conformer in which the ester function is axial, in which case only the secondary hydrogens are available to form a pseudoheterocyclic transition state. The hydroxy function in *cis*-2-methylcyclohexanol is assigned the axial position due to the apparent deshielding of the proton geminal to the hydroxy group in the *trans* (equatorial) isomer, relative to the proton geminal to the hydroxy group of the *cis* isomer.<sup>12</sup> The resonances of the counterpart protons in the *cis*- and *trans*-diphenylphosphinic esters bear the same relative relationship (in DCCl<sub>3</sub>) as in the case of the alcohols;<sup>13</sup> this suggests the axial position for the ester function of the *cis* isomer. There is, of course, no requirement that the actual transition state resemble the ground-state configuration. The predominance of the 1-alkene product contrasts markedly with the re-

(8) H. R. Nace, *J. Amer. Chem. Soc.*, **81**, 5428 (1959).

(9) A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell, and Z. Jacura [*J. Amer. Chem. Soc.*, **82**, 1750 (1960)] equilibrated 1-methylcyclohexene and methylenecyclohexene in the presence of *p*-toluenesulfonic acid in acetic acid. Only the *exo* and *endo* isomers were found; no other methylcyclohexenes were detected. The implication is that under the mildly acidic conditions employed in our pyrolysis no isomerization to the 3 isomer occurs. The low solubility of diphenylphosphinic acid in the 3- and 1-methylcyclohexene may be the reason that no isomerization of the 3 isomer was observed.

(10) For a review of these pyrolyses, see C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431, 438 (1960).

(11) W. J. Bailey and C. N. Bird, abstracts of papers presented at the 131st National Meeting of the American Chemical Society, Miami Beach, Fla., April 1957, p 44-O.

(12) E. L. Eliel, M. H. Gianni, and Th. D. Williams, *Tetrahedron Lett.*, 741 (1962).

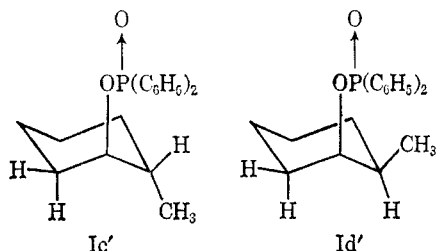
(13) 3.05 ppm for *trans*-2-methylcyclohexanol, 3.77 ppm for *cis*-2-methylcyclohexanol, 4.07 ppm for *trans*-2-methylcyclohexyl diphenylphosphinate, 4.53 ppm for *cis*-2-methylcyclohexyl diphenylphosphinate.

sults of the pyrolysis of the acetic ester in which the 3-alkene is reported to be the sole product.<sup>14</sup> Loss of the diphenylphosphinate anion to give the secondary carbonium ion followed by loss of the acidic proton from C-1 could yield the product, 1-methylcyclohexene, observed in our work.

Botteron and Shulman<sup>15</sup> have found essentially the same ratio of 1-:3-methylcyclohexene (56:44) when the corresponding *trans*-2-methylcyclohexyl methylxanthate was pyrolyzed. An observed increase in the ratio of 1:3 isomer on addition of benzoyl peroxide was suggested to imply a free-radical mechanism. Several observations do not offer support for a free-radical mechanism during pyrolysis of the phosphinates. Pyrolysis of Ic in diphenyl ether in the presence of added hydroquinone, a known radical scavenger, produced no change in the ratio of methylcyclohexenes. When 2-phenylethyl diphenylphosphinate (Ie) was pyrolyzed, no polymerization of styrene was found.<sup>5</sup> Examination of the pyrolysate from benzyl diphenylphosphinate revealed toluene and diphenylmethane (possible radical products).<sup>16</sup> However, in this case absence of  $\beta$  hydrogen precludes operation of a concerted *cis*-elimination pathway.

The results (99% 3-methylcyclohexene) obtained when *trans* ester Ic was pyrolyzed in DMSO precludes the possibility of a *cis*-concerted process in this case. Although the *trans*-diaxial conformation in Ic is certainly not the expected ground-state conformation, it is conceivable that under conditions of the pyrolysis elimination may occur in this conformation by an E2-type pathway. The observed ratio (56.13:43.87) of 3-:1-methylcyclohexene obtained from the *cis* ester Id also is explicable by this pathway. Heating 1-methylcyclohexene to 170° in DMSO in the presence of diphenylphosphinic acid for 3 hr causes isomerization to an 85:15 mixture of 1- and 3-methylcyclohexene. Addition of 0.5% water to DMSO causes a considerable increase in the rate of isomerization. At 135° for 2 hr under the latter condition converts 1-methylcyclohexene into a 59:41 1:3 isomer mixture. Nevertheless, the times for these isomerizations to occur are considerably longer (2-3 hr) than the time that it takes the pyrolyses themselves to occur (approximately 0.25 hr at maximum). Thus only a small part of the 3-methylcyclohexene from either Ic or Id could have formed by isomerization.

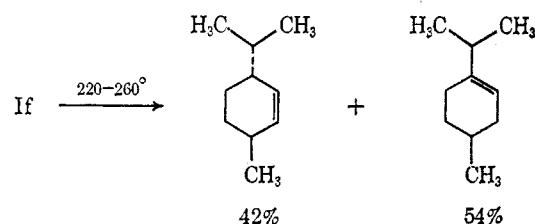
The difference in observed ratios of the products obtained by pyrolysis of Ic or Id neat and in diphenyl ether compared with those in DMSO could possibly be attributed in part to the greater ease of formation of the conformers Ic' and Id'' in DMSO, respectively. Also



the ability of DMSO to abstract a proton may be important. It is noteworthy that the *cis*- and *trans*-2-

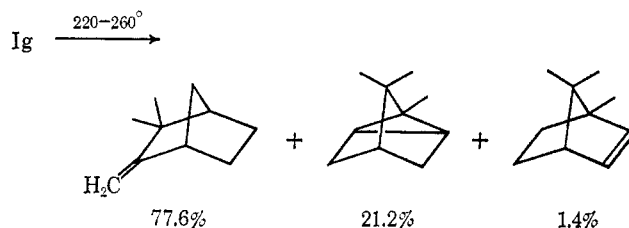
methylcyclohexyl *p*-toluenesulfonates were found to give essentially the same product ratio of alkenes (as we observed) when treated with potassium *t*-butoxide in DMSO at 55°.<sup>17</sup> We cannot rule out the possibility that a subtle mechanism is operative in pyrolyses of Ic or Id in DMSO.<sup>18</sup>

Pyrolysis of menthyl diphenylphosphinate (If) produces (88% conversion) *p*-menth-3-ene (54%), *trans*-*p*-menth-2-ene (42%), and other isomers (4%). This compares with a 75:25 ratio for the 3 *vs.* the 2 isomer for the menthenes from methylmenthyl xanthate with no other menthene isomers produced.<sup>19</sup>



Optical rotation values for the menthenes (from pyrolysis of If) in diethyl ether were measured using a micropolarimeter tube for preparatively chromatographed samples. The rotations are  $[\alpha]^{22D} + 77.3^\circ$  for the 3 isomer and  $[\alpha]^{22D} + 162^\circ$  for the 2 isomer. These compare with literature values of  $[\alpha]^{16D} + 109^\circ$  and  $[\alpha]^{16D} + 132.5^\circ$  (homogeneous), respectively.<sup>20</sup> From the percentage composition and the measured optical rotations, a rotation of  $109.6^\circ$  was calculated for the mixture compared with the  $[\alpha]^{21D} 107.5^\circ$  value measured directly on the original sample. The disparity of the product ratios, the presence of traces of extraneous menthene isomers, and the inferior value for the optical rotation of the *p*-menth-3-ene again cast doubt as to whether the mechanism could be considered strictly *cis* concerted.

Pyrolysis of bornyl diphenylphosphinate (Ig) gave principally camphene and tricyclene (77.6 and 21.2%)



(17) D. H. Froemsdorf and M. E. McCain, *J. Amer. Chem. Soc.*, **87**, 3983 (1965).

(18) Rutherford and Fung have suggested some carbonium ion character in the transition state in the pyrolyses of the hydrogen phthalate of *trans*-1,2-dimethylcyclohexanol. All three expected isomers were obtained, however, in the ratio of 19:46:35; see K. G. Rutherford and D. P. C. Fung, *Can. J. Chem.*, **42**, 2657 (1964). A referee has suggested a *trans*-concerted elimination (1,2) with Ic and Id but we feel that the following arguments are valid. Assuming that the six atoms, HCCOP $\rightarrow$ O, are not required to approach coplanarity in the transition state, surely for a *trans*-concerted elimination the activation energy arising from torsional effects between one departing group and a residual group on the vicinal carbon atom as the double bond is developing is higher than for *cis*-concerted elimination.

(19) The menthene isomer ratios were determined by quantitative gas chromatography on samples prepared in this laboratory. The literature values for the 3:2 isomer ratio is 70:30, this result being obtained by selective racemization of the *p*-menth-3-ene by *p*-toluenesulfonic acid: see W. Huckel and W. Tappe, *Ann.*, **537**, 113 (1939).

(20) N. McNiven and J. Read, *J. Chem. Soc.*, 153 (1952). This reference contains the highest value for the rotations of the menthene isomers. Nothing was found in the literature to indicate that pure (+)-*p*-menth-3-ene has ever been isolated and measurements taken on it directly. Likewise, if the previous samples of *trans*-*p*-menth-2-ene were less than homogeneous, the discrepancy between the literature value for its rotation and that obtained in this laboratory would be explained.

(14) W. Huckel and D. Rucker, *Ann.*, **666**, 43, (1963).

(15) D. G. Botteron and G. P. Shulman, *J. Org. Chem.*, **27**, 2007 (1962).

(16) Unpublished results of K. D. Berlin and W. C. Pivonka, Oklahoma State University, 1965.

and a trace of bornylene (1.4%). The camphene formed is approximately 38% optically pure. The results contrast with the yields of bornylene (70, 61, and 24.5%) obtained from the methyl xanthate,<sup>21</sup> acetate,<sup>22</sup> and benzoate,<sup>21</sup> respectively. Heating 95% bornylene (the balance is camphene plus a trace of tricyclene) to 220–260° for 45 min in the presence of diphenylphosphinic acid (sealed tube) causes isomerization to camphene and tricyclene leaving only 4.6% bornylene unchanged (Table III). This amount of bornylene, however, is in excess of that formed in the pyrolysis of Ig where the contact time at the elevated temperature is considerably shorter (15-min maximum). Heating the bornylene to 220–260° in the absence of the acid causes no isomerization. These results are probably best explained by some charge formation in the transition state from Ig to products.

In conclusion, the experimental results from the pyrolysis of a number of alkyl diphenylphosphinates are not entirely in accord with the proposition of a simple *cis*-concerted mechanism. However, the low pyrolysis temperatures, the high conversion, and the relatively simple compositions of many of the product mixtures argue against a wholly ionic transition state. The diphenylphosphinyl function might be viewed as capable of forming the hydrogen-bridged pseudoheterocyclic transition state, albeit with a certain degree of charge separation therein. When for steric or other reasons the concerted transition state has difficulty in forming, the mechanism passes over into an ionic mode, perhaps involving an associated ion pair. In the case of highly reactive carbonium ion species, hydride migration or skeletal rearrangements may occur competitively with proton abstraction by the anion, such as in the case of Ia, If, and Ig.

As a method of alkene preparation, pyrolysis of diphenylphosphinic esters is still attractive since the esters are crystalline solids which are easily prepared and purified. Moreover, conversions are excellent and, unlike the case of other commonly pyrolyzed esters, the product needs little purification. With alkenes extremely sensitive to skeletal rearrangement in the presence of even weak acids or where small amounts of isomeric products are undesirable, xanthate or acetate pyrolysis may still be of equivalent value or superior.

### Experimental Section

**Materials.**—The following chemicals were obtained from commercial sources: *cis*-stilbene, *trans*-stilbene, 3-methylcyclohexene, 1,2-diphenylethanol, *trans*-2-methylcyclohexanol (ir maxima 9.40, 9.50, and 9.63  $\mu$ )<sup>23</sup> *cis*-2-methylcyclohexanol (ir maxima 9.82, 10.23, and 10.58  $\mu$ ),<sup>23</sup> borneol ( $[\alpha]^{25}_D -20.8^\circ$ ) and menthol ( $[\alpha]^{25}_D -44.7^\circ$ ). Samples of methylcyclohexene, 3-phenyl-1-propene, and *cis*- and *trans*-1-phenyl-1-propene were generously supplied by Dr. E. J. Eisenbraun. We also express our thanks to Dr. Don H. Burpo who helped in the preparation of If and Ig.

**Preparation of Diphenylphosphinic Chloride.**—Dried (H<sub>2</sub>SO<sub>4</sub>) oxygen was bubbled through diphenylphosphinous chloride (neat) at 135–140° for 28 hr.<sup>24</sup> Oxidation was monitored by observing the decrease in refractive index to a constant value of

$n^{24}_D 1.6080$ . The resulting dark yellow-orange liquid distilled *in vacuo* at 137–138° (0.03–0.06 mm) [lit.<sup>24</sup> 140° (0.1 mm) to give 86% yield of diphenylphosphinic chloride,  $n^{24}_D 1.6083$  (lit.<sup>25</sup>  $n^{25}_D 1.6095$ ).

**Preparation of 1,2-Diphenylethyl Diphenylphosphinate (Ib).** **Method I.**—A solution of 11.8 g (0.05 mol) of diphenylphosphinic chloride in 50 ml of anhydrous ether was added dropwise with stirring over 0.5 hr to a solution of 9.9 g (0.05 mol) of 1,2-diphenylethanol and 10.1 g (0.1 mol) of triethylamine in 75 ml of anhydrous ether. During addition, the temperature rose so as to cause gentle refluxing. After addition of ether (150 ml) to facilitate stirring of the heavy slurry, the mixture was heated under reflux for 1.5 hr. The precipitate was collected by filtration, washed with water to remove triethylamine hydrochloride, and recrystallized from benzene–hexane to yield 14.4 g (72.7%) of 1,2-diphenylethyl diphenylphosphinate. The compound was identified by elemental and spectral analysis (Table I).

The work-up in the above procedure was modified slightly for the 2-methylcyclohexyl esters. After removal of the amine hydrochloride and the solvent, the residual oil crystallized on standing. The solid was then recrystallized twice from hexane (Table I).

**Preparation of Menthyl Diphenylphosphinate (If).** **Method II.**—Sodium (2.76 g, 0.12 g-atom), menthol (15.63 g, 0.10 mol,  $[\alpha]^{25}_D -44.7^\circ$ ), and 50 ml of toluene (dried over sodium) were stirred vigorously for 7 hr at 100–105°. After the mixture had cooled to room temperature, the excess sodium was mechanically removed. Diphenylphosphinic chloride (26.0 g, 0.11 mol) in 50 ml of toluene was added dropwise to the sodium mentoxide with ice bath cooling to keep the reaction temperature below 40°. After the addition of the diphenylphosphinic chloride was complete, the reaction mixture was heated to 85° for 4 hr, then cooled and extracted with 5% sodium bicarbonate and with water. To remove unreacted menthol, the organic layer was steam distilled until 1.5 l. of distillate was collected. The non-volatile residue was extracted with ether, and the ether layer was dried (MgSO<sub>4</sub>) and evaporated. Crystallization of the resulting oil from *n*-hexane yielded 18.25 g (51.2% If, mp 72–73°). The compound was identified by elemental and spectral analysis (Table I).

**Pyrolysis of *trans*-2-Methylcyclohexyl Diphenylphosphinate (Ic).**—The procedure employed for pyrolysis during this study is essentially the same as that reported by Berlin and Austin<sup>6</sup> with some modifications. The method employed for *trans*-2-methylcyclohexyl diphenylphosphinate will be described.

The reaction was carried out in a 10-ml pear-shaped flask equipped with a thermometer, magnetic stirrer, and nitrogen inlet which was connected to a pyrolysis train. The train consisted of three traps connected in series, the first being air cooled and the latter two immersed in Dry Ice–acetone traps. Each of the traps was filled with ether to approximately 1 in. above the lower end of the inlet tube. The system was protected with a drying tube (CaCl<sub>2</sub>) and was swept with dried N<sub>2</sub>. The reaction vessel was charged with 1.200 g (0.0038 mol) of ester Ic, and heat was applied slowly until the ester had melted (75°). The temperature was raised to 200° at which point liquid droplets were observed in the connecting tube. The temperature was held between 200 and 220° for 0.75 hr. After 15 min no further condensation was observed. The system was allowed to cool to room temperature. The slightly discolored solid in the flask was dissolved in 10% NaOH and the yellow alkaline solution was extracted several times with ether. Contents of the three traps were combined with the ether extract, condensed, and diluted to 25.0 ml with ether for glpc analysis.

The aqueous solution, when acidified with 6 N HCl, gave a white solid which, after drying at 25° *in vacuo* for 24 hr, melted at 193–194° (lit.<sup>26</sup> mp 192–193.5°). The infrared spectrum was identical with that of an authentic sample of diphenylphosphinic acid.

**Preparation of Menthene Standards.**—Carbon disulfide and then methyl iodide were added, in order, to an ice-cooled solution of sodium mentoxide (prepared from sodium and menthol in toluene) in anhydrous ether. The ether solution was boiled 1 hr between respective additions. The ether was removed by distillation and the resulting residual oil was crystallized from ethanol to give methyl menthyl xanthate (86%).<sup>27</sup> The xanthate

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(22) E. U. Emovon, *J. Chem. Soc., B*, 588 (1966).

(23) Reported values: *trans*-2-methylcyclohexanol 9.39, 9.50, and 9.63  $\mu$ ; *cis*-2-methylcyclohexanol 9.83, 10.23, and 10.60  $\mu$  [E. L. Eliel and C. A. Lukach, *J. Amer. Chem. Soc.*, **79**, 5986 (1957)].

(24) R. A. Baldwin and R. M. Washburn, *J. Org. Chem.*, **30**, 3864 (1965).

(25) T. H. Austin, Ph.D. Thesis, Oklahoma State University, 1965.

(26) G. M. Kosolapoff and R. F. Struck, *J. Chem. Soc.*, 3950 (1959).

(27) D. Malcolm and J. Read, *ibid.*, 1037 (1939).

(10.0 g, 0.042 mol) was distilled through a water-cooled condenser from a sand bath heated to 200°. The resulting liquid was heated over 2 g of sodium for 11 hr and then distilled at 65–72° (aspirator vacuum). The produced menthene (3.1 g, 55%) had a standard rotation of  $[\alpha]^{25}_D$  113.7° (ether) [lit.<sup>27</sup>  $[\alpha]^{14}_D$  +114.1° (alcohol)] and contained (by glpc) *p*-menth-3-ene (70.0%), *trans-p*-menth-2-ene (23.2%), and unidentified components (6.8%). *trans-p*-Menth-2-ene was identified by mixed injection on glpc with an authentic sample of *trans-p*-menth-2-ene prepared by base-catalyzed elimination on menthyl *p*-toluenesulfonate.<sup>28, 29</sup>

**Gas Chromatography of Alkenes.**—A 6 ft  $\times$  1/8 in. 5% SE-30 on 60/80 mesh, acid-washed, DMCS treated Chromosorb G column served to separate all alkene mixtures with the exception of the menthenes. A 1 m  $\times$  0.25 in. column packed with 30% silver nitrate in ethylene glycol (25%) on 60–80 mesh, acid-washed firebrick performed well in separating 2- and 3-*p*-menthenes. (Retention volumes for the 2- and 3-menthenes are 1.21 and 3.17, respectively, relative to toluene.)<sup>30</sup> The column

(28) N. Mori, *Nippon Kagaku Zasshi*, **78**, 36 (1957); *Chem. Abstr.*, **53**, 5320 (1959).

(29) A. K. MacBeth and W. G. P. Robertson, *J. Chem. Soc.*, 895 (1953).

(30) J. Herling, J. Shabtai, and E. Gil-av, *J. Chromatogr.*, **8**, 349 (1962).

was operated at room temperature with a helium flow rate of 60–90 ml/min. A 0.5-in.-o.d. version of this column was used to chromatograph the isomers preparatively.

**Optical Purity of Camphene from Bornyl Diphenylphosphinate.**—I<sub>g</sub> was pyrolyzed by the standard method and the alkene products were taken up in ether. The ether solution was analyzed quantitatively by glpc and the concentration found to be 1.11 g of alkene/10.0 ml. The rotation due to the 1.4% bornylene (lit.<sup>31</sup>  $[\alpha]^{18}_D$  –21.69°) was assumed to be negligible. Thus from the observed rotation,  $\alpha^{25}_D$  –3.41°, of the alkene mixture, assuming all rotation due to the 78.2% camphene, a specific rotation,  $[\alpha]^{25}_D$  –39.4°, was calculated. Taking  $[\alpha]^{17}_D$  –104.7° (ether) for pure (–)-camphene,<sup>32</sup> an optical purity of 38% is calculated for the camphene.

**Registry No.**—I<sub>a</sub>, 19639-45-3; I<sub>b</sub>, 19639-46-4; I<sub>c</sub>, 19639-93-1; I<sub>d</sub>, 19669-14-8; I<sub>f</sub>, 19639-94-2; I<sub>g</sub>, 19639-95-3.

(31) J. Bredt and H. Sandkuhl, *Ann.*, **366**, 1 (1909).

(32) J. L. Simonsen, "The Terpenes," Vol. II, 2nd ed, University Press, Cambridge, 1949, p 289.

## Bis(perfluoroalkyl)acetylenes. VI. Thermal and Photochemical Additions of Perfluoro-2-butyne to Aromatic Compounds

ROBERT S. H. LIU<sup>1</sup> AND CARL G. KRESPAN

Contribution No. 1487 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

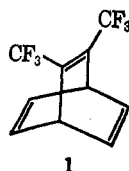
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1,4 adducts have been isolated from thermal addition of perfluoro-2-butyne to benzene, toluene, and *o*-, *m*-, and *p*-xylenes. These thermal adducts are unstable at elevated temperatures. The photochemical addition of perfluorobutyne to aromatic compounds and the photosensitized rearrangement of the thermal adducts have also been investigated.

The high reactivity of bis(perfluoroalkyl)acetylenes as dienophiles was demonstrated in their addition to aromatic compounds to form 1,4 adducts.<sup>2a</sup> The addition to simple benzenoid compounds to form isolable 1,4 adducts was, however, limited to durene.<sup>2a</sup> We wish to report here the generality of the reaction as demonstrated by isolation of adducts from reactions of perfluoro-2-butyne (PFB) with benzene and other simple benzenoid compounds. The photochemical addition of PFB to several aromatic compounds and the photorearrangements of the thermal 1,4 adducts have also been investigated.<sup>2b</sup>

### Results and Discussion

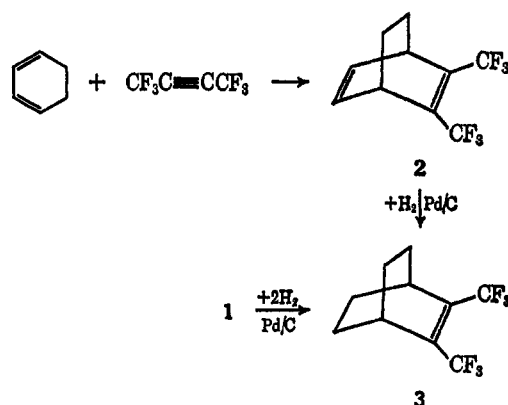
**Thermal Addition Reactions.**—The earlier investigation<sup>2a</sup> of the reaction of PFB with benzene at 250° under pressure did not result in detection of the 1,4 adduct 1. However, the isolation of 1,2-bis(trifluoro-



1

methyl)benzene strongly suggested the transient existence of 1. Compound 1 has now been isolated when the reaction is run under autogeneous pressure and at slightly lower temperatures (180–200°). Even at these temperatures, thermolysis of 1 and further reaction of 1 with PFB competes with formation of 1. Therefore, even under optimum conditions, 1 could be isolated in only 7–10% yield. The structural assignment of 1 was based on the chemical transformations shown in Scheme I. Elemental analyses and spectro-

SCHEME I



3

(1) To whom inquiries should be addressed: Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822.

(2) (a) C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Amer. Chem. Soc.*, **83**, 3428 (1961). (b) Part of this work was described previously in a preliminary report: R. S. H. Liu, *ibid.*, **90**, 215 (1968).

scopic data agree with the assignment. Further, the assignment is supported by the excellent agreement between the observed and calculated 100-Mc proton magnetic resonance (pmr) spectra.<sup>2b</sup>