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COPPER COUPLING OF 1-CHLORO-2-IODO- AND 1,2-DI-IODO-PERFLUOROCYCLOALKENES

ROBERT L. SOULEN,* SAM K. CHOI AND JOSEPH D. PARK

Department of Chemistry, University of Colorado, Boulder, Colo. 80302 (U.S.A.)

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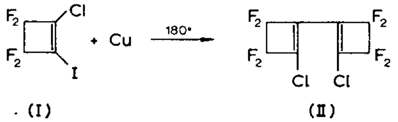
SUMMARY

Reductive coupling of 1-chloro-2-iodoperfluorocyclobutene (I), cyclopentene (III) and cyclohexene (VI) has been carried out with copper powder and a trace amount of dimethylformamide to give the corresponding 2,2′-dichloroperfluoro-(bi-1-cycloalken-1-yl) derivatives in 69%, 36% and 73% yield, respectively. A reduced by-product, 2*H*,2′*H*-dodecafluoro-(bi-1-cyclopenten-1-yl) was also obtained in the copper coupling of (III). Coupling of 1,2-di-iodoperfluorocyclobutene (IX) and cyclopentene (XII) under similar conditions gave good yields of cyclic trimers and tetramers. Mass spectra, infrared and ^{19}F NMR data are discussed.

INTRODUCTION

Recent studies in these laboratories on an improved method of preparation of 1-chloro-2-iodo- and 1,2-di-iodo-perfluorocycloalkenes has prompted our investigation of these novel fluorocarbons[1]. An area of particular interest has been the coupling of these vinylic iodides with copper. For example, we have previously reported that 1-chloro-2-iodo-3,3,4,4-tetrafluorocyclobutene (I) undergoes a dimeric coupling reaction with copper metal at 180° yielding 2,2′-dichloro-octafluoro-(bi-1-cyclobuten-1-yl) (II) in 58% yield[2].



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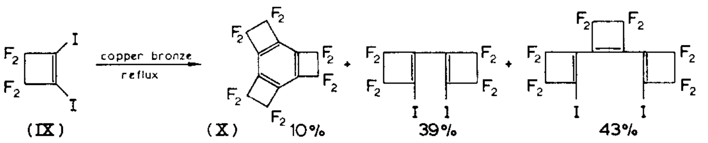
* Professor of Chemistry, Southwestern University, Georgetown, Texas 78626 (U.S.A.).

The coupling of perfluorovinyl iodides with copper bronze was initially disclosed by Tatlow[4]; however, it was only recently shown that this technique could be used to produce cyclic perfluoroalkyl derivatives of benzene and cyclooctatetraene[3, 5].

In contrast to the results reported below, Camaggi[3] has recently observed the formation of both linear and cyclic oligomers in the coupling reaction of the 1,2-di-iodides of perfluorocyclobutene (IX) and perfluorocyclopentene (XII). He reports that linearly coupled products are the predominate products from (IX) whereas a cyclic trimer and tetramer composed 90% of the reaction products from (XII) and copper bronze[3].

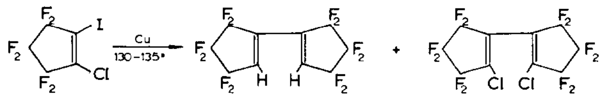


It is interesting to compare the ease of synthesis and the greater stability of the cyclic perfluoroalkenes with the corresponding hydrocarbon series which have been so carefully studied by Wittig[6]. Cycloalkyne hydrocarbon trimers of type (X) are unknown for cyclobutyne and have been found in only 2% and 8% yield in reactions of cyclopentyne and cyclohexyne respectively[7].

RESULTS AND DISCUSSION

Copper coupling of 1-chloro-2-iodoperfluorocycloalkenes leads to dimeric products in high purity and good yields. Since our initial disclosure of this reaction, it has been found that the addition of trace amounts of anhydrous dimethylformamide (DMF) increases yields and allows the reaction to proceed at a lower temperature; thus, for example, heating (I), which contained approximately 0.5% DMF, with purified copper powder at 130–135° for 24 h gave 69% of nearly pure (II). The only contaminate shown by VPC analysis was the starting material which was easily separated by recrystallization from n-hexane. It was most convenient to carry out these reactions in a sublimation apparatus so that the liquid starting materials dripped down on to the copper powder but the solid products remained on the condensing surfaces. This, of course, avoided prolonged contact of the products with the copper catalyst and reduced unwanted side-reactions.

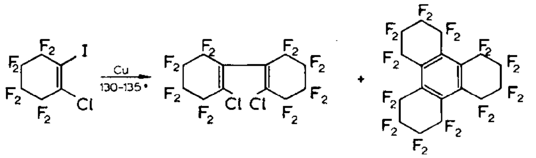
Copper coupling of 1-chloro-2-iodoperfluorocyclopentene (III) gave a 32% yield of a reduced product 2*H*,2'*H*-dodecafluoro-(bi-1-cyclopenten-1-yl) (IV) as well as the expected product 2,2'-dichlorododecafluoro-(bi-1-cyclopenten-1-yl) (V) in 36% yield.



(III) (IV) (V)

At higher temperatures (150°), copper coupling of (III) gave only the reduced product (IV) in 59% yield. The unusual propensity for the five-membered ring to abstract a proton in the coupling reaction has been noted by others[3]. Careful drying of all reagents and the apparatus did not seem to greatly affect the amount of (IV) obtained in these reactions; thus it can be assumed that the proton was abstracted from the DMF.

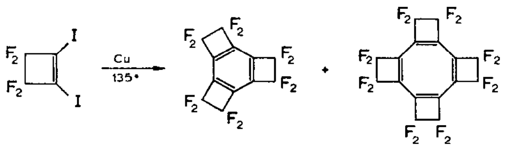
Coupling of 1-chloro-2-iodoperfluorocyclohexene (VI) with copper powder gave 2,2'-dichlorohexadecafluoro-(bi-1-cyclohexen-1-yl) (VII) in 73% yield and a small amount (4%) of perfluorododecahydrotriphenylene (VIII).



(VI) (VII) (VIII)

The appearance of (VIII) was unexpected and could have arisen from a small amount of 1,2-di-iodoperfluorocyclohexene in the starting material.

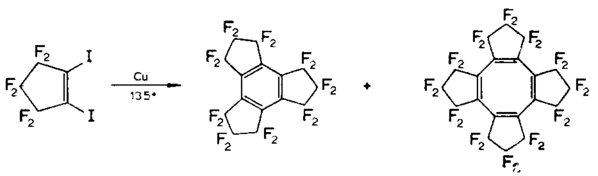
The ability of DMF to promote the copper-coupling reaction was best demonstrated in the reactions of the 1,2-di-iodides of perfluorocycloalkenes. Copper bronze in refluxing (IX) (*ca.* 155°) has been reported to yield 10% of the cyclic trimer (X), 39% of a linear dimer and 43% of a linear trimer[3]. We have found that the addition of as little as 0.5 wt. % of DMF to (IX) permitted the coupling reaction to occur at 130° or lower and produced only cyclic products, *i.e.*, perfluorobenzo[1,2:3,4:5,6]tricyclobutene (X) in 50% yield and a deep red crystalline product (XI) (34% yield) which has not been observed previously.



(IX) (X) (XI)

The structure of the tetramer (XI) has been tentatively assigned to a substituted cyclo-octatetraene and will be discussed below.

Coupling of 1,2-di-iodoperfluorocyclopentene (XII) with copper and a trace of DMF gave improved yields of the cyclic trimer (XIII) (42%) and tetramer (XIV) (28%) but none of the linear coupled products reported by Camaggi[3].



(XII) (XIII) (XIV)

Structure proof of the linear and cyclic products reported above was based on mass spectra, infrared, ultraviolet and ^{19}F NMR spectra as well as on elemental analysis and subsequent chemical reactions.

Mass spectra of the linearly coupled products (II), (IV), (V) and (VII) gave weak to moderate molecular ions characteristic of ions containing two chlorine atoms ((II), (V) and (VII)). The principal fragmentation pathway for (II) and (V) was loss of chlorine ($M^+ - Cl$) from the molecular ion, which accounts for 80% and 88% of the products respectively. Loss of CF_3 from (IV) (70%) and C_2F_4 from (VII) (28%) was also a major fragmentation path and is characteristic of these molecules[8]. In each case, strong metastable peaks supported the fragmentation paths.

Mass spectra of the cyclic coupled products (VIII), (X), (XI), (XIII) and (XIV) gave pronounced molecular ions (100%) and principal fragmentation ions corresponding to loss of fluorine (50–60%) and loss of CF_3 (60–90%). Loss of CF_3 as a one-step process was supported by strong metastable ions. Fragmentation of the molecular ion with loss of CF_2 was a significant pathway in (X) and (XI) (30–40%) but minor ($<5\%$) in (VIII), (XIII) and (XIV). Characteristic loss of C_2F_5 (35–45%) from the molecular ion was observed in the five- and six-membered ring derivatives (VIII), (XIII) and (XIV)[8]. Metastable ions indicated that loss of C_2F_5 occurred *via* one-step and two-step processes ($-CF_3$ then $-CF_2$).

The infrared spectra of (II), (IV), (V) and (VII) were typical of conjugated 1,3-dienes, showing strong carbon–carbon double-bond absorption between 6.35 and 6.05 μm. Olefinic absorption in (II) was strongest and shifted to the lower frequencies indicating a highly conjugated *transoidal* relation of the double bonds. This preferred configuration is also suggested by chemical reactions as a number of unsuccessful attempts have been made to produce a new five-membered ring through reaction of the two vinylic chlorine atoms of (II)[9].

Ring-strain effects were noted in the olefinic carbon–carbon vibrations of the cyclic trimers (VIII), (X) and (XIII). Only the double-degenerate "semicircle-stretching" vibration appeared in all three compounds at 7.25, 7.14 and 6.87 μm respectively. The normally inactive "quadrant-stretching" vibration occurred as a moderate-intensity band at 6.15 μm in the perfluorocyclobutene trimer (X) and the perfluorocyclopentene trimer (XIII) but was absent in the less-strained perfluorocyclohexene trimer (VIII). The infrared spectra of the cycloalkene tetramers (XI) and (XIV) gave very little information concerning the extent of unsaturation in these products. Compound (XI) gave very weak bands at 6.11 and 5.82 μm.

Similarly, the tetramer (XIV) showed a broad very weak absorption at about 6.18 μm. The Raman spectra of (XI) and (XIV), however, gave strong polarized absorptions at 6.25 and 5.91 μm respectively, indicating the symmetrical nature of the olefinic stretching modes. The appearance of the Raman band at 6.25 μm in (XI) is of considerable importance as it indicates substantial conjugation of the olefinic π-electron cloud. Assuming that the external bond angle of the cyclo-octatetraene ring is 90° within the cyclobutene ring, the internal cyclo-octatetraene angle becomes 135°. It would thus appear that four cyclobutene rings fused to the cyclo-octatetraene ring force the molecule into a co-planar state and allow interaction of the π electrons. Crystals and fresh alcohol solutions of (XI) are a deep reddish purple color giving additional support to the concept of a highly conjugated co-planar 8 π-electron system.

The ^{19}F NMR spectra were particularly helpful in structure determinations and offered a rather straightforward analysis in the case of the linear dimers (II), (IV) and (V). The spectrum of (II) appeared as two quartets of equal area at 111.1 and 117.6 ppm, ($J = 10$ Hz). The higher-field signal has been assigned to the geminal fluorines adjacent to the vinylic chlorine atom[10].

Compounds (IV) and (V) gave similar ^{19}F NMR spectral patterns for three singlets (1:1:1 ratio) at 110.0, 111.9, 132.1 ppm and 109.3, 115.3, 131.2 ppm respectively. The allylic CF_2 group absorption of (IV) at 110.0 and 111.9 ppm could not be assigned with any certainty. However, the 109.3 ppm $(=\overset{|}{C}-CF_2-)$, 115.3 ppm $(=CCl-CF_2)$ and 131.2, 132.1 ppm $(-CF_2-\underline{CF}_2-CF_2-)$ signal assignments seem unambigous on the basis of earlier work[11]. The ^{1}H NMR signal of (IV) appeared as a singlet at 6.93 ppm.

The ^{19}F NMR spectrum of (VII) gave a series of complex AB doublets due to the fairly rigid cyclohexene ring and the resulting quasi-axial-quasi-equatorial-fluorine interactions. Allylic CF_2 groups at C_3 and C_6 appeared as complex doublets at 101.7, 107.7 and an overlapping pair of doublets at 115.8 ppm ($J =$ *ca.* 295 Hz). The lower-field signal at 101.7 ppm and one of the pairs of doublets at 115.8 ppm were assigned to the C_6 fluorines after comparison with a series of known perfluorocyclohexene derivatives[12]. Homoallylic CF_2 group signals from C_4 and C_5 also appeared as complex multiplets at 127.7, 130.1, 138.9 and 140.4 ppm with the characteristic coupling $J = 278$ Hz. It does not appear possible to give unique assignments to the geminal fluorine atoms of C_4 and C_5 without extensive spin decoupling studies.

The cyclic trimer (X) and tetramer (XI) of perfluorocyclobutene gave ^{19}F NMR absorption singlets at 104.9 and 118.5 ppm respectively. The low-field shift of the geminal fluorine atoms of (X) is typical of benzylic fluorine signals[13] and is the expected result of aromatic ring current. The 118.5 ppm signal from (XI) is more typical of allylic fluorine and compares quite favorably with the 117 ppm value reported for a similar 8 π-electron system, octafluoro-2,7-dithiatricyclo-decadiene[14].

Our observed ^{19}F NMR signals for the cyclic tetramer (XIV) are very close to those reported previously[3] and consisted of four multiplets at 107.7, 115.8 ppm ($J = 285$ Hz) and 129.9, 134.7 ppm ($J = 265$ Hz), signal ratio 2:1. Of the possible structures for a cycloalkene tetramer[6], only a cyclo-octatetraene or a cubane structure would yield a spectrum in which the fluorine absorptions appear in two patterns in a 2:1 ratio. The cubane structure appeared to be most reasonable as (XIV) gave no indication of double-bond absorption in the IR (see above) and failed chemical tests normally indicative of a double bond, *e.g.*, Br_2/CCl_4, potassium permanganate and tetranitromethane. Attempts to determine double bonds by catalytic microhydrogenation failed as fluorine substitution reactions competed successfully with the desired double-bond saturation. Confirmation of the proposed cyclo-octatetraene structure for (XIV) was obtained from the Raman spectrum which has been discussed above.

The absence of typical double-bond properties in (XIV) has been observed previously[3] and cannot be easily explained. Similar lack of double-bond reactivity was found in (X) and (XIII) but this, of course, is expected for aromatic systems.

Except for ^{19}F NMR absorption values, the physical properties found for (XIII) agree with those reported by Camaggi[3]. We have found a slightly broadened triplet at 107.2 ppm and an unresolved multiplet at 131.7 ppm (2:1 ratio). The appearance of the benzylic fluorine signal at 107.2 ppm agrees more favorably with previously reported values[13].

EXPERIMENTAL

Melting points were determined in sealed capillary tubes on a Thomas–Hoover apparatus and are uncorrected. Infrared and ultraviolet spectra were recorded on a Perkin–Elmer 337 spectrophotometer and a Cary 17 spectrophotometer respectively. ^{1}H NMR spectra were determined on a Varian A-60A spectrometer using tetramethylsilane as an external standard while the ^{19}F NMR spectra were run on a Varian HA-100 spectrometer using CCl_3F as an internal standard. Mass spectra were obtained on an Atlas CH-4 instrument using 70 eV as the ionization potential. Analytical and preparative vapor-phase chromatography were performed on an F&M Model 300 Gas Chromatograph using a 4.8 m × 6 mm aluminum column packed with Chromosorb W coated with 20 wt. % SF-1265. Chemical analyses were performed by Huffman Laboratories of Wheatridge, Colorado. Carbon and fluorine analyses invariably appeared 1–2% low on the cyclic trimers and tetramers although other elements, namely iodine, hydrogen, chlorine and oxygen, could not be detected in any appreciable quantity ($<0.2\%$). Hydrogen and chlorine analyses on the linear dimers were within experimental error and are reported below.

Copper coupling of 1-chloro-2-iodoperfluorocyclobutene (I)

A small sublimation apparatus was charged with 25.58 g of dry copper powder (Matheson CX-1925) and 1.17 g (4.1 mmol) of 1-chloro-2-iodotetrafluorocyclobutene containing a trace of DMF. The lower portion of the apparatus was heated by an oil bath to 130–135° for 24 h, then the crystalline product was collected from the cold finger and the sides of the apparatus. The crude sublimate (0.45 g, 69%) was almost pure (II) and contained starting material as the only contaminate. Recrystallization from hexane gave pure (II) (m.p. 69.5–70.5°). The mixed melting point with an authentic sample of (II)[2] was not depressed. The following spectral absorptions were determined on a VPC purified sample (m.p. 69.5–70.5°): IR (KBr): 6.35(s), 7.55(s), 8.00(s), 8.9(s) (doublet), 11.5(s), 13.1(s), 17.2(m) and 20.1(s) μm; ^{19}F NMR: 112.7 ppm, quartet (J = 10 Hz) and 116.2 ppm, quartet (J = 10 Hz) in a 1:1 ratio. The mass spectrum gave molecular ions at 318 (39%), 320 (22%) and 322 (3.8%) with the following fragmentation ions; M^+—F (13%), M^+—Cl (100%), M^+—CF_3 (31%), M^+—2Cl (52%), M^+—CF_2Cl (49%) and $C_2F_2Cl_2^+$ (45%). (Found: Cl, 21.97%. $C_8Cl_2F_8$ requires Cl, 22.23%).

Copper coupling of 1-chloro-2-iodohexafluorocyclopentene (III)

In a similar manner to that described above, 1.31 g (3.9 mmol) of (III) and 21.0 g of copper powder were heated at 130–135° for 24 h. The crude product was dissolved in CH_2Cl_2 and separated into two products by preparative VPC. The first product peak (0.22 g, 32%) was identified as 3,3,3′,3′,4,4,4′,4′,5,5,5′,5′-dodecafluoro-(bi-1-cyclopenten-1-yl) (nc) (IV): m.p. 84.0–85.0°; IR (KBr): 3.25(m), 6.25(m), 7.45(s), 7.7(s), 8.0(s), 8.3(s), 8.9(s), 9.2(m), 10.2(s), 11.3(m), 13.6(m), 13.9(m), 19.6(m) and 20.8(m) μm; ^{19}F NMR: 110.0 (singlet), 111.9 (singlet), 132.1 ppm (singlet) in a 1:1:1 ratio; ^1H NMR: 6.93 ppm (singlet). The mass spectrum gave the molecular ion at 350 (49%) and the following fragmentation ions; M^+—F (32%), M^+—CF_2 (7%), M^+—CF_3 (70%), M^+—C_2F_5 (100%). (Found: H, 0.53%. $C_{10}H_2F_{12}$ requires H, 0.57%).

The other product peak (0.29 g, 36%) was identified as 2,2′-dichlorododecafluoro-(bi-1-cyclopenten-1-yl) (nc) (V): b.p. 148.5–149.0°/618 mmHg; n_D^{25} = 1.3738; IR (NaCl neat): 6.18(w), 7.50(s), 7.75(s), 7.85(s), 8.08(m), 8.25(s), 8.55(s), 8.90(m), 9.10(s), 9.40(s), 10.0(s), 10.5(w), 11.3(s) and 13.9(w) μm; ^{19}F NMR: 109.3 ppm (singlet) $(=\overset{|}{C}{-}\underline{CF_2})$, 115.3 ppm (singlet) $(=CCl{-}\underline{CF_2}{-}CF_2{-})$ and 131.1 ppm (singlet) $({-}CF_2{-}\underline{CF_2}{-}CF_2{-})$ in a 1:1:1 ratio. The mass spectrum gave a molecular ion peak at 418 (100%) with the following fragmentation ions; M^+—Cl (37.1%), M^+—CF_3 (57.1%) and M^+—CF_3Cl (20%). (Found: Cl, 17.13%. $C_{10}Cl_2F_{12}$ requires Cl, 16.93%).

Copper coupling of 1-chloro-2-iodo-octafluorocyclohexene (VI)

A mixture consisting of 10.0 g of copper powder and 0.909 g (2.35 mmol) of (VI) containing a trace of DMF was heated at 140° for 24 h. After this time, only a small amount of sublimate had collected on the cold finger so additional copper powder (5.0 g) was added. The amount of sublimate increased rapidly but became constant after 6 h. The crude product (0.469 g, 77%) was purified by resublimation at 40°/630 mmHg yielding 0.445 g (73%) of 2,2′-dichlorohexadecafluoro-(bi-1-cyclohexen-1-yl) (nc) (VII) (m.p. 51.5–52.0°) and 0.014 g (4%) of the less volatile perfluorododecahydrotriphenylene (nc), (VIII) (m.p. 184–185°).

The mass spectrum of (VII) gave molecular ions at 518 (15%), 520 (9.6%) and 522 (1.6%) with the following fragmentation ions; M^+—F (13%), M^+—C_2F_4 (28%), M^+—C_2F_4Cl (24%), CF_2Cl^+ (53%) and CF_3^+ (100%). Spectral peaks were observed as follows: IR (KBr): 6.05(m), 6.15(m), 7.48(m), 7.85(s), 8.05(s), 8.25(s), 8.80(s), 9.60(s), 10.20(s), 11.5(s), 11.6(s), 15.3(m) and 20.2(m) μm; ^{19}F NMR: (see discussion). (Found: Cl, 13.91%. $C_{12}Cl_2F_{16}$ requires Cl, 13.66%).

The mass spectrum of (VIII) gave a molecular ion at 672 (28%) and the following fragmentation ions; M^+—F (26%), M^+—CF_2 (1.7%), M^+—CF_3 (19%), M^+—C_2F_5 (39%) and CF_3^+ (100%). Spectral bands were observed as follows: IR (KBr): 6.1(vw), 7.25(m), 7.73(s), 8.1–8.2(s), 8.60(s), 9.7(s), 12.7(m), 15.1(m), 21.0(m) μm; UV: $\lambda_{max.}$ 264nm (ε 200) and 275nm (ε 233).

Copper coupling of 1,2-di-iodotetrafluorocyclobutene (IX)

A mixture consisting of 1.00 g (2.65 mmol) of (IX) containing less than 0.5% DMF and 2.50 g of activated copper powder[15] was heated to 130–135° for 24 h. The crude sublimate (0.311 g, 95%) partially dissolved in hot heptane leaving 0.112 g (34%) of a deep red solid (XI) (nc).

The heptane-insoluble material was purified by fractional sublimation in a sealed tube giving deep red platelets (XI), m.p. 201.0–201.5°. The mass spectrum gave a molecular ion at 496 (100%) and a fragmentation pattern similar to that of the trimer (XI), M^+—F (48%), M^+—CF_2 (30%) and M^+—CF_3 (61%). Spectral bands were observed as follows: IR (KBr): 6.11(w), 7.50(s), 7.90(s), 8.10(m), 8.45(s), 10.7(m), 12.0(m) and 20.7(m) μm; Raman: 6.25(s), 7.81(w), 10.5(m) and 15.3(s) μm; ^{19}F NMR (dioxane): broad singlet at 118.5 ppm.

The heptane solution was concentrated and then fractionated by preparative VPC yielding 0.163 g (50%) of a white volatile solid identified as perfluorobenzo-[1,2:3,4:5,6]tricyclobutene (X), m.p. 135–136°. The mass spectrum gave a molecular ion at 372 (100%) and a characteristic fragmentation pattern with prominent metastable ions: M^+—F (54%), M^+—CF_2 (47%) and M^+—CF_3 (58%). Spectral bands were observed as follows: IR (KBr): 6.15(w), 7.14(w), 7.68(s), 8.00(s), 8.40(s), 8.80(s), 12.30(s), 16.9(m) and 21.0(s) μm; UV: $\lambda_{max.}$ 252.8 (ε 447) and 259.0 nm (ε 455); ^{19}F NMR: (CH_2Cl_2) sharp singlet at 104.9 ppm [lit.[3], m.p. 133–134°; UV: $\lambda_{max.}$ 253 and 259 nm (ε 240 and 240)].

Copper coupling of 1,2-di-iodohexafluorocyclopentene (XII)

Copper powder (10.0 g) and 0.921 g (2.5 mmol) of (XII) containing one drop of DMF was heated at 140° for 24 h. A crystalline sublimate began to appear within 30 min and reached a constant amount in about 12 h. The crude sublimate (0.283 g, 74%) was dissolved in $CF_2Cl–CFCl_2$ (F-113) and separated by preparative VPC at 175°. In addition to a trace amount of starting material, only two products appeared. The first product from the VPC column was identified as perfluoro-(dodecahydrotetracyclopenteno-cyclo-octatetraene) (XIV) (40 wt. %), m.p. 81.0–82.5°, and gave the following spectral absorptions: IR (KBr): 6.18(vw), 7.48(s), 7.85(s), 8.13(m), 8.25(m), 9.20(m), 9.80(s), 11.8(m) and 19.8(s) µm; Raman: 5.91(s), 7.81(m), 7.87(m), 8.64(m), 10.7(m), 14.9(m), 15.6(m), 26.0(m) and 27.8(m) µm; UV: $\lambda_{max.}$ 253 nm (ε 483); ^{19}F NMR: (hexane) 107.7 ppm and 115.8 ppm ($=C–\underline{CF_2}–$), $J = 285$ Hz, 129.9 ppm and 134.7 ppm ($–CF_2–\underline{CF_2}–CF_2–$), $J = 265$ Hz [lit.[3], m.p. 78°; UV: $\lambda_{infl.}$ 250–270 nm (ε 470–310); ^{19}F NMR: 107.9, 115.1 ppm, $J = 280$ Hz and 130.0, 134.1 ppm, $J = 244$ Hz]. The mass spectrum of (XIV) gave the molecular ion at 696 (100%) and the following fragmentation ions; $M^+–F$ (60%), $M^+–CF_2$ (5%), $M^+–CF_3$ (56%) and $M^+–C_2F_5$ (35%).

The second product (60 wt. %) was identified as perfluorotrindane (XIII), m.p. 117–118°, and gave the following spectral absorptions: IR (KBr): 6.15(vw), 6.87(vw), 7.50(m), 7.75(s), 7.95(m), 8.25(s), 8.47(m), 9.50(s), 12.50(m) and 19.3(m) µm; UV: $\lambda_{max.}$ 256.0 nm (ε 204) and 263.6 nm (ε 236); ^{19}F NMR (hexane) gave a broad triplet at 107.2 ppm and an unresolved multiplet at 131.7 ppm, ratio 2:1 [lit.[3], m.p. 114°; IR: 1630 and 1460 cm^{-1}; UV: $\lambda_{max.}$ 256 nm (ε 226) and 263 nm (ε 260); ^{19}F NMR: 114 ppm and 131.1 ppm, ratio 2:1].

The mass spectrum of (XIII) gave a molecular ion at 522 (100%) and the following fragmentation ions; $M^+–F$ (62%), $M^+–CF_3$ (94%) and $M^+–C_2F_5$ (46%).

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