Pyrolysis of 1,1,3,3-Tetrafluoroacetone

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The pyrolysis of 1,1,3,3-tetrafluoroacetone was studied in a flow system at 575–690°. The principal products of the pyrolysis are CO, CF_2H_2, CF_2HCF_2H, CF_2CFH, CF_3CHCF_2, $CF_2HCF_2CF_2H$, and HF (as SiF_4). Evidence has been obtained for the insertion of CF_2 into HF, elimination of HF from excited CF_2HCF_2H, and the intermediacy of difluoroketene.

The principal products of the pyrolysis of acetone in flow systems at about 600° are carbon monoxide, methane, ethane, and ketene.[1] Important steps in the mechanism are thought to be

$$CH_3COCH_3 \longrightarrow CH_3\cdot + \cdot COCH_3$$

$$\cdot COCH_3 \longrightarrow CH_3\cdot + CO$$

$$CH_3\cdot + CH_3COCH_3 \longrightarrow CH_4 + \cdot CH_2COCH_3$$

$$\cdot CH_2COCH_3 \longrightarrow CH_2CO + \cdot CH_3$$

$$2\cdot CH_3 \longrightarrow C_2H_6$$

One might therefore expect that the pyrolysis of 1,1,3,3-tetrafluoroacetone (TFA) would give difluoroketene, a compound which has not previously been isolated.[2] Although we did not obtain difluoroketene as a product of the pyrolysis of TFA in a flow system at 575–690°, we did find evidence that it was an intermediate. Furthermore, the pyrolysis of TFA revealed two elementary steps of importance: the elimination of hydrogen fluoride from excited difluoromethyl dimers and the insertion of difluoromethylene into hydrogen fluoride to form trifluoromethane.

$$CF_2HCF_2H^* \longrightarrow CF_2{=}CFH + HF$$

$$CF_2 + HF \longrightarrow CF_3H$$

TFA was completely pyrolyzed at 690° with a contact time of 3.3–4.5 sec. At 575° only 5% of the TFA was pyrolyzed. Semiquantitative analysis of condensable products of the 690° pyrolysis gave the following product distribution (mole %): CF_2H_2 (32), CF_2HCF_2H (11), $CF_2HCF_2CF_2H$ (10), CF_3CHCF_2 (10), CF_2CFH (8), CF_3H (7) (less at lower temperatures), SiF_4 (4), CF_2HCF_3 (4), CFH_2CF_3 (4), $CF_2HCF_2CF_2CF_2H$ (2), CF_2HCOF (1) (more at lower temperatures), CF_2CH_2 (0.7), CF_2O (0.04), unidentified (6), CF_2CF_2 (trace) (significantly more at lower temperatures). Infrared and molecular weight data suggest that the major unidentified products are fluorobutanes and fluorobutenes. When CO analyses were performed, a semiquantitative agreement between CO production and TFA pyrolysis was found.

Steps analogous to the formation of methane and ethane in the pyrolysis of acetone account for the large amounts of CF_2HCF_2H and CF_2H_2. However, when difluoromethyl radicals combine, the excited dimer, in addition to undergoing collisional deactivation to stable CF_2HCF_2H, can also eliminate HF to form trifluoroethylene, a process also observed by Pritchard and Bryant in the photolysis of TFA.[3] These investigators argued on the basis of RRK unimolecular kinetics theory that the yield of CF_2CFH should increase with temperature, a prediction supported by our observations. The importance of this process is underscored by the formation of CF_3CFH_2 which can be explained by the addition of HF to CF_2CFH. The formation of CF_3CFH_2 lends support to the notion that symmetric fluoroethanes will be converted to asymmetric ones if a mechanistic pathway is provided. Although the thermodynamic functions for some of the tetrafluoroethanes have not been reported, data on trifluoroethanes [CF_3CH_3, $\Delta H_f°$ (298°) = -178.2 kcal/mol; CF_2HCFH_2, $\Delta H_f°$ (298°) = -158.9 kcal/mol][4] suggest that the asymmetric isomer is the more stable. An estimate of the enthalpies of formation of the tetrafluoroethanes using the group substitution methods[5] gives the supporting results: $\Delta H_f°$ (CF_3CFH_2) = -210 kcal/mol and $\Delta H_f°$ (CF_2HCF_2H) = -199 kcal/mol. A similar calculation on the trifluoroethanes gives $\Delta H_f°$ (CF_3CH_3) = -171 kcal/mol and $\Delta H_f°$ (CHF_2CH_2F) = -149 kcal/mol, in fair absolute and good relative agreement with the experimental values.[6]

Some higher molecular weight products result from difluoromethyl–olefin reactions

$$\cdot CF_2H + CF_2CF_2 \longrightarrow CF_2HCF_2CF_2\cdot$$

$$CF_2HCF_2CF_2\cdot + CF_2HCOCF_2H \longrightarrow \underset{\mathbf{1}}{CF_2HCF_2CF_2H} + CF_2HCOCF_2\cdot$$

$$CF_2HCF_2CF_2\cdot + \cdot CF_2H \longrightarrow \underset{\mathbf{2}}{CF_2HCF_2CF_2CF_2H}$$

A photolysis of a TFA–CF_2CF_2 mixture yielding **1** and **2** (as well as CF_2H_2 and CF_2HCF_2H) as major products was performed to check this mechanism. Extension of the chain by means of HF elimination and addition provides a reasonable explanation for higher molecular weight products. Trifluoroethylene–difluoromethyl-radical reactions are not needed to account for the identified products but may play a role in the formation of minor higher molecular weight products. Photolysis of a TFA–CF_2CFH mixture yielded mostly CF_2H_2 and CF_2HCF_2H with only trace amounts of unidentified higher molecular weight products.

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(6) From the enthalpy of formation of CF_2CF_2 at 25°, -157.6 kcal/mol (ref 4), and the enthalpy of hydrogenation of CF_2CF_2 at 120°, -42.26 kcal/mol (J. R. Lacher and J. D. Park, AF-AFOSR Report 810-67), the enthalpy of formation of CF_2HCF_2H at 25° is calculated to be -200.6 kcal/mol. The adjustment of the enthalpy of hydrogenation of CF_2CF_2 to 25° (-0.6 kcal/mol) was made using the heat capacities [CF_2CF_2 and H_2, JANAF Thermochemical Tables, 1965; CF_2HCF_2H, calculated by statistical thermodynamics from infrared data of P. Klaboe and J. R. Nielsen, *J. Chem. Phys.*, **32**, 899 (1960)]. Entropy differences between fluoroethane isomers are assumed to be essentially zero.

Although difluoroketene was not isolated, its role as an intermediate is indicated by the isolation of CF_2CF_2 (and its addition products), CF_3H, and CF_2HCOF. By analogy to the known chemistry of ketenes,[7] difluoroketene would be expected to decompose to CF_2 and CO. C_2F_4 arises from the well-known dimerization of CF_2. A secondary route for the formation of CF_2 could be the following reaction.[7]

$$CF_2 + CF_2CO \longrightarrow CF_2CF_2 + CO$$

CF_3H arises from the insertion of CF_2 into HF, a reaction previously unreported. The insertion of CF_2 into HCl has been reported.[8] We have observed that CF_3H is a product of the pyrolysis of a mixture of HF and difluorodiazirine (a thermal source of CF_2).[9] The formation of $CF_2HCF_2CF_2CF_2H$ cannot be attributed to the insertion of CF_2 into $CF_2HCF_2CF_2H$ as Mitsch has shown that CF_2, a species more discriminating and less reactive than methylene, does not insert into C–H bonds.[10] Insertion of CF_2 into C–F bonds is also ruled out as it has not been observed in simpler systems.[10] Reaction of CF_2 with CF_2H, for which $\Delta H = -53$ kcal/mol,[11] could be another route to CF_2HCF_2H and to $CF_2HCF_2CF_2H$. However, no products, such as $CF_2HCF{=}CF_2$, were isolated that would be characteristic of this mechanism. A hypothetical decomposition of CF_2HCOF, a product presumed to arise from addition of HF to CF_2CO, is not a likely alternative pathway to CF_3H (and CO). Although CF_2HCOF is a product of the pyrolysis of difluoroacetic anhydride, CF_3H is not. The isolation of CF_2HCOF is more direct evidence of the CF_2CO intermediate. A reaction of HF with CF_2CO parallels ketene chemistry; for example, HCl reacts with ketene to produce acetyl chloride.[12]

In their paper on the pyrolysis of hexafluoroacetone, Batey and Trenwith propose that the observed trifluoroacetyl fluoride results from the primary step in the decomposition[13]

$$CF_3COCF_3 \longrightarrow CF_3COF + CF_2$$

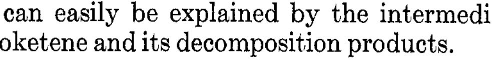
Such a route in the TFA pyrolysis would require the production of fluoromethylene (CFH) as an intermediate which could combine to form 1,2-difluoroethylene. Since neither 1,2-difluoroethylene nor its HF addition products were observed, this route for CF_2HCOF production seems unlikely. CF_2H_2 could be interpreted as an insertion product of CFH into HF, but the large excess of CF_2H_2 over CF_2HCOF and COF_2, a possible decomposition product, rules this out as as major mechanistic pathway. However, the ketene route, in which each mole of CF_2H_2 is accompanied by 1 mol of CF_2, following ketene decomposition, is supported within the accuracy of the semiquantitative data by the mass balance between CF_2H_2 and CF_2 derived products. At 690°, $CF_2H_2 = 32$ mol %; $2CF_2CF_2 + CF_2HCF_2CF_2H + 2CF_3CF_2H + CF_2CHCF_2 + CF_3H + CF_2HCOF + 2CF_2HCF_2CF_2CF_2H = 40$ mol %. Finally, the Batey–Trenwith mechanism does not account for products which can easily be explained by the intermediacy of difluoroketene and its decomposition products.

When CF_2CFH itself is pyrolyzed between 500 and 700°, the principal products are CF_3CHCF_2 and $CF_3CH{=}CHCF_3$ with the butene being generally twice as large in amount.[14] Knunyants, German, and Rozhkov have explained these products with the mechanism

$$CF_2CFH \longrightarrow CF_3CH\!:$$

$$2CF_3CH\!: \longrightarrow (CF_3CH\!:)_2$$

$$CF_2CFH \longrightarrow CF_2\!: + CFH\!:$$



$$CF_2CFH + CF_2\!: \longrightarrow \underset{CF_2}{CF_2\text{—}CFH} \longrightarrow CF_3CHCF_2$$

Since studies of the pyrolysis of fluorocyclopropanes (*vide infra*) would seem to rule out pentafluorocyclopropane as an intermediate in the formation of CF_3-$CHCF_2$, it seems likely that the CF_3CHCF_2 found in the pyrolysis of TFA results more directly from the reaction

$$CF_3CH\!: + CF_2\!: \longrightarrow CF_3CHCF_2$$

$CF_3CH{=}CHCF_3$ was not observed as a product in the TFA pyrolysis, suggesting that the proposed CF_3CH: was trapped by difluoroketene-originated CF_2: before dimerization could occur.

The instability of difluoroketene relative to ketene is probably due in part to the enhanced stability of difluoromethylene relative to methylene. Difluoromethylene is stable enough to allow determination of its microwave spectrum.[15] Furthermore, whereas activated perfluorocyclopropane eliminates CF_2,[16] cyclopropane isomerizes to propene without elimination.[17] The activation energy for the former process is 38.6 kcal, considerably less than the 65.5 kcal which is required for the latter. Other excited highly fluorinated molecules such as 1,1,2,2-tetrafluorocyclopropane[18] and perfluoroethylene oxide[19] also eliminate CF_2.

Although CF_2 is known to add to olefins to form cyclopropanes,[9,10] no evidence for fluorocyclopropanes was found in the pyrolysis products. This does not rule out the intermediacy of highly fluorinated cyclopropanes since these compounds have been shown to decompose readily at 300°,[16,18,20] a temperature considerably below the pyrolysis temperature. However, these references and the thermochemical estimates of O'Neal and Benson[21] show that highly fluorinated cyclopropanes do not isomerize to propylenes, ruling these compounds out as a route to higher olefins. In particular, pentafluorocyclopropane cannot be the source of $CF_3CH{=}CF_2$ for it decomposes to CF_2CFH and CF_2CF_2 at 250°.

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(11) $\Delta H_f°$ (kcal/mol): CF_2 (−40), CF_2H (−56), and CF_2HCF_2 (−149). See ref 4 and 21. Subsequent elimination of a hydrogen atom from the hot ethyl radical is not possible since $\Delta H = 44$ kcal/mol for this step.

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Experimental Section[22]

1,1,3,3-Tetrafluoroacetone.—TFA was prepared by reaction of 70 g of $CF_2ClCOCF_2Cl$ (Allied Chemical Co.) and H_2 on a palladium-on-charcoal catalyst in a monel flow system at 200°.[23] Fractionation of the crude product, followed by preparative vpc of the 57-61° cut on the DBP-FP column[22] at 75° gave material free of other acetones, 23 g (50%), but still containing some HCl and water. HCl was removed by passing the TFA as a gas over solid K_2CO_3, and water was removed by passage over P_4O_{10}: ir 3550 (w), 1785 (s), 1390 (m), 1345 (s), 1175 (s), 1115, 1100 (vs), 860 (m), 675 (m), 565 (m), 525 (m), 435 cm^{-1} (m). The wet TFA has additional gas phase bands at 3620, 3020, 1320, 980, and 780 cm^{-1}; pmr δ 6.1 (t with complex substructure, J_{HF} (gem) = 54 Hz).

Difluoroacetyl Fluoride.—CF_2HCOF was made by reaction of KHF_2 and difluoroacetic anhydride (DFAA), which was obtained by refluxing difluoroacetic acid (Columbia Chemical Co.) over P_4O_{10}.[24] DFAA (5.1 g) and KHF_2 (0.65 g) were stirred and heated at 130° for 2.5 hr while the product acid fluoride distilled into a trap held at −80°, yield 0.16 g. The identity of the acid fluoride, bp 2°, was established from its gas density and ir spectrum: mol wt 99 g/mol (calcd 98 g/mol); ir 2980 (s), 1895, 1880, 1870 (vs), 1365, 1360 (s), 1250 (s), 1145 (vs), 1110, 1100, 1090 (vs), 915 (s), 860 (s), 740 (m), 575 cm^{-1} (s); ir of DFAA 3000 (m), 1870, 1800 (s), 1350 (s), 1220 (s), 1140, 1110, 1070 (vs), 930 cm^{-1} (s).

1,1,2,2-Tetrafluoroethane and Pentafluoroethane.—CF_2HCF_2H and CF_3CF_2H were prepared by overnight photolysis with a medium-pressure mercury lamp of an equimolar gaseous mixture of TFA and hexafluoroacetone in a 3-l. Pyrex flask.[25] In addition to the desired ethanes the products included CF_2H_2, CF_3H, and CF_3CF_3. Pure CF_2HCF_2H and 95% pure CF_3CF_2H were isolated by repeated vpc on the DBP-FB column at 0°. Elution times: CF_3CF_3, 1.0; CF_3H, 1.6; CF_3CF_2H, 2.4; CF_2H_2, 3.9; and CF_2HCF_2H, 9.7.

1,1,1,2-Tetrafluoroethane.—CF_3CFH_2 was isolated from the TFA pyrolysis products by vpc at 0° on the DBP-FB column followed by the HC-FB column and identified by its ir spectrum.

1,1,2,2,3,3-Hexafluoropropane and 1,1,2,2,3,3,4,4-Octafluorobutane.—$CF_2HCF_2CF_2H$ was obtained from photolysis of a gaseous 100:16 Torr mixture of TFA and CF_2CF_2 (Peninsular ChemResearch Co.). This propane (29 mg) was isolated by vpc on the HC-FB column at 0°. The propane was identified by its gas density and its pmr[26] and ir spectra: mol wt 146 g/mol (calcd 152 g/mol); pmr δ 5.9 (t of t, J_{HF} = 53, 5.5 Hz); ir 3000 (m), 1415 (s), 1380 (s), 1345 (s), 1295 (s), 1270 (vs), 1215 (vs), 1185 (vs), 1120 (vs), 1085 (vs), 875 (s), 775 (m), 710 (s), 645 (m), 575 (m), 450 cm^{-1} (m).

A smaller fraction of moderate purity obtained from this photolysis was tentatively identified as $CF_2HCF_2CF_2CF_2H$ on the basis of its gas density (11-mg sample) and ir spectrum: mol wt 181 g/mol (calcd 202 g/mol); ir 3000 (m), 1395 (m), 1350, 1255, 1235 (s), 1150 (vs), 1120 (vs), 1065 (s), 840 (m), 790 (m), 700 (m), 565 cm^{-1} (m).

1,1,3,3,3-Pentafluoropropene-1 and 1,1,2,2,3,3-Heptafluoropropane.—A fluoroalkane and a fluoroalkene, separated from the products of pyrolysis of TFA by the HC-FB and DBP-FB columns at 0°, were identified as CF_3CHCF_2 and $CF_3CF_2CF_2H$ by their ir spectra.

Other Fluorocarbons.—Analytical samples of CF_2H_2, CF_3H, CF_2CF_2, CF_2CFH, and SiF_4 were obtained from commercial sources.

Pyrolysis of Difluorodiazirine with Hydrogen Fluoride.—A 60:240 Torr gaseous mixture of CF_2N_2[9] and HF (Matheson Co.) was heated for 4 hr at 155° in a monel cylinder. Products, in addition to nitrogen, were CF_3H (10%) and CO_2 (90%), based on available CF_2. The monel cylinder was not given a prior treatment to remove any oxide film from the interior, and water may have been present in the HF.

Pentafluorocyclopropane.—c-C_3F_5H was prepared by heating a mixture of CF_2N_2 and CF_2CFH.[27] c-C_3F_5H (0.8 mmol, 30% yield) was separated from the other condensable product, perfluorocyclopropane, by vpc: ir 3140 (m), 1530 (m), 1325, 1320 (s), 1270 (vs), 1250 (vs), 1225, 1215 (vs), 1180, 1175 (m), 970, 965 (s), 830 (s), 780 (s), 685, 675 (w), 600 (m), 530 (m), 430 cm^{-1} (m). c-C_3F_5H was heated in a Pyrex tube at 250° yielding CF_2CFH and CF_2CF_2 as principal products with some perfluorocyclopropane.

Pyrolysis of Tetrafluoroacetone.—TFA was pyrolyzed in a flow system, which was built onto a conventional vacuum system, with He as a carrier gas. Reaction took place in a 20 × 1.6 cm carbonized quartz tube. (Although TFA pyrolyzed readily at 650° in the quartz tube, no pyrolysis was observed in a monel tube even at 830°.) Helium, at atmospheric pressure, bubbling through TFA in a trap maintained at room temperature, picked up the acetone at a pressure of about 100 Torr. Products were collected in three traps. The trap next to the furnace was maintained at −30°, somewhat above the freezing point of TFA; the other two were at −195°. Noncondensable gases were continuously vented to the atmosphere. The flow rate of He ranged from 8.7 to 6.0 l./hr, giving a contact time of 3.3–4.5 sec. Temperature was measured with two thermocouples placed inside the furnace.

Condensable products were analyzed primarily by infrared spectrometry, using literature spectra for identification whenever possible.[28] The 10-cm gas cell was constructed with a monel body and 5-cm KBr windows sealed with O rings. During an analysis, involatile deposits, absorbing at 1120–1020, 730, and 475 cm^{-1}, built up on the cell windows, making frequent repolishing necessary. Products condensed in the two −195° traps were combined in a mixing flask, from which were obtained gaseous samples for representative spectra at various pressures. Generally, the overlap of useful, strong absorption bands, particularly in the 1400–1000-cm^{-1} region, was such that a second step was necessary to obtain an analysis. The entire −195° fraction was condensed in a bulb, and gaseous aliquots were taken in sequence for ir spectra by allowing the material to warm slowly from −195°. This procedure gave significantly simplified spectra of mixtures of products having similar boiling points. Analytical vpc, using HC-FB and DBP-FB columns at 0°, with ir analyses on various fractions was also used to complement the boil-off method. In the −30° trap, essentially only unreacted TFA was found.

CO, the only noncondensable product, was determined by diluting a portion of the gaseous He–CO mixture from each trap with a measured quantity of air and then analyzing by vpc. A 4 m × 1.0 cm activated charcoal column at room temperature was used. From the CO–N_2 ratio, the He (plus CO)–N_2 ratio, the flow rate of He, and the duration of the run, the amount of CO was calculated.

Registry No.—TFA, 360-52-1; CF_2HCOF, 2925-22-6; $CF_2HCF_2CF_2H$, 680-00-2; $CF_2HCF_2CF_2CF_2H$, 377-36-6; c-C_3F_5H, 872-58-2.

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(22) Gas phase ir spectra were run on a Perkin-Elmer Model 621 spectrometer, and nmr spectra were run on a Varian A-60 spectrometer with TMS as an internal standard and $CFCl_3$ as a solvent. Preparative and analytical vpc was performed with 4 m × 1.0 cm columns packed with 20% dibutyl phthalate on either Fluoropak 80 (DBP-FP) or firebrick (DBP-FB) and halocarbon oil on firebrick (HC-FB).

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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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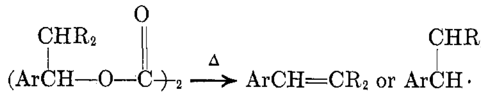
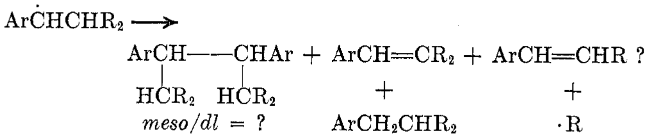
Products from the low-pressure gas phase pyrolysis of di(α-substituted benzyl) oxalates are reported. Di(α-substituted benzyl) oxalates which contain β hydrogen atoms undergo an elimination reaction in addition to homolytic decomposition to α-substituted benzyl radicals. Coupling of α-substituted benzyl 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



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

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



$$\mathrm{Ar\dot{C}HCHR_2} \longrightarrow \underset{meso/dl\ =\ ?}{\mathrm{Ar}\underset{\mathrm{HCR_2}}{\underset{|}{\mathrm{C}}}\mathrm{H{-}{-}}\underset{\mathrm{HCR_2}}{\underset{|}{\mathrm{C}}}\mathrm{HAr}} + \underset{\mathrm{ArCH_2CHR_2}}{\underset{+}{\mathrm{ArCH{=}CR_2}}} + \underset{\cdot\mathrm{R}}{\underset{+}{\mathrm{ArCH{=}CHR}}}\ ?$$

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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