Acknowledgments.—G. Frederick Hatch made the initial studies of this system, and Eric A. Gislason prepared and characterized CF_2HCOF. We are indebted to Dr. R. A. Mitsch of the 3M Co. for the CF_2N_2 sample. C. D. J. and W. E. S. were supported by National Science Foundation Summer URP Grants.

Organic Oxalates. VI. Pyrolysis of Di(α-substituted benzyl) Oxalates[1]

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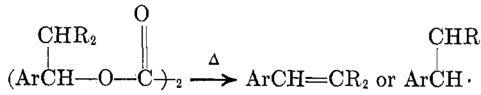
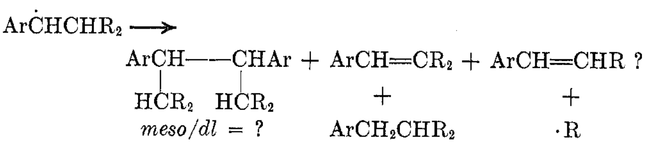
Products from the low-pressure gas phase pyrolysis of di(α-substituted benzyl) oxalates are reported. Di(α-substituted benzyl) oxalates which contain β hydrogen atoms undergo an elimination reaction in addition to homolytic decomposition to α-substituted benzyl radicals. Coupling of α-substituted benzyl radicals occurs only when the α substituent is a methyl or trifluoromethyl group. When the α substituent is a trichloromethyl, an ethyl, a pentafluoroethyl, or an isopropyl group, β scission is the chief reaction of the radicals. No evidence for disproportionation of the radicals is presented. The *meso/dl* ratios for the coupling products from the α-methylbenzyl and α-trifluoromethylbenzyl radicals are 52:48 and 42:58, respectively. Mechanistic implications of these results are discussed.

Recently we reported that pyrolysis of ring-substituted dibenzyl oxalates under vacuum gave exclusively bibenzyls resulting from coupling of benzyl radicals.[2] These oxalates did not contain β hydrogen atoms and consequently could not undergo elimination reactions such as those observed by Karabatsos and coworkers who pyrolyzed dialkyl oxalates that possessed β hydrogen atoms in the liquid phase.[3] In this paper we report the study of di(α-substituted benzyl) oxalates. One objective of this study was to determine if the pyrolysis of an oxalate that contains β hydrogen atoms under our conditions leads to an elimination reaction or benzyl radical formation. Another objective was to determine the fate of α-substituted benzyl radicals in cases where they are produced. Specifically, we wished to know whether



$$(\mathrm{Ar}\overset{\mathrm{CHR_2}}{\mathrm{C}}\mathrm{H{-}O{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\!\!\rightarrow\!)_2 \xrightarrow{\Delta} \mathrm{ArCH{=}CR_2}\ \text{or}\ \mathrm{Ar}\overset{\mathrm{CHR_2}}{\mathrm{C}}\mathrm{H}\cdot$$

these radicals couple, disproportionate, or undergo β scission under our conditions, and the *meso/dl* ratio of the coupling products when coupling occurs.



$$\mathrm{Ar\dot{C}HCHR_2} \longrightarrow \underset{\mathit{meso/dl}\,=\,?}{\mathrm{Ar}\underset{\mathrm{HCR_2}}{\mathrm{CH}}{-\!-\!-}\underset{\mathrm{HCR_2}}{\mathrm{CH}}\mathrm{Ar}} + \underset{\mathrm{ArCH_2CHR_2}}{\overset{}{\mathrm{ArCH{=}CR_2}}\atop +} + \underset{\cdot\mathrm{R}}{\mathrm{ArCH{=}CHR}\atop +}\ ?$$

Results

Glpc and nmr analyses of the pyrolysate of di-α-methylbenzyl oxalate at 570° showed that styrene was the main product and benzaldehyde and *meso*- and *dl*-2,3-diphenylbutanes were minor products obtained in comparable amounts. Pyrolyses carried out from 400 to 650° showed that the ratio of styrene to 2,3-diphenylbutanes ranged from 4.9 to 9.0. The large amount of styrene probably comes from a concerted cyclic elimination pathway, the usual pyrolytic route of esters,[4] since disproportionation of the α-methylbenzyl radical should lead to ethylbenzene in addition to styrene and only a negligible amount of ethylbenzene was detected. Thus di-α-methylbenzyl oxalate seems to decompose chiefly by the elimination route and the main reaction of the α-methylbenzyl radicals which are produced is coupling to form the 2,3-diphenylbutane diastereomers. The origin of benzaldehyde is not clear, and it may come from the mono-α-methylbenzyl oxalate which results from the elimination reaction.

The *meso/dl* ratio of the 2,3-diphenylbutanes produced at 480° was found to be 52/48. The meso isomer was passed through the oven heated to 480° with negligible isomerization to the *dl* isomer.

Pyrolysis of di-α-trifluoromethylbenzyl oxalate at 650° gave the two isomers of 2,3-diphenyl-1,1,1,4,4,4-hexafluorobutane (DPHFB) in 40% yield. These isomers were separated by glpc (SE-30 column) and their structures were confirmed by nmr, ir, and mass spectra and elemental analyses. The lower melting isomer, mp 73–75°, was assigned the *dl* structure and the other isomer, mp 156–158°, was assigned the meso structure since the symmetry of the unit cell of the higher melting isomer demands that the molecule has an inversion center. Only the meso isomer can have a center of symmetry. Weissenberg photographs of a single crystal of the high melting isomer showed the D_{2h} Laue symmetry appropriate for the orthorhombic crystal class. The cell constants, measured from Weissenberg photographs, are $a = 14.43 \pm 0.08$, $b = 7.41 \pm 0.01$, $c = 13.28 \pm 0.05$ Å.

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[1] (a) Part V: W. S. Trahanovsky and P. W. Mullen, *Chem. Commun.*, 102 (1971). (b) 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 the National Science Foundation (NSF) Grant GP 1715 and a grant from the Iowa State Alumni Research Fund. We thank these organizations for their support. (c) Based on work by C. C. O. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University. (d) Preliminary communication: Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, 33-P. (e) Alfred P. Sloan Research Fellow, 1970–1972. (f) NSF Undergraduate Research participant, summer 1970.

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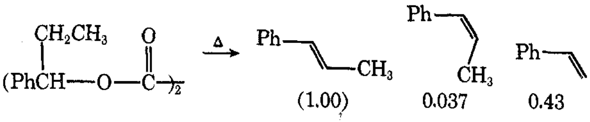
The systematic extinctions on *h*0*l* (absent if $l = 2n + 1$), 0*kl* (absent if $k = 2n + 1$), and *hk*0 (absent if $h = 2n + 1$) uniquely determine the space group as *P*bca (D_{2h}^{15}). The density, determined by flotation in aqueous potassium iodide, is 1.42 g/cm^3. This implies that there are four molecules per unit cell. The calculated density for $Z = 4$ is 1.49 g/cm^3. Since space group *P*bca requires 8 molecules of the isomer if no molecular symmetry were used in the crystal, the two halves of the molecule must be related by the crystallographic inversion center. Thus, in the absence of disorder, the high melting dimer must be the meso and it must pack in the anti conformation which has an inversion center.

Our assignment of stereochemistry is consistent with the generalization that the more symmetrical isomer melts at a higher temperature than the less symmetrical isomer.[5] Moreover, the *dl* isomer is eluted before the meso isomer on an SE-30 column which is the same behavior exhibited by the 2,3-diphenylbutanes, but polarity differences of the two sets of isomers make their glpc behavior difficult to predict. The average *meso/dl* ratio of DPHFB obtained from seven runs of the pyrolysis of di-α-trifluoromethylbenzyl oxalate was 42.1/57.9 = 0.728 ± 0.024. The pyrolysis temperature of these runs ranged from 420 to 650°. No significant temperature variation of the *meso/dl* ratio was noted; however, at low pyrolysis temperatures where the yields of DPHFB became low, the glpc peak of an impurity which was eluted at the same rate as the *dl* isomer became important. Using a 17-ft 20% SE-30–3-ft 20% SE-95 column the peaks for the impurity and *dl* isomer were resolved. Using this column, a *meso/dl* ratio of 42.5/57.5 was obtained for a run carried out at 420°. In this run, only 7% of these products were obtained relative to recovered starting material.

The *meso/dl* ratio was the same for runs that were made using a mixture of the meso and *dl* oxalates or one of the pure, crystalline isomers of the oxalate. The meso DPHFB was found not to isomerize significantly when passed through the furnace at 500°.

Unlike the di-α-trifluoromethylbenzyl oxalate, di-α-trichloromethylbenzyl oxalate gave rise to the elimination product, not the product from the coupling reaction. A 32% yield of β,β-dichlorostyrene was obtained from the pyrolysis of di-α-trichloromethylbenzyl oxalate at 500 and 680°.[6]

Pyrolysis at 570° of di-α-ethylbenzyl and di-α-isopropylbenzyl oxalates gave the olefins that result from elimination reactions of the oxalates and fragmentation reactions of the substituted benzyl radicals. Relative yields of these products are presented in eq 1 and 2 and in both cases the absolute yield of these products was >60%. No evidence for coupling products from the benzyl radicals was obtained.



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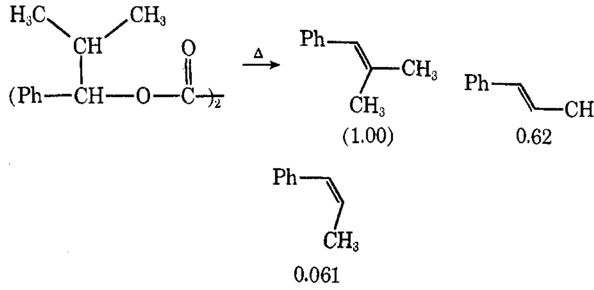
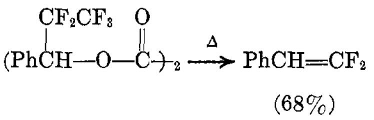


(2)

Attempts to prepare di-α-*tert*-butylbenzyl oxalate were unsuccessful.

Pyrolysis of di-α-pentafluoroethylbenzyl oxalate at 650° gave almost exclusively β,β-difluorostyrene. Nmr analysis of the pyrolysate showed that 1.36 mol of β,β-difluorostyrene was formed per mol of oxalate pyrolyzed. Glpc analysis showed the presence of three high boiling components. Two of these components might by the coupling products of the intermediate radical but their low yield prevented their identification. Undoubtedly the β,β-difluorostyrene was formed from β scission of the α-pentafluoroethylbenzyl radical.



$$\left(\mathrm{Ph}\overset{\mathrm{CF_2CF_3}}{\mathrm{CH}}\mathrm{—O—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\right)_2 \xrightarrow{\Delta} \underset{(68\%)}{\mathrm{PhCH{=}CF_2}}$$

Pyrolysis of di-α,α-dimethylbenzyl oxalate gave a quantitative yield of the elimination product, α-methylstyrene.

Discussion

We have reported previously that the major mode of thermal decomposition of ring-substituted dibenzyl oxalates in the gas phase is homolytic cleavage to form benzyl radicals which couple to form bibenzyls.[2] From the present study it is clear that di(α-substituted benzyl) oxalates which contain β hydrogen atoms undergo an elimination reaction in addition to homolytic decomposition to benzyl radicals. Indeed, the elimination reaction becomes the exclusive pathway of decomposition of di-α,α-dimethylbenzyl oxalate.

The most reasonable mechanism for the elimination reaction is that proposed for monoester pyrolyses, a concerted cyclic pathway.[4] An ion pair mechanism as proposed by Karabatsos and coworkers[3] for the thermal decomposition of oxalates in the liquid phase cannot be entirely ruled out but is less likely than the concerted cyclic process for a gas phase reaction.

Although the elimination reaction is the dominant one during the gas phase pyrolysis of di(α-alkyl-substituted benzyl) oxalates that contain β hydrogen atoms, formation of α-alkyl-substituted benzyl radicals does occur. Coupling of these radicals take place, however, only when the α substituent is a methyl group. When the α substituent is an ethyl or isopropyl group, β scission is the chief reaction of the radicals. No evidence for disproportion of the radicals was obtained in any case.

Replacement of the hydrogen atoms on the α substituent with fluorines prevents the elimination reaction but the α-perfluoroalkyl-substituted benzyl radicals

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[5] K. Wiberg, "Laboratory Techniques in Organic Chemistry," McGraw-Hill, New York, N. Y., 1960, pp 77–79.

[6] This oxalate was pyrolyzed at lower pressures (10^{-4}–10^{-5} mm) than was used for the other oxalates since a different pyrolysis apparatus was used.

undergo reactions similar to the hydrocarbon radicals. It is interesting to note that the α-pentafluoroethylbenzyl radical undergoes β scission just like the α-ethylbenzyl radical to give a fair yield of β,β-difluorostyrene. The α-trichloromethylbenzyl radical, unlike the α-trifluoromethylbenzyl radical, undergoes β scission to give a fair yield of β,β-dichlorostyrene.

Fragmentation of alkyl radicals, especially α-alkylbenzyl radicals has not been extensively investigated. Only a few scattered examples are cited in the literature such as fragmentation of lower alkyl radicals,[7] bond scission of aryl-substituted alkyl radicals during high temperature cracking of alkylbenzene,[8] and reversibility of radical addition to olefins.[9,10] Recently, Bartlett and McBride[11] have reported that the 1-phenyl-1-methylisobutyl radical undergoes exclusively dimerization and disproportionation. The fact that we have obtained exclusively β scission products from similar radicals is undoubtedly due to the high temperature of our reactions.

Coupling of the α-methyl- and α-trifluoromethylbenzyl radicals leads to meso and *dl* products. Since we measured these *meso*/*dl* ratios from pyrolyses carried out under conditions that did not isomerize one of the pure isomers, our ratios should measure the rates of formation of these two isomers and not their thermodynamic stabilities. α-Methylbenzyl radicals have been generated from several sources and under a variety of conditions and the latest results indicate that statistically distributed α-methylbenzyl radicals couple to give approximately equal amounts of *meso*- and *dl*-2,3-diphenylbutanes.[12,13] Thus our results agree with those previously published and indicate that the activation energies for the formation of the *meso*- and *dl*-2,3-diphenylbutanes are equal which indicates that no great steric or polar differences exist in the two diasteromeric transition states.

In contrast to the *meso*/*dl* ratio found for the products from α-methylbenzyl radicals, the *meso*/*dl* ratio of the products from the coupling of the α-trifluoromethylbenzyl radicals was found to be 42/58. This difference in yields of meso and *dl* isomers from the coupling of the α-trifluoromethylbenzyl radicals suggests that there is a substantial polar effect which favors formation of one diastereomer over the other. However, it is difficult to understand the predominance of the *dl* isomer since the most favored transition state that leads to coupling would seem to be the one that has the two trifluoromethyl groups as far apart as possible so that their dipole moments cancel, and the two phenyl groups as far apart as possible in order to minimize steric interactions. This transition state would lead to the meso isomer. Thus, the greater yield of the *dl* isomer indicates that some other types of polar or steric factors must be important which causes the *dl* transition state to be more stable than the meso transition state.

The *meso*/*dl* ratios of products from other radicals that have been studied are usually close to 1.[12i,j,14] There are only a few cases which are reported to give unequal amounts of meso and *dl* coupling products, and, in these cases, usually the meso isomer was obtained in higher yield.[12h,14a,15]

The yield of the two 2,3-diphenyl-1,1,1,4,4,4-hexafluorobutanes was 40% from a pyrolysis at 650°. This reaction illustrates the synthetic utility of oxalate pyrolyses since we have not been able to synthesize these compounds by other routes. The Grignard coupling reaction is often used to produce bibenzyls[2] but α-fluoro Grignard and lithium reagents are quite unstable and difficult to work with.[16]

Experimental Section

Materials and Methods.—Most equipment, some materials, and methods have been previously described.[2,17]

In addition to using the previously described pyrolysis apparatus, a high-vacuum pyrolysis apparatus was also used. This apparatus was constructed as follows. The pyrolysis tube consisted of a 31 × 2.8 cm Vycor tube filled with short pieces (∼6 mm) of 7-mm Vycor tubing. It was sealed on one end to an inner H.V.S., ground, Pyrex, ₸ 40/35, o-ring joint with a silicone rubber o-ring (Scientific Glass Apparatus) for attachment to the sample holder; the other end was sealed to a 90° angle portion of Pyrex tubing and then an o-ring seal, 2.5-cm i.d., joint for attachment to the product trap. The sample was held in a small boat inside the constrictured outer portion of the ₸ 40/35 joint and could be externally heated by an aluminum cylinder wrapped with heating tape and asbestos tape. The product trap joints were both 2.5-cm i.d., o-ring seal. The furnace was an 800-W Lindberg Hevi-Duty "Mini Mite," with input control and pyrometer. The temperature was measured only at the center of the tube. A two-stage oil diffusion pump (H. S. Martin and Son) was used and was monitored with a cold cathode gauge (H. S. Martin and Son). The stopcocks (Scientific Glass) to the roughing line and between the product trap and vacuum line were both Teflon sized 0–10 and 0–15 mm, respectively.

α-Methylbenzyl, α-ethylbenzyl, α-isopropylbenzyl, and α,α-dimethylbenzyl alcohols were obtained from Aldrich.

α-Trifluoromethylbenzyl alcohol was prepared by the lithium aluminum hydride reduction of trifluoroacetophenone (Pierce Chemical Co.): yield 80%; bp 70–74° (15 mm) [lit.[18] bp 64–65° (5 mm)]; nmr ($CDCl_3$) δ 7.32 (s, 5), 4.82 (q, 1, $J = 7$ Hz), and 3.33 (s, 1).

α-Pentafluoroethylbenzyl Alcohol.—Pentafluoroethyl phenyl ketone was prepared by the method of Simmons, Black, and Clark[19] by the Friedel–Crafts reaction of pentafluoropropionyl chloride (Pierce Chemical Co.) with benzene in the presence of aluminum trichloride, yield 30%, bp 159–160° (lit.[19] bp 161–

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TABLE I

YIELDS, MELTING AND BOILING POINTS, ELEMENTAL ANALYSES, NMR SIGNALS, AND IR ABSORPTION BANDS OF DI(α-SUBSTITUTED BENZYL) OXALATES (PhCHROCO$\rightarrow_2$)

R	Registry no.	Yield, %	Mp or bp, (mm) °C	Found, %		Calcd, %		Chemical shifts, δ, ppm[a]			Ir frequency,[b] cm^{-1} >C=O
				C	H	C	H	Aromatic H	—CH—	Other	
CH$_3$	24523-30-6	65	172–176 (1.5)	71.79	5.98[c]	72.45	6.09	7.3 (m)	5.96 (q)	1.57 (d, J = 7 Hz, CH$_3$)	1770 1740
CH$_3$CH$_2$	31164-21-3	56	170–172 (0.4)	73.67	6.92[d]	73.58	6.79	7.3 (m)	5.78 (t, J = 7 Hz)	1.83 (quintet, CH$_2$) 0.88 (t, J = 7 Hz, CH$_3$)	1775 1730
(CH$_3$)$_2$CH	31164-22-4	68	160–163 (0.2)	74.46	7.43[c]	74.53	7.40	7.3 (s)	5.61 (d, J = 7 Hz)	2.21 (m, CH) 1.0 (d, J = 7 Hz, CH$_3$) 0.82 (d, J = 7 Hz, CH$_3$)	1770 1740
CF$_3$	31164-23-5	45	140–143 (0.3) 63–87 97–99[e]	52.80	2.87[d]	53.18	2.98	7.3 (s)	6.2 (q, J = 7 Hz)		1795 1770
CF$_3$CF$_2$	31208-73-8	60[f]	. . .[g]	47.28	2.58[c]	47.42	2.39	7.3 (s)	6.3 (q, separations between peaks are 9, 6, and 9 Hz)		1790 1770
CCl$_3$	31164-24-6	66	102–117[h]	42.81	2.15[i]	42.81	2.39	7.5[j] (m)	6.4 (s)		1790[j] 1765

[a] Solvent was CDCl$_3$. [b] Solvent was CHCl$_3$. [c] Analyzed by Spang Microanalytical Laboratory, Ann Arbor, Mich. [d] Analyzed by MHW Laboratories, Garden City, Mich. [e] The distilled oxalate was presumably a mixture of the meso and *dl* isomers. One isomer (mp 97–99°) could be purified by recrystallization from 95% ethanol. [f] Estimated approximately from nmr spectrum. [g] No pure product was isolated. The analytical sample was purified by glpc. [h] Presumably this material was a mixture of the meso and *dl* isomers. [i] Analyzed by Chemalytics, Inc., Tempe, Ariz. [j] Solvent was CCl$_4$.

162°). The ketone was reduced to the alcohol with lithium aluminum hydride: 80% yield; bp 45–50° (2.8 mm) [lit.[18] bp 52° (3 mm)]; nmr (CDCl$_3$) δ 7.35 (s, 5), 5.03 (q, each peak separated by 8 Hz, 1) and 4.26 (s, 1).

α-Trichloromethylbenzyl Alcohol.—Phenyltrichloromethyl ketone was prepared according to the procedure of Cohen, Wolinski, and Scheuer[20] by chlorination (with excess Cl$_2$) of acetophenone first in glacial acetic acid at 50–60° and then at 95–100° in the presence of added sodium acetate: crude yield 95%, slightly colored viscous liquid; nmr (CCl$_4$) δ 8.2 (m, 2) and 7.5 (m, 3) with no evidence for mono- or dichloroacetophenone. The crude ketone (22.3 g) was reduced to the alcohol with aluminum isopropoxide according to the procedure of Bergkvist:[21] crude yield 94%; slightly colored viscous liquid; nmr (CCl$_4$) δ 7.4 (m, 5), 5.03 (d, 1, CHOH, J = 4.5 Hz), and 3.92 (d, 1, OH, J = 4.5 Hz).

Preparation of Di(α-substituted benzyl) Oxalates.—Methods I,[2] II,[2] and III[17] have been previously described. In Table I are presented pertinent data for each new di(α-substituted benzyl) oxalate. These oxalates were prepared by method III.

Di-α,α-dimethylbenzyl oxalate was prepared as described previously:[3a] yield 91%; mp 68–70° (from ethanol); ir (CHCl$_3$) 1772 and 1740 cm^{-1} (C=O); nmr (CDCl$_3$) δ 7.32 (s, 5) and 1.85 (s, 6).

Anal. Calcd for C$_{20}$H$_{22}$O$_4$: C, 73.58; H, 6.80. Found: C, 73.12; H, 6.85.

***meso-* and *dl*-2,3-diphenylbutanes** were prepared by the method of Barber, Slack, and Woolman[22] by a Grignard coupling reaction of α-chloroethylbenzene, prepared as described by Shirley.[23]

Procedure for pyrolysis of oxalates at high temperatures under vacuum has been illustrated by that of dibenzyl oxalate.[2]

Pyrolysis of Di-α-methylbenzyl Oxalate.—Glpc analysis of the pyrolysate of di-α-methylbenzyl oxalate run at 570° showed the presence of at least eight components. Nmr analysis showed that the components were styrene, benzaldehyde, *dl*- and *meso*-2,3-diphenylbutanes, possibly the formate of α-methylbenzyl alcohol, and other unknowns. The identity of 2,3-diphenylbutanes was confirmed also by glpc peak enhancement [8 ft × 0.25 in. 20% SE-30 column (column A) at 135°]. The ratio of styrene and 2,3-diphenylbutanes was based on nmr analysis. The relative ratio of the diastereomers was determined from the glpc peak areas with the assumption that their thermal conductivities were equal.[12i] *meso*-2,3-Diphenylbutane was passed through the pyrolysis apparatus with different furnace temperatures and the *meso/dl* ratios were obtained by nmr analysis. Less than 5% *dl* isomer was obrained when the furnace was heated to 500° or less and 15% *dl* isomer was obtained when the furnace was at 540°.

Pyrolysis of Di-α-ethylbenzyl Oxalate.—Di-α-ethylbenzyl oxalate was pyrolyzed at 570° with a head temperature of 135–140°. Nmr analysis of the pyrolysate showed the presence of 0.76 mol of *trans*-methylstyrene, 0.026 mol of *cis*-methylstyrene, 0.31 mol of styrene, and other unknown components using dimethyl oxalate as an internal standard. The identity and ratio of the components were also confirmed by glpc analysis (column A at 90°).

Pyrolysis of Di-α-isopropylbenzyl Oxalate.—Di-α-isopropylbenzyl oxalate was pyrolyzed at 570°. Glpc analysis of the pyrolysate indicated the presence of a small amount of styrene and an unknown and the three olefins given in eq 2 which were identified by glpc peak enhancement. Nmr analysis of the pyrolysate using dimethyl oxalate as an internal standard showed that 0.36 mol of *trans*-β-methylstyrene was formed per mol of oxalate pyrolyzed.

Pyrolysis of Di-α-trifluoromethylbenzyl Oxalate.—Di-α-trifluoromethylbenzyl oxalate was pyrolyzed at 420–650° with a head temperature of 130–135°. Glpc analysis of the pyrolysate showed the presence of six components. The two major components were collected by glpc [5 ft × 0.25 in. 20% SE-30 column (column B) at 190°]. Mass spectra of both components showed parent ion peak at m/e 318 corresponding to the assigned structure of 2,3-diphenyl-1,1,1,4,4,4-hexafluorobutane (DPHFB). The ir spectra of both components were similar with broad absorptions from 1350–1050 cm^{-1}. The product with the shorter

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retention time was assigned the *dl* structure (see Results): nmr ($CDCl_3$) δ 7.3–6.8 (m, 5) and 4.0 (m, 1);[24] mp 73–75°.

Anal. Calcd for $C_{16}H_{12}F_6$: C, 60.35; H, 3.82. Found: C, 60.49; H, 3.90.

The product with the longer retention time was assigned the meso structure (see Results): nmr ($CDCl_3$) δ 7.4 (s, 5) and 4.0 (m, 1);[24] mp 156–158°.

Anal. Calcd for $C_{16}H_{12}F_6$: C, 60.35; H, 3.82. Found: C, 60.42; H, 3.84.

In a large-scale run, the combined pyrolysate from 30 g of oxalate, pyrolyzed in 3-g portions at 650°, was dissolved in hot ethanol. Upon cooling, the impure meso isomer separated as white crystals, mp 160–162°, leaving the ethanol rich in the *dl* isomer. Recrystallization of these crystals from ethanol gave 5 g of the meso isomer, mp 161–162°. Evaporation of the initial mother liquor gave a residue which, when recrystallized from petroleum ether (bp 30–60°), gave 3 g of white crystals, mp 65–70°. This low-melting material was further purified by chromatography on alumina using petroleum ether as the eluent giving white crystals of the *dl* isomer, mp 72–74°.

Single crystals of the high-melting isomer suitable for X-ray diffraction were grown by slow evaporation of a petroleum ether (bp 30–60°) solution. These crystals melted at 161–162°. A crystal of approximate dimension 0.2 mm on an edge was chosen and mounted along the *a* axis. Weissenberg photographs were taken with Ni-filtered Cu K_α radiation (1.5418 Å) of the 0*kl* and 1*kl* zones. A second crystal was mounted and the *h*0*l* and *h*1*l* zones were recorded.

The ratio of the two DPHFB isomers obtained from a pyrolysis at 500° was based on glpc analysis. The thermal conductivities of the two isomers were found to be identical. The absolute yield of the DPHFB isomers was obtained from the pyrolysate based on nmr analysis using bibenzyl as an internal standard. Less than 5% *dl*-DPHFB was obtained when *meso*-DPHFB was passed through the pyrolysis apparatus with the furnace heated to 500°.

Pyrolysis of Di-α-pentafluoroethylbenzyl Oxalate.—Pyrolysis of di-α-perfluoroethylbenzyl oxalate took place at 650° with a head temperature of 135–140°. The characteristic nmr spectrum of the β,β-difluorostyrene was the main feature of the nmr spectrum of the pyrolysate.[25] The yield of β,β-difluorostyrene was determined by nmr analysis using bibenzyl as an internal standard. Glpc analysis of the pyrolysate showed the presence of at least three high-boiling components in small amounts (column A).

Pyrolysis of di-α-trichloromethyl oxalate was carried out at 500 and 680° at 10^{-4}–10^{-5} mm with a head temperature of 135°.[6] The nmr spectrum (CCl_4) of the pyrolysate showed essentially a single product, β,β-dichlorostyrene, present in 32% yield relative to an internal standard, 1,1,2,2-tetrachloroethane (δ 6.00): nmr (CCl_4) δ 7.37 (m, 5, C_6H_5) and 6.78 (s, 1, $CH{=}CCl_2$) [lit.[26] nmr ($CDCl_3$) δ 7.25 (m, 5) and 6.72 (s, 1)]. Glpc analysis of the product mixture (column B) showed one main peak and several smaller peaks, the smaller peaks accounting for less than 5% of the crude mixture assuming equal thermal conductivities. A mass spectrum of the crude mixture gave a parent ion peak at *m/e* 172.

Pyrolysis of Di-α,α-dimethylbenzyl Oxalate.—The nmr spectrum of the pyrolysate run at 340° showed exclusively the characteristic spectrum of α-methylstyrene. Nmr analysis using bibenzyl as an internal standard showed that a quantitative yield of the styrene was obtained. The identity of the product was further confirmed by glpc analysis (column B).

Registry No.—Di-α,α-dimethylbenzyl oxalate, 31164-25-7; *dl*-DPHFB, 31208-74-9; *meso*-DPHFB, 31164-26-8.

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The Thermal Decomposition of β-Hydroxy Esters

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The products and kinetics of the thermal decomposition of several β-hydroxy esters have been studied. It has been shown that all of the β-hydroxy esters studied pyrolyze to form a mixture of the corresponding ester and aldehyde or ketone and that the decomposition follows first-order kinetics and appears to be homogenous and unimolecular. Based on these data a six-membered cyclic transition state is proposed for the reaction. The absence of large substituent effects indicates that little charge separation occurs during the breaking of the carbon–carbon double bond.

It has recently been shown[1] that ethyl 3-hydroxy-3-methylbutanoate decomposes thermally in xylene solution to a mixture of acetone and ethyl acetate (eq 1).

$$(CH_3)_2COHCH_2CO_2C_2H_5 \longrightarrow (CH_3)_2C{=}O + CH_3CO_2C_2H_5 \quad (1)$$

It was proposed that the reaction involves a cyclic six-membered transition state similar to that thought to be involved in other similar thermal decomposition reactions such as the thermolysis of β-hydroxy ketones,[2] β-hydroxy olefins,[3] β-hydroxy alkynes,[4] and esters.[5] The present paper reports the products and kinetics of the thermolysis in the gas phase of several other β-hydroxy esters.

Results

The β-hydroxy esters listed in Table I were pyrolyzed in evacuated, sealed glass tubes. All of the β-hydroxy esters pyrolyzed to a mixture of the ester and aldehyde or ketone according to eq 2.

$$R_2COHCHRCO_2C_2H_5 \longrightarrow R_2CO + RCH_2CO_2C_2H_5 \quad (2)$$

The products of the reaction were identified by their glc retention times and by the formation of 2,4-dinitrophenylhydrazones of the aldehyde or ketone from the products of the reaction. No other major products of reaction were observed by glc, and quantitative glc measurements using *p*-xylene as an internal standard indicated that the above reaction occurred to at least 90% for all of the β-hydroxy esters studied. No peak due to water was observed indicating that under the conditions of reaction no dehydration occurred. Also in the case of the ethyl esters no peak due to ethylene was observed indicating that a possible side reaction, the pyrol-

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