

## Organic Oxalates. II. Formation of Bibenzyls by Pyrolysis of Benzyl Oxalates<sup>1a-d</sup>

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**Abstract:** Several benzyl oxalates were converted to the corresponding bibenzyls in good yield by pyrolysis in the gas phase. Since oxalates are readily prepared from benzyl alcohols, pyrolysis of oxalates offers a convenient way of converting benzyl alcohols to bibenzyls. Pyrolyses of the unsymmetrical oxalates, benzyl *p*-chlorobenzyl oxalate and benzyl benzyl- $\alpha,\alpha$ -*d*<sub>2</sub> oxalate, indicate that the mechanism of the reaction requires statistical scrambling of the benzyl groups, which is consistent with the formation of benzyl radicals. Gas-phase pyrolysis of oxalates appears to be a means of generating relatively stable radicals, such as benzyl radicals, in the absence of any very reactive radicals or molecules.

Recently Montaudo and Purrello<sup>2</sup> studied the thermal decomposition of neat benzyl oxalate at 280° in sealed tubes. Unreproducible yields of benzyl alcohol, benzaldehyde, benzyl ether, bibenzyl, and polybenzyl were obtained. These authors postulated a radical mechanism to account for their results.

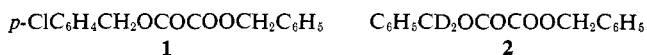
In continuation of our study<sup>1c</sup> of the thermal decomposition of oxalates that possess no  $\beta$  hydrogens and hence cannot undergo elimination, we studied the pyrolysis of benzyl oxalates.<sup>3</sup> Pyrolysis of neat benzyl oxalate under nitrogen in a flask and pyrolysis of the oxalate dissolved in benzene on a hot column through which nitrogen was flowing gave us unreproducible amounts of the same products obtained by Montaudo and Purrello. In an effort to control experimental conditions more exactly, benzyl oxalate was vaporized by heating (up to 125°) under low pressure and passed through a hot (660°) tube. Products of the reaction were condensed in a cold trap cooled with liquid nitrogen. Under these conditions, the major product is bibenzyl. Similar results were obtained with other benzyl oxalates.

### Results

The oxalic esters, prepared in high yield from oxalic acid<sup>5</sup> or oxalyl chloride and the corresponding benzyl alcohol, are white crystalline solids that contain a characteristic doublet in the carbonyl region (1790–1760 and 1755–1740 cm<sup>-1</sup> in chloroform) of their infrared spectra. Physical properties of these oxalates are given in Table I. These oxalates were pyrolyzed in the vapor phase at 660° under reduced pressure. Most of

the oxalates were pyrolyzed in gram quantities over a 1–2-hr period. Analysis of the crude product mixtures by nmr showed that they were composed of at least 90% of the corresponding bibenzyl and small amounts (<5%) of the oxalate and corresponding benzyl alcohol, benzaldehyde, toluene, and benzyl ether. In large-scale runs the pure bibenzyl was obtained by chromatography of the crude pyrolysate on a silica gel column followed by recrystallization of the chromatographed bibenzyls. For small-scale runs yields of bibenzyls were determined by addition of an internal standard to the product mixture followed by nmr or glpc analyses. The yields of bibenzyls are reported in Table II. The melting points of the bibenzyls agreed with reported values, and the nmr spectra of all the bibenzyls (except *p,p'*-dicyanobibenzyl which was too insoluble) had a four-proton singlet at  $\delta$  3.0–2.6. The structure of *p,p'*-dicyanobibenzyl was confirmed by its ir and mass spectra. Yields of the bibenzyls were 40–76%, except from *m*-nitrobenzyl oxalate which gave poor yields or *p*-methoxybenzyl oxalate which gave none.

In order to determine if the formation of the bibenzyls is inter- or intramolecular, two unsymmetrical benzyl oxalates, benzyl *p*-chlorobenzyl oxalate (**1**) and benzyl benzyl- $\alpha,\alpha$ -*d*<sub>2</sub> oxalate (**2**), were pyrolyzed. The



stability of the bibenzyls under the reaction conditions was established by sublimation of *p*-chlorobibenzyl through the tube heated to 650° which produced only 12% of each symmetrical bibenzyl. Since the residence time of *p*-chlorobibenzyl in the pyrolysis tube under these conditions should be no less than that of *p*-chlorobibenzyl formed from oxalate **1**, decomposition of **1** by an intramolecular pathway should lead to mainly *p*-chlorobibenzyl, but an intermolecular pathway should lead to bibenzyl, *p*-chlorobibenzyl, and *p,p'*-dichlorobibenzyl in the ratio 1:2:1. Glpc analysis of the product mixture showed that the unsubstituted, monochlorinated, and dichlorinated bibenzyls were formed in the ratio 1.00:2.04:1.00. Further confirmation of the intermolecular nature of the reaction was obtained from the pyrolysis of **2**. An intramolecular reaction with no more than 50% decomposition of the bibenzyl to free bibenzyl radicals and an intermolecular reaction with

(1) (a) This work was partially supported by Public Health Service Grant GM 13799 from the National Institute of General Medical Sciences and Grant 3219-A from the Petroleum Research Fund administered by the American Chemical Society. The mass spectrometer was purchased with funds from National Science Foundation Grant GP 1715 and a grant from the Iowa State Alumni Research Foundation. (b) Based on work by C. C. Ong in partial fulfillment of the requirement for the Ph.D. degree at Iowa State University. (c) Part I: W. S. Trahanovsky, J. A. Lawson, and D. E. Zabel, *J. Org. Chem.*, **32**, 2287 (1967). (d) Preliminary communication, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, 33-P. (e) National Science Foundation Undergraduate Research Participant, 1966.

(2) G. Montaudo and G. Purrello, *Ann. Chim. (Rome)*, **51**, 876 (1961).

(3) The mass spectrometry of benzyl oxalates has recently been reported.<sup>4</sup>

(4) T. H. Kinstle and R. L. Muntz, *Tetrahedron Letters*, 2613 (1967).

(5) C. Lespagnol, *Bull. Soc. Chim. France*, 110 (1960).

**Table I.** Method of Preparation, Yields, Melting Points, Elemental Analyses, Nmr Signals, and Ir Absorption Bands of Benzyl Oxalates

R	Prepn	Yield, %	Mp, °C <sup>a</sup>	% <sup>b</sup> found		
				C	H	Other
C <sub>6</sub> H <sub>5</sub>	I	92	79–80 <sup>f</sup>			
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	I	86	118.5–120	56.67	3.56	21.02 (Cl)
<i>o</i> -ClC <sub>6</sub> H <sub>4</sub>	I	71	77–79	56.57	3.56	20.90 (Cl)
<i>m</i> -ClC <sub>6</sub> H <sub>4</sub>	I	88	104–106	56.59	3.59	20.71 (Cl)
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	II	75	136–138	44.78	2.88	37.35 (Br)
<i>p</i> -FC <sub>6</sub> H <sub>4</sub>	I	58	107–109	62.96 <sup>g</sup>	3.96 <sup>g</sup>	
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	I	54	99–100	72.26	6.15	
<i>p</i> -NCC <sub>6</sub> H <sub>4</sub>	II	41	194–197 <sup>i</sup>	67.32	3.80	8.71 (N)
α-Naphthyl	II	58	104–106	77.47 <sup>g</sup>	4.92 <sup>g</sup>	
<i>m</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	I	88	133–135 <sup>m</sup>	53.53	3.37	7.65 (N)
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	II <sup>n</sup>	64	133–114.5	65.41	5.39	

<sup>a</sup> Recrystallized from 95% ethanol unless otherwise specified. <sup>b</sup> Analyses by Spang Microanalytical Laboratory, Ann Arbor, Mich., unless otherwise specified. <sup>c</sup> Chloroform-*d*<sub>1</sub> was used as solvent unless otherwise specified. <sup>d</sup> s = singlet, q = quartet, m = multiplet. <sup>e</sup> Chloroform was used as solvent unless otherwise specified. <sup>f</sup> Lit.<sup>5</sup> mp 79–80°. <sup>g</sup> Analysis by M-H-W Laboratories, Garden City, Mich. <sup>h</sup> The

**Table II.** Gas-Phase Pyrolysis of Benzyl Oxalates (RCH<sub>2</sub>OCOCOOCH<sub>2</sub>R) to Bibenzyls (RCH<sub>2</sub>CH<sub>2</sub>R)<sup>a</sup>

R	Yields of bibenzyls, % <sup>b</sup>	Mp of bibenzyls, °C	Lit. mp, °C
C <sub>6</sub> H <sub>5</sub>	59, 61	51–52	51.5–52.5 <sup>c</sup>
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	69, 66	100–101	100 <sup>d</sup>
<i>o</i> -ClC <sub>6</sub> H <sub>4</sub>	69, 73, 76 <sup>e</sup>	59–61	62 <sup>d</sup>
<i>m</i> -ClC <sub>6</sub> H <sub>4</sub>	62, 58, 66 <sup>e</sup>	48–50	52 <sup>d</sup>
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	40, <sup>e</sup> 44 <sup>e</sup>	112–114	114 <sup>d</sup>
<i>p</i> -FC <sub>6</sub> H <sub>4</sub>	72, 72 <sup>e</sup>	87–89	90 <sup>f</sup>
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	47, 51, 57 <sup>e</sup>	78–80	79–81 <sup>g</sup>
<i>p</i> -NCC <sub>6</sub> H <sub>4</sub>	44, <sup>h</sup> 43 <sup>h</sup>	196–198	198 <sup>i</sup>
α-Naphthyl	46, <sup>e</sup> 52 <sup>e</sup>	159–161	162 <sup>j</sup>
<i>m</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	<i>k</i>		
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<i>l</i>		

<sup>a</sup> The head temperature was 110–145°. The pressure of the system was 0.07–0.1 mm. <sup>b</sup> Isolated yields of recrystallized bibenzyls unless otherwise noted. <sup>c</sup> S. Cannizzaro and A. Rossi, *Ann.*, **121**, 251 (1862). <sup>d</sup> K. M. Johnston and G. H. Williams, *J. Chem. Soc.*, 1168 (1960). <sup>e</sup> Yield obtained by addition of a standard (methyl oxalate) and nmr analysis. <sup>f</sup> M. Szwarc and J. S. Roberts, *J. Am. Chem. Soc.*, **70**, 2831 (1948). <sup>g</sup> D. J. Cram and H. Steinberg, *ibid.*, **73**, 5691 (1951). <sup>h</sup> Yield obtained by addition of a standard (bibenzyl) and glpc analysis. <sup>i</sup> P. Kattwinkel and R. Wolfenstein, *Ber.*, **37**, 3215 (1904). <sup>j</sup> Ng. Ph. Buu-Hoi and Ng. Hoan, *J. Org. Chem.*, **14**, 1023 (1949). <sup>k</sup> From nmr analysis, at least two different bibenzyls were produced in poor yield, which is consistent with thermal decomposition of the aromatic nitro group such as reported by E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **89**, 3224 (1967). <sup>l</sup> Nmr analysis of the product mixture showed no bibenzyl present.

completely random distribution of benzyl groups should lead to bibenzyls with the isotope distributions shown in Table III. The experimental isotope distribution of the bibenzyl produced from **2** clearly coincides with that calculated for an intermolecular process.

**Table III.** Isotopic Distribution (%) in Bibenzyl Obtained from the Pyrolysis of Benzyl Benzyl-α,α-d<sub>2</sub> Oxalate<sup>a</sup>

	<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>	<i>d</i> <sub>3</sub>	<i>d</i> <sub>4</sub>
Exptl	26.4	14.2	37.3	10.3	11.8
Calcd					
Intermolecular	29.3	11.7	39.1	7.6	12.3
Intramolecular <sup>b</sup>	8.3–18.9	16.7–21.6	54.7–70.1	0–3.8	0–6.2

<sup>a</sup> The oxalate was 8.3% *d*<sub>0</sub>, 21.6% *d*<sub>1</sub>, and 70.1% *d*<sub>2</sub>. <sup>b</sup> With no more than 50% decomposition of the bibenzyl to benzyl radicals which would combine statistically.

## Discussion

Several methods are known for the preparation of bibenzyls in good yields. The methods most often used are the reduction of a Grignard reagent and the Wurtz reaction. However, both of these reactions cannot be used with certain functional groups. For bibenzyls that contain these functional groups, pyrolysis of benzyl oxalates is probably the method of choice. For example, *p,p'*-dicyanobibenzyl could not be obtained from reduction of the Grignard reagent<sup>6</sup> and was obtained only in poor yields by other reactions,<sup>7</sup> but was obtained in fair yield from *p*-cyanobenzyl oxalate.<sup>8</sup> The oxalate pyrolysis should also be useful for the preparation of large quantities of bibenzyls since expensive reagents and anhydrous conditions can be avoided.

Pyrolysis under vacuum of compounds that are only slightly volatile makes reaction in the vapor phase more likely and consequently enables experimental conditions to be better controlled,<sup>9</sup> as witnessed by the striking difference between the reproducible yields of bibenzyls obtained by pyrolysis under vacuum compared to the unreproducible yields of many products obtained by pyrolysis in the condensed phase or in the conventional flow system.

Oxalate pyrolysis under our conditions is not a good method for the preparation of bibenzyls that contain polar functional groups or strongly electron-donating groups. Both types of functional groups lead to decomposition of the oxalate before it can be vaporized. With the polar functional group, the vapor pressure of the oxalate is very low and thus the head temperature must be quite high before vaporization takes place. In the case of an electron-donating group, such as *p*-methoxy, the oxalate decomposes at such a low temperature that it cannot be vaporized without decomposition.

A reasonable mechanism for pyrolysis of benzyl oxalates is formation of a benzyl radical, one molecule

(6) R. C. Fuson, *J. Am. Chem. Soc.*, **48**, 835 (1926).

(7) (a) See Table II, footnote i; (b) W. S. Lindsay, P. Stokes, L. G. Humber, and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 943 (1961).

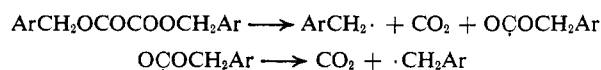
(8) We have recently prepared *meso*- and *dl*-2,3-diphenyl-1,1,1,4,4,4-hexafluorobutanes in good yields from the appropriate oxalate. These bibenzyls could not be prepared from Grignard reagents.

(9) R. F. C. Brown and R. K. Solly, *Australian J. Chem.*, **19**, 1045 (1966).

(RCH<sub>2</sub>OCO-)<sub>2</sub>

C	% calcd		Chemical shifts, $\delta$ , <sup>c,d</sup> ppm		Ir frequency, cm <sup>-1</sup> <sup>e</sup>
	H	Other	Aromatic H	-CH <sub>2</sub> -	C=O
56.66	3.57	20.91 (Cl)	7.28 s	5.28 s	1780, 1740
56.66	3.57	20.91 (Cl)	7.30 s	5.22 s	1770, 1745
56.66	3.57	20.91 (Cl)	7.27-7.66 m	5.42 s	1770, 1755
44.87	2.83	37.35 (Br)	7.46-7.22 m	5.26 s	1780, 1743
62.73	3.95	12.41 (F)	7.38 q	5.24 s	1768, 1740
72.43	6.09		6.88-7.55 m	5.25 s	1770, 1740
			7.04-7.36 m	5.12 s <sup>h</sup>	1770, 1742
					1770 <sup>i</sup>
67.48	3.77	8.75 (N)	k		1755 <sup>i,l</sup>
77.81	4.90		7.25-8.1 m	5.75 s	1770, 1740
53.32	3.36	7.77 (N)	k		1745 <sup>i</sup>
65.43	5.49		7.4-6.78 q	5.2 s <sup>o</sup>	1760, 1740

CH<sub>3</sub> peak appeared at  $\delta$  2.31 s. <sup>i</sup> A KBr pellet was used. <sup>j</sup> Recrystallized from hot dichloromethane. <sup>k</sup> Insoluble in common spectra solvents. <sup>l</sup> The CN absorption appeared at 2240 cm<sup>-1</sup>. <sup>m</sup> Recrystallized from hot benzene. <sup>n</sup> No triethylamine was used. <sup>o</sup> The OCH<sub>3</sub> peak appeared at  $\delta$  2.78 s.



of carbon dioxide, and a benzyloxycarbonyl radical which rapidly decomposes to a benzyl radical and a molecule of carbon dioxide. An alternative mechanism is three-bond cleavage to give two molecules of carbon dioxide and two benzyl radicals. The two-bond cleavage mechanism is analogous to that proposed for the thermal decomposition at 200–275° of benzhydryl oxalates in solution.<sup>1c</sup> Both mechanisms account for the intermolecular nature of the reaction. That no phenylacetic ester was noticed in the high-temperature experiments, in contrast to the diphenylacetic ester which was formed in the low-temperature experiments, indicates that the benzyloxycarbonyl radical must rapidly decarboxylate at high temperatures if indeed it is formed. Thus it appears that the gas-phase pyrolysis of oxalates offers a convenient source of relatively stable free radicals, such as benzyl radicals, in the absence of any very reactive radicals or molecules.<sup>10</sup>

## Experimental Section

**Materials and Methods.** Routine equipment and methods have been previously described.<sup>11</sup> Infrared spectra were taken using chloroform as the solvent unless otherwise specified. All nmr spectra were taken using chloroform-*d*<sub>1</sub> or carbon tetrachloride as solvent and tetramethylsilane as an internal standard.

The pyrolysis apparatus consisted of a 2 × 30 cm Vycor tube packed with Pyrex helices or Vycor rings and encased in a 30-cm electric furnace. At one end of the tube was attached by a standard-taper ground-glass joint a 2 × 4.5 cm tube closed at one end. This tube which held the starting material was encased in a slightly larger test tube wrapped with heating tape. On the other end of the pyrolysis tube was attached by means of a ball and socket joint a U-shaped trap made from 38 cm of 1.2-cm Pyrex tubing with indentations. The trap was connected directly to a vacuum system. Temperature of the hot tube was monitored with a thermocouple and a Leeds and Northrup potentiometer.

Oxalic acid dihydrate was obtained from Baker Chemical Co., oxalyl chloride was obtained from Columbia Chemical Co., and triethylamine was obtained from Matheson Coleman and Bell and was dried over barium oxide before use.

The sources of benzyl, *o*-chlorobenzyl, *p*-methylbenzyl, *m*-nitrobenzyl, *p*-bromobenzyl, and *p*-methoxybenzyl have been previously described.<sup>12</sup> *m*-Chlorobenzyl alcohol was obtained from Aldrich. *p*-Chlorobenzyl and *p*-fluorobenzyl alcohols and  $\alpha$ -naph-

thylmethanol were prepared from the benzyl chlorides obtained from Aldrich by a method similar to that of Hartman and Rahr.<sup>13</sup> *p*-Cyanobenzyl alcohol was prepared in a similar fashion<sup>13</sup> from the benzyl chloride, obtained from K & K Chemical Co.

**Preparation of Symmetrical Benzyl Oxalates.** Method I is patterned after that of Lespagnol<sup>5</sup> and has been previously described for the preparation of benzhydryl oxalate.<sup>1c</sup> Method II is illustrated by the preparation of *p*-bromobenzyl oxalate. A quantity of 0.9 ml (0.0103 mol) of oxalyl chloride was added slowly to an ice-cooled, stirred solution of 3.74 g (0.02 mol) of *p*-bromobenzyl alcohol and 4 ml (0.03 mol) of triethylamine in 100 ml of anhydrous ether. Ten minutes later the mixture was filtered, and the precipitate was washed with water and recrystallized from 95% ethanol to give 3.2 g (75%) of white leaflets. In Table I are presented pertinent data for each symmetrical benzyl oxalate.

**Benzyl *p*-Chlorobenzyl Oxalate (1).** This mixed ester was made by dropwise addition of benzyl chloroglyoxylate into an equimolar amount of *p*-chlorobenzyl alcohol in the presence of triethylamine and dry ether, adapting details of a published method.<sup>14</sup> After filtration and evaporation of solvent, the residue was crystallized from 95% alcohol; 42% yield of white crystals, mp 96–98°; ir (CHCl<sub>3</sub>) 1770 and 1745 cm<sup>-1</sup> (C=O); nmr (CDCl<sub>3</sub>)  $\delta$  7.25 (s, 9), 5.28 (s, 2), and 5.22 (s, 2).

*Anal.* Calcd for C<sub>16</sub>H<sub>13</sub>O<sub>4</sub>Cl: C, 63.00; H, 4.39; Cl, 11.62. Found: C, 63.08; H, 4.46; Cl, 11.36.

**Bibenzyl- $\alpha,\alpha$ -*d*<sub>2</sub> (2)** was prepared from benzyl chloroglyoxylate and benzyl alcohol- $\alpha,\alpha$ -*d*<sub>2</sub><sup>15</sup> by the same method used to prepare benzyl *p*-chlorobenzyl oxalate. Recrystallization of the crude product gave 2.25 g (76%) of white crystals, mp 79–80°; ir (CHCl<sub>3</sub>) 1770 and 1740 cm<sup>-1</sup> (C=O). Mass spectral analysis of the thrice recrystallized oxalate showed that it was 8.3% *d*<sub>0</sub>, 21.6% *d*<sub>1</sub>, and 70.1% *d*<sub>2</sub>. Pertinent mass spectral data are presented in Table IV. In agreement with the mass spectral data an nmr spectrum of the oxalate showed that 20% of the benzyl hydrogens were protons.

**Pyrolysis of the benzyl oxalates** is illustrated by that of benzyl oxalate. The furnace was heated to 660°. A quantity of 1 g (3.7 mmol) of benzyl oxalate in an aluminum foil pan was placed in the head of the apparatus and the system was evacuated to 0.05 mm. The cold trap was cooled with liquid nitrogen and the head was heated to 115–125°. Over a period of 2 hr all of the oxalate had sublimed. The liquid nitrogen bath was removed and the system was opened to the atmosphere. The crude pyrolysate was washed out of the trap with the use of a small amount of pentane and then acetone. The solvent was evaporated, an nmr spectrum of the pyrolysate was taken, and the peaks at  $\delta$  2.32 (toluene), 2.82 (bibenzyl), 4.48 (benzyl alcohol), 4.50 (benzyl ether), 5.22 (benzyl oxalate), and 10.0 (benzaldehyde) were integrated. The assignment of these peaks was confirmed by nmr spectra of authentic samples. At least 90% of these products was bibenzyl.

Recrystallization from 95% ethanol of the bibenzyl obtained from chromatography of the pyrolysate on a silica gel column using pentane as the eluent gave 0.396 g (2.18 mmol, 59%) of bibenzyl, mp 51–52°, lit.<sup>16</sup> mp 51.5–52.5°.

Yields and melting points for the bibenzyls that were prepared by this method are given in Table I. The ir spectrum of *p,p'*-

(10) Biallyl has been obtained from the gas-phase pyrolysis of allyl oxalate in high yield.

(11) W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, **32**, 146 (1967).

(12) W. S. Trahanovsky, L. B. Young, and G. L. Brown, *ibid.*, **32**, 3865 (1967).

(13) W. W. Hartman and E. J. Rahr, "Organic Synthesis," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., pp 650–653.

(14) S. Rhoads and R. Mischels, *J. Am. Chem. Soc.*, **85**, 585 (1963).

(15) We thank Professor G. A. Russell for this sample.

(16) See Table I, footnote c.

Table IV. Mass Spectral Data for Natural and Deuterated Benzyl Oxalate

	<i>m/e</i>	Intensity of natural sample <sup>a</sup>	Intensity of deuterated sample <sup>b</sup>	Calcd peaks for		
				<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>
P	270	100	2.5	2.5		
P + 1	271	19.8	7	0.50	6.5	
P + 2	272	3.36	22.5	0.084	1.29	21.13

<sup>a</sup> Ionization voltage was 70 eV. <sup>b</sup> Ionization voltage was 23 eV.

Table V. Mass Spectral Data for Bibenzyl from Deuterated Benzyl Oxalate

	<i>m/e</i>	Intensity <sup>a</sup> of natural sample	Intensity <sup>a</sup> of deuterated sample	Calcd peaks for				
				<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>	<i>d</i> <sub>3</sub>	<i>d</i> <sub>4</sub>
P	182	100	23.5	23.5				
P + 1	183	15.6	16.3	3.7	12.6			
P + 2	184	1.13	35.5	0.3	2.0	33.2		
P + 3	185		14.5		0.1	5.2	9.2	
P + 4	186		12.3			0.4	1.4	10.5

<sup>a</sup> Ionization voltage was 18 eV.

dicyanobibenzyl showed no carbonyl peaks, and its mass spectrum showed a molecular peak of *m/e* 232.

**Pyrolysis of benzyl *p*-chlorobenzyl oxalate (1)** was carried out in the usual manner. Glpc analysis of the pyrolysate on a 7 ft × 0.25 in. column containing 20% SE No. 30 showed three main peaks in the ratio of 1:00:2.04:1.00. The first and last peaks were identified as bibenzyl and *p,p'*-dichlorobibenzyl by peak enhancement with authentic samples. The product giving rise to the second glpc peak was collected and identified as *p*-chlorobibenzyl by its melting point, 47–49° (lit.<sup>17</sup> mp 49°), and consistent nmr spectrum. Since the relative thermal conductivity of bibenzyl to *p,p'*-dichlorobibenzyl was found to be 1:1.03, the relative thermal conductivities used for the three peaks was 1:1:1.

**The thermal stability of *p*-chlorobibenzyl** was tested by passing 10-mg quantities of *p*-chlorobibenzyl (collected by glpc from the pyrolysate of 1) through the pyrolysis tube heated to 650° (0.1–0.07

mm) with a head temperature of 125 or 75°. Glpc analysis of the pyrolysate of two runs showed it to be 12.2 ± 1.6% bibenzyl, 76.0 ± 2.6% *p*-chlorobibenzyl, and 11.8 ± 1.0% *p,p'*-dichlorobibenzyl.

**Pyrolysis of benzyl benzyl- $\alpha,\alpha$ -*d*<sub>2</sub> oxalate (2)** was carried out in the usual manner. The chromatographed and recrystallized bibenzyl was submitted to mass spectral analysis. In Table V are presented pertinent mass spectral data from which percentages of *d*<sub>0</sub>–*d*<sub>4</sub> species were calculated and presented in Table III.

The percentages of *d*<sub>0</sub>–*d*<sub>4</sub> species of the bibenzyl expected from an intermolecular process were calculated as follows. The benzyl oxalate was 8.3% *d*<sub>0</sub>, 21.6% *d*<sub>1</sub>, and 70.1% *d*<sub>2</sub>. Therefore, 54.15% of the benzyl groups that the oxalate contained were *d*<sub>0</sub>, 10.8% were *d*<sub>1</sub>, and 35.05% were *d*<sub>2</sub>. The probabilities of forming bibenzyls-*d*<sub>0</sub>–*d*<sub>4</sub> are: *d*<sub>0</sub>, (0.5415)(0.5415) = 0.293; *d*<sub>1</sub>, (0.5415)(0.108) + (0.108)(0.5415) = 0.117; *d*<sub>2</sub>, (0.5415)(0.3505) + (0.3505)(0.5415) + (0.108)(0.108) = 0.391; *d*<sub>3</sub>, (0.108)(0.3505) + (0.3505)(0.108) = 0.759; *d*<sub>4</sub>, (0.3505)(0.3505) = 0.123. Multiplying these probabilities by 100 gives the calculated percentages for an intermolecular process.

(17) F. Bergman, J. Weizman, and D. Schapiro, *J. Org. Chem.*, **9**, 408 (1944).