SYNTHESIS AND ISOMERIZATION OF 2,5- AND 2,6-SUBSTITUTED F-HEXADIENES AND HEPTADIENES [1]*

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SUMMARY

The reaction of 2,2,3,3,4,4-hexafluoro-1,5-diphenylpentane-1,5-dione, 4,4,5,5-tetrafluorooctane-3,6-dione and 4,4,5,5,6,6,-hexafluorononane-3,7-dione with excess triphenylphosphine and dibromodifluoromethane in triglyme at 70 °C gave modest yields (50-60%) of the corresponding dienes and enones (10-20%). No isomerized olefins were observed. Subsequent treatment of the dienes with tetraethylammonium fluoride gave the internal olefins, and thermal isomerization of 2,6diphenyl-1,1,3,3,4,4,5,5,7,7-decafluoro-1,6-heptadiene to the internal isomeric olefins was observed at 250 °C.

INTRODUCTION

Several years ago we attempted to prepare substituted fluorinated dienes via the Wittig reaction of difluoromethylenetriphenylphosphorane (generated from lithium chlorodifluoroacetate and triphenylphosphine) and suitably substituted <u>F</u>-diones [2]. This approach failed to give the desired dienes. When $R = C_6H_5$,

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Dedicated to Emeritus Professor W.K.R. Musgrave on the occasion of his 70th birthday.

only trace amounts of unidentified products were observed. When $R = C_2H_5$, cyclization of the diones occurred to give α,β unsaturated cyclic ketones via an intramolecular Aldol-type condensation process. The cyclization reaction was promoted by the dimethylamine produced via decomposition of DMF under the reaction conditions utilized for the thermolysis of lithium chlorodifluoroacetate. The choice of lithium chlorodifluoroacetate in this approach was predicated on earlier reports [3,4] which indicated that the lithium salt was the best choice to suppress fluoride ion catalyzed isomerization of the products.

Subsequent work in our laboratory demonstrated that triphenylphosphine and dibromodifluoromethane in glyme solvents could be employed for the conversion of aldehydes and ketones to 1,1-difluoroolefins [5,6]. More importantly, this methodology did not produce significant amounts of fluoride ion, and the synthesis of 1,1-difluoroolefins could be readily achieved without concomitant formation of isomerized olefins [6]. Thus, we were prompted to attempt the conversion of polyfluorinated diones to substituted F-dienes via this latter approach. The absence of DMF in this method could prevent the Aldol cyclization problem, and the mild reaction conditions and absence of fluoride ion could preclude isomerization of the resultant dienes. Earlier work in our laboratory had demonstrated that fluoride ion easily isomerized <u>F</u>-olefins substituted at the 2-position with an aryl group [7,8].

RESULTS AND DISCUSSION

Suitably substituted <u>F</u>-diones were prepared via procedures described by Groth [9], Yakubovich [10] and Zawistowski [11].

 $RMgX + HOOC(CF_2)_nCOOH \longrightarrow RC(O)(CF_2)_nC(O)R$ $R = C_6H_5, C_2H_5$ n = 2,3

These diones were reacted with excess triphenylphosphine and dibromodifluoromethane in triglyme (TG) at 70 °C to give the respective dienes and enones. The reaction conditions were chosen to maximize formation of the diene product. No attempt was made to maximize the enone product.

As noted in Table I, the dienes were isolated in modest yields. A small amount of the enone product was also isolated. In the case of 2,2,3,3-tetrafluoro-1,4-diphenyl-1,4-dione the diene was formed in a 60% GLPC yield, however all attempts to isolate this product in high purity failed. Most importantly, no isomerized dienes were detected either by ¹⁹F NMR or GLPC analysis. Thus, this methodology successfully avoids the isomerization and cyclization problems associated with the lithium chlorodifluoroacetate procedure [2].

When $R = C_6 H_5$, the reaction was also carried out by metal dehalogenation of bromodifluoromethyltriphenylphosphonium bromide with either cadmium or zinc. This approach has also been demonstrated to be effective as a route to difluoromethylenetriphenylphosphorane intermediates [12]. With cadmium, results similar to the Ph_3P/CF_2Br_2 methodology were observed, and with zinc this approach was less efficient. These results are tabulated in Table I.

RC(0)(CF₂)_nC(0)R + xs Ph₃P + xs CF₂Br₂ \downarrow 70 °C, TG

R	n	۶ Diene ^a	۲ Enone ^a	Metal
с ₆ н ₅	3	55 ^b (Ia)	15 (IIa)	
С ₂ Н ₅	3	54 ^b (Ib)	9 (IIb)	
С ₂ Н ₅	2	48 (IC)	16 (IIC)	
C ₆ H ₅	2	(60) ^C (Id)		
C ₂ H ₅	2	50 (IC)	trace	cdd
с ₂ н ₅	2	(21) ^C (IC)	(6) ^C (IIC)	Zn ^d

 $F_2C=C(R)(CF_2)_nC(R)=CF_2 + F_2C=C(R)(CF_2)_nC(O)R$

a isolated yields

b average yield from three different preparations

C GLPC yield

d reaction carried out in TG at 25-30 °C

Thermal reactions

In order to determine whether intramolecular cycloaddition would occur, the diene (Ia) was heated in a sealed ampule at high temperatures. The optimum conditions for this reaction were in the range of 250-280 °C for 40-50 hours. Below 200 °C, no reaction occurred after 3 days, and temperatures above 400 °C resulted in decomposition.

As noted below, no products of intramolecular cycloaddition were found. However, (Ia) did undergo isomerization, and the following isomerized dienes were detected and characterized.



The ratio of (IIIa):(IIIb):(IIIc):(IIId):(Ia) was 8.0:6.5:3.1:5.5:1.0.

The dienes (Ib) and (Ic) did not undergo thermal isomerization at or below 300 °C, and at temperatures greater than 400 °C, only polymer film formed on the wall of the ampule.

Fluoride ion reactions

The dienes (Ia) and (Ib) were treated with tetraethylammonium fluoride in DMF at room temperature [8].



Within 30 minutes isomerization was complete. Of the three possible geometrical isomers, only two were observed. No (E,E)-isomer was detected in either case. Perhaps with longer reaction times, the (E,E)-isomer could be formed, but no attempt was made to study the equilibration of these internal dienes.

The ease of isomerization of (Ia) and I(b) illustrates the value of the Ph_3P/CF_2Br_2 approach, which yielded only the terminal dienes.

EXPERIMENTAL

¹H NMR spectra were obtained with either a Varian A-60 or Varian HA-100 instrument with tetramethylsilane (TMS) as an internal reference, and chemical shifts are reported in δ ¹⁹F NMR spectra were obtained with values downfield from TMS. a Varian HA-100 instrument operating at 94.075 MHz with fluorotrichloromethane (CFCl₃) as an internal standard. Chemical shifts are reported in Φ^* values upfield from CFCl₂ and are assigned negative chemical shift values. All NMR spectra were recorded in CCl₄ or CDCl₃. Mass spectra were recorded on a Hitachi-Perkin Elmer RMU-66 spectrometer at 70 eV. Infrared spectra were recorded on a Perkin-Elmer Model 21 double beam recording spectrophotometer or a Beckman IR-20A spectrophotometer using a neat film between sodium chloride plates. Quantitative elemental analyses for carbon and hydrogen were performed by service personnel in this department. Fluorine microanalyses were obtained from Micro-Tech Laboratory, Inc., Skokie, Illinois. Refractive indices were determined at 20±0.1 °C with a Bausch and Lomb Abbe-3L refractometer. Boiling points were determined during distillation by means of a partial immersion thermometer and are uncorrected. Micro boiling points were determined by the Siwoloboff procedure [13]. Analyses by gas-liquid phase chromatography (GLPC) were obtained on a Hewlett-Packard Model

5750 Dual Column Gas Chromatograph equipped with thermal conductivity detectors with helium as the carrier gas. Preparative GLPC (SE 30, 30%, 10'x0.5" column) was carried out on a Varian Aerograph Model 700 instrument with a pressure drop of 50 to 60 psi across the column (flow rates of 150 to 200 mL per minute). Triglyme (Ansul Ether 161) was dried by distillation at reduced pressure from a sodium-benzophenone ketyl and stored over 3 Å molecular sieves in capped bottles under nitrogen. Bromodifluoromethyltriphenylphosphonium bromide was prepared by the method of Naae [5]. The diones utilized in this work were prepared by the method of Groth [9] and Yakubovich [10] as described by Zawistowski [11]. Tetraethylammonium fluoride was prepared as described by Headley [8].

Preparation of 2,6-Diphenyl-1,1,3,3,4,4,5,5,7,7-decafluoro-1,6-heptadiene (Ia)

A 300 mL three necked flask was equipped with a mechanical stirrer and a reflux condenser attached to a dry nitrogen flow system. The flask was charged with 15.7 g of triphenylphosphine (60 mmols), 3 g of 2,2,3,3,4,4-hexafluoro-1,5-diphenylpentane-1,5-dione (8.5 mmols) and 32 mL dry triglyme. This mixture was stirred at room temperature until a homogeneous solution was obtained. Then, 5.4 g of dibromodifluoromethane (25 mmols) was added to the solution, and the reaction mixture was heated at 60-70 °C for 50-60 h. After cooling, the reaction mixture was poured into water (145 mL) and ether was added in portions until all the solid material dissolved. The ether layer was separated and the aqueous layer was extracted with 3x30 mL of ether. The combined ether layers were cooled in an ice bath to precipitate most of the triphenylphosphine oxide. The supernatant ether solution was then washed with 4x30 mL of 80% aqueous NaCl. The ether solution was then dried over anhydrous 'MgSO, filtered, and the ether removed by distillation. The remaining light brown residue was dissolved in 70 mL benzene and washed with concentrated H2SO4 until any remaining Ph3P or Ph3PO had been removed. The benzene solution was then washed with 5% NaHCO3 (1x20 mL, 2x30 mL), dried over anhydrous $MgSO_A$, filtered, and

the benzene removed by distillation to give 2.6 g of solid residue. Chromatographic separation on silica gel (hexane eluent) gave pure diene (Ia) and pure enone (IIa). From several runs, the yields of diene and enone were in the range of 50-60% and 10-20%, respectively. Recrystallization of solid residue from hexane also gave pure diene, but pure enone could not be obtained by recrystallization.

сđ C=C (Ia) : 89-90 °C mp Analysis: C19H10F10 Calcd: %C 53.27; %H 2.34; %F 44.39 Found: %C 52.67; %H 2.29; %F 45.01 IR : 5.85µ (C=CF₂) ¹H NMR : $\delta 7.31$ (broad singlet) ¹⁹F NMR : F_a -73.6 ppm (2F, dtt) F_b -75.3 ppm (2F, tdt) F_{C} -106.3 ppm (4F, d,d) $F_{d} = 119.9 \text{ ppm} (2F, d, d)$ Jab 12.8 Hz Jac 8.8 Hz Jad 2.9 Hz J_{bc} 27.6 Hz J_{bd} 11.7 Hz Mass Spectrum: M⁺ 428 m/e сғ₂сғ₂сғ₂сс₆н₅ (IIa) mp : 51-52 °C Analysis: C₁₈H₁₀F₈O Calcd: %C 54.82; %H 2.58 Found: %C 54.01; %H 2.72 IR : 5.85µ (C=CF₂, C=O) ¹H NMR : δ7.31

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<sup>19</sup>F NMR : F_a -73.7 \text{ ppm (1F, dtt)}

F_b -74.9 \text{ ppm (1F, ttdt)}

F_c -106.7 \text{ ppm (2F, dtd)}

F_d -113.1 \text{ ppm (2F, dd)}

F_e -120.8 \text{ ppm (2F, dd)}

J_{ab} 9.7 \text{ Hz}

J_{ac} 9.7 \text{ Hz}

J_{ac} 1.2 \text{ Hz}

J_{bc} 29.4 \text{ Hz}

J_{be} 11.3 \text{ Hz}

J_{bd} 1.5 \text{ Hz}

J_{cd} 13.6 \text{ Hz}

Mass Spectrum: M<sup>+</sup> 394 m/e
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Preparation of 2,6-Diethyl-1,1,3,3,4,4,5,5,7,7-decafluoro-1,6heptadiene (Ib)

A 1 L three necked flask was equipped with a mechanical stirrer and a reflux condenser attached to a dry nitrogen flow The flask was charged with 32 g of 4,4,5,5,6,6system. hexafluorononane-3,6-dione (120 mmols), 221.8 g of triphenylphosphine (847 mmols) and 600 mL of dry triglyme. This mixture was stirred at room temperature until a homogeneous solution was obtained. Then 76.1 g of dibromodifluoromethane (332 mmols) was added to the solution, and the mixture was heated at 60-70 °C for 65 h. After cooling, 50 mL of ether was added to the reaction mixture, and the products were separated via steam distillation. The organic layer of the distillate was separated, dried over anhydrous magnesium sulfate, filtered, and fractionated thru a 10 cm Vigreaux column to give 22 g of material, bp 62-65 °C/17.5 mm Hg. GLPC analysis showed that this material consisted of 80% of (Ib) and 20% of 2-ethyl-1,1,3,3,4,4,5,5-octafluoro-1-octene-6-one (IIb). Separation of (Ib) and (IIb) was achieved by preparative GLPC. From several reactions carried out as described above, the isolated yields of (Ib) and (IIb) were in the range of 50-60% and 8-10%, respectively.

c d c CF2CF2CF2 C=C (Ib) C2H5 C2H5 bp (micro): 164-165 °C/747 mm Hg n_D²⁰ : 1.3576 Analysis : C₁₁H₁₀F₁₀: Calcd: %C 39.76; %H 3.03; %F 57.21 Found: %C 40.62; %H 3.21; %F 56.53 IR : 5.75µ (C=CF₂) ¹H NMR : δ1.1 (3H, t) δ2.2 (2H, q) J_{HH} 7.1 Hz

¹⁹F NMR : F_a -80.6 ppm (1F, dt) $F_{\rm b}$ -77.2 ppm (1F, tdt) F_{C} -110.2 ppm (2F, dd) F_{d} -124.2 ppm (1F, d) Jab 23.1 Hz

J_{bd} 10.6 Hz Mass Spectrum: no M⁺; m/e 141 highest fragment observed $(C_2H_5C(=CF_2)CF_2)$

$$\begin{array}{c} c & e & d & o \\ F_b & CF_2CF_2CF_2CC_2H_5 \\ c=c & (IIb) \\ F_a & C_2H_5 \end{array}$$

bp (micro): 173-174 °C/729 mm Hg n_D^{20} 1.3605 : IR : 5.70µ (C=CF₂, C=O) ¹H NMR : $\delta 1.13$ (6H, two overlapped t) δ2.13 (CH₂, 2H, q) δ2.75 (CH₂', 2H, q) $J_{HH} = J_{HH}$, 7.5 Hz ¹⁹F NMR : F_a -80.0 ppm (1F, dt) F_b -76.3 ppm (1F, tdt) $F_{\rm C}$ -109.6 ppm (2F, dtd)

 $F_{d} = -124.1 \text{ ppm } (2F, t)$ $F_{e} = -120.9 \text{ ppm } (2F, d)$ $J_{ab} = 20.0 \text{ Hz}$ $J_{ac} = 8.7 \text{ Hz}$ $J_{bc} = 21.5 \text{ Hz}$ $J_{be} = 12.0 \text{ Hz}$ $J_{cd} = 10.0 \text{ Hz}$ Mass Spectrum: 279 m/e (M-F)

Preparation of 2,5-Diethyl-1,1,3,3,4,4,6,6-octafluoro-1,5hexadiene (Ic)

A 150 mL flask was equipped with a Teflon coated stir bar and a reflux condenser attached to a dry nitrogen flow system. The flask was charged with 2 g of 4,4,5,5-tetrafluorooctane-3,6-dione (9.34 mmols), 19.9 g of triphenylphosphine (75.6 mmols) and 40 mL of dry triglyme. This mixture was stirred at room temperature until a homogenous solution was obtained. Then, 6.8 g of dibromodifluoromethane (32.3 mmols) was added to the solution, and the reaction mixture was heated at 70 °C for 72 h. The volatile products were then removed via vacuum distillation (50 °C/1 mm Hg) to give 1.65 g of products. GLPC analysis showed this material to consist of 78% of (Ic) and 22% of 2-ethyl-1,1,3,3,4,4-hexafluoro-1-hepten-5-one (IIc). Preparative GLPC gave (Ic) and (IIc) in 48% and 16% isolated yields, respectively.

c c' F_b C=C $C_2F_2CF_2$ C=C F_b' (Ic) F_a C_2H_5 C_2H_5 F_a' bp (micro): 151-152 °C/747 mm Hg n_D^{20} : 1.3668 Analysis : $C_{10}H_{10}F_8$: Calcd: %C 42.56; %H 3.57; %F 53.86 Found: %C 43.09; %H 3.68; %F 53.09 IR : 5.75 μ (C=CF₂) ¹H NMR : δ 1.12 (3H, t) : δ 2.14 (2H, q)

:
$$J_{HH}$$
 7.5 Hz
¹⁹F NMR : F_a -81.0 ppm (2F, dtt)
 F_b -77.8 ppm (2F, dtt)
 F_c -111.3 ppm (4F, dd)
 J_{ab} 25.6 Hz
 J_{bc} 25.3 Hz
 J_{ac} 10.1 Hz
 J_{bc} , 12.6 Hz
 J_{ac} , 2.5 Hz
Mass Spectrum: no M⁺; m/e 141 highest fragment observed
 $(C_2H_5C(=CF_2)CF_2)$

c d 0

$$F_{b_{c}} = C_{2}CF_{2}CC_{2}H_{5}$$
 (IIc)
 $F_{a} = C_{2}H_{5}$
bp (micro): 151-152 °C/747 mm Hg
 n_{D}^{20} : 1.3668
Analysis : $C_{9}H_{10}F_{6}$ 0: Calcd: %C 43.55; %H 4.06; %F 45.93
Found: %C 43.80; %H 4.76, %F 44.70
IR : 5.74 μ (C=CF₂, C=O)
¹H NMR : δ 1.1 (6H, t)
 δ 2.2 (2H, q)
 δ 2.8 (2H, q)
 J_{HH} 7.5 Hz
¹⁹F NMR : F_a -80.4 ppm (1F, dt)
F_b -77.1 ppm (1F, dt)
F_c -110.4 ppm (2F, dd)
F_d -121.6 ppm (2F, dd)
J_{ab} 24.9 Hz
J_{bc} 24.0 Hz
J_{bd} 10.1 Hz
Mass Spectrum: M⁺ 248 m/e

Reaction of 4,4,5,5-Tetrafluorooctane-3,6-dione and Bromodifluoromethyltriphenylphosphonium Bromide and Cadmium or Zinc in Triglyme

A 50 mL flask was equipped with a Teflon coated stir bar and a condenser attached to a dry nitrogen flow system. The flask was charged with 2 g of 4,4,5,5-tetrafluorooctane-3,6dione (9.3 mmols), 15.9 g of bromodifluoromethyltriphenylphosphonium bromide (30.4 mmols), 4.7 g of cadmium (41.8 mmols) and 35 mL of dry triglyme. The reaction mixture was heated with stirring at 30-40 °C until the exothermic reaction was initiated. Heat was then removed and the temperature of the reaction mixture allowed to return to room temperature. Vacuum distillation of the reaction mixture (50 °C/1 mm Hg) gave 1.3 g (50% yield) of (Ic) in excellent purity with only a trace of enone. (Ic) was identified by its infrared spectrum.

A reaction with identical quantities of materials as described above, except that zinc was substituted for cadmium, gave 0.7 g of products after vacuum distillation of the reaction mixture. GLPC analysis of this product mixture showed that it consisted of 80% (Ic) and 20% (IIc).

Attempted Thermal Isomerization of (Ib) and (Ic)

A dry 2 mL ampule was charged with 1 g of either (Ib) or (Ic) and sealed. The ampule was heated at 250 °C in a furnace for 48 h. GLPC analysis of the recovered material showed only (Ib) or (Ic). No isomerized product was detected. Similar results were found when (Ib) was heated at 300 °C for 50 h.

Thermal Isomerization of 2,6-Diphenyl-1,1,1,3,4,4,5,7,7,7decafluoro-(Z,Z)-2,5-heptadiene (IIIb)

A dry 2 mL ampule was charged with 0.5 g of (IIIb) and sealed. The ampule was heated at 320 °C for 42 h. GLPC analysis of the recovered material showed that it consisted of 90% (IIIb) and 10% (IIIc).

Thermal Isomerization of (Ia)

A dry 2 mL ampule was charged with 2 g of (Ia) and sealed. The ampule was heated at 250 °C for 48 h in a furnace. A dark red viscous liquid was recovered. GLPC analysis of this liquid showed four new products and a small amount of (Ia). Preparative GLPC effected separation of these products and these structures were assigned as 2,6-diphenyl-1,1,3,3,4,4,5,7,7,7-decafluoro-(Z)-1,5-heptadiene (IIIa), 2,6diphenyl-1,1,1,3,4,4,5,7,7,7-decafluoro-(Z,Z)-2,5-heptadiene (IIIb), 2,6-diphenyl-1,1,1,3,4,4,5,7,7,7-decafluoro-(Z,E)-2,5heptadiene (IIIc), and 2,6-diphenyl-1,1,3,3,4,4,5,7,7,7decafluoro-(E)-1,5-heptadiene (IIId). The ratio of (IIIa):(IIIb):(IIIc):(IIId):(Ia) was found to be 8:0:6.5:3.1:5.5:1.0 by GLPC analysis.

а (IIIa) С đ mp : 58-59 °C IR : 5.80μ (C=CF₂) ¹H NMR : $\delta 7.3$ (m) ¹⁹F NMR: F_a -61.4 ppm (3F, dt) F_b -110.2 ppm (1F, qt) F_c -112.4 ppm (2F, not totally resolved) F_d -107.3 ppm (2F, not totally resolved) F. -74.1 ppm (1F, ttd) F_{f} -75.0 ppm (1F, td) Jab 27.1 Hz J_{bc} 11.1 Hz J_{ef} 10.5 Hz Jac 1.2 Hz J_{de} 26.6 Hz J_{df} 10.5 Hz J_{CP} 11.1 Hz J_{cd} 9.9 Hz

Mass Spectrum: M⁺ 428 m/e a сс а (IIIb) CF2 C6H5 ь bp (micro): 271-272 °C/737 mm Hg n_D^{20} : 1.4601 IR : 5.9µ (C=C, W) ¹H NMR : δ7.3 (m) ¹⁹F NMR F_a -61.3 ppm (6F, dt) : F_b -96.6 ppm (2F, t heptets) : : F_c -110.2 ppm (2F, qt) : J_{ab} 2.3 Hz : J_{ac} 25.6 Hz : J_{bc} 13.4 Hz Mass Spectrum: M⁺ 428 m/e b e d (IIIc) CF2 C6H5 С n_D²⁰ : 1.4643 IR : 5.80 μ (C=C, w) and 5.59 μ (C=C, w) ¹H NMR : $\delta7.1(s)$ and $\delta7.4(s)$ ¹⁹F NMR: F_a -56.9 ppm (3F, dt) F_b -61.3 ppm (3F, dt) F_{C} -96.7 ppm (2F, ddqq) F_d -105.2 ppm (1F, qt) F_e -110.4 ppm (1F, qt) J_{ac} 12.3 Hz J_{ad} 13.1 Hz

 J_{bc} 2.1 Hz

J_{be} 23.8 Hz

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J<sub>cd</sub> 12.3 Hz
Mass Spectrum: M<sup>+</sup> 428 m/e
       C=C F^{C_6H_5} C=C F^{b} (IIId)
 CF3
 а
             f
n_20
        : 1.4693
          : 5.76\mu (C=CF<sub>2</sub>, s) and 5.95\mu (C=C, w)
IR
<sup>1</sup>H NMR : \delta7.1 (s) and \delta7.3 (s)
<sup>19</sup>F NMR: F<sub>a</sub> -56.1 ppm (3F, tdt)
              F_b -74.0 ppm (1F, dt)
               F<sub>c</sub> -75.2 ppm (1F, tdt)
               F<sub>d</sub> -105.9 ppm (1F, qt)
               Fe -107.5 ppm (2F, broad m)
               F<sub>f</sub> -114.5 ppm (2F, broad m)
              J<sub>ad</sub> 12.3 Hz
               J<sub>af</sub> 18.0 Hz
              Jae 5.7 Hz
              J<sub>bc</sub> 9.8 Hz
              Jbe 9.8 Hz
              J<sub>Ce</sub> 26.2 Hz
              J<sub>cf</sub> 9.8 Hz
              J<sub>df</sub> 11.4 Hz
Mass Spectrum: M<sup>+</sup> 428 m/e
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Fluoride Ion Catalyzed Isomerization of (Ia)

A 10 mL flask was equipped with a Teflon coated magnetic stir bar and a reflux condenser attached to a dry nitrogen flow system. The flask was charged with 0.4 g of (Ia) and 5 mL of dry DMF. Then, 0.5 mL of a DMF solution, saturated with tetraethylammonium fluoride [8] was added to this solution via syringe. After 20 minutes at room temperature, GLPC analysis of the reaction mixture indicated a quantitative conversion of (Ia) to a mixture of (IIIb) and (IIIc) in a ratio of 4:1.

Fluoride Ion Catalyzed Isomerization of (Ib)

A 10 mL flask was equipped with a Teflon coated magnetic stir bar and a reflux condenser attached to a dry nitrogen flow system. The flask was charged with 2 g of (Ib) and 5 mL of dry DMF. Then 2 mL of a DMF solution, saturated with tetraethylammonium fluoride [8], was added to this mixture via syringe. The reaction mixture was stirred at room temperature for 30 minutes and quenched by the addition of an equal volume of water. The lower organic layer was separated and washed once with an equal volume of water. GLPC analysis of the organic layer (85% recovery) showed only the two isomerized products, 3,7-bistrifluoromethyl-4,5,5,6-tetrafluoro-(Z,Z)-3,6nonadiene and 3,7-bistrifluoromethyl-4,5,5,6-tetrafluoro-(Z,E)-3,6-nonadiene in a 1.35:1 ratio, respectively. Preparative GLPC did not adequately separate these two isomers, although analytical GLPC (SE-30) did provide total separation.

Properties (Mixture):

IR : 5.88 μ (C=C, w) and 5.89 μ (C=C, w) n_D²⁰ : 1.3551 ¹H NMR: δ 1.2 (3H, t) δ 2.4 (2H, unresolved q) J_{HH} 7.4 Hz

e'd' С and b a١ ¹⁹F NMR: F_a -61.1 ppm (6F, dt) F_a, -57.9 ppm (3F, m) $F_{\rm b}$, -61.1 ppm (3F, d) F_b -100.4 ppm (2F, tm) F_{C} -112.9 ppm (2F, m) $F_{C1} - 98.9 \text{ ppm} (2F, m)$ Jac 21.8 Hz F_d, -111.8 ppm (1F, m) Jab 2 Hz Fet -112.9 ppm (1F, m) J_{bc} 15 Hz Jate 13.9 Hz J_{a'd}, 13.9 Hz J_{b'e'} 21.8 Hz

Mass Spectrum: M⁺ 282 m/e

CONCLUSION

The reaction of polyfluorinated diones with triphenylphosphine and dibromodifluoromethane in triglyme is a useful method for the formation of substituted <u>F</u>-dienes without concomitant fluoride ion isomerization.

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