The Unexpected Formation of a Novel Fluorinated Triene

Igor Shevchenko,*[a] Vasyl Andrushko,[a] Enno Lork,[b] and Gerd-Volker Röschenthaler*[b]

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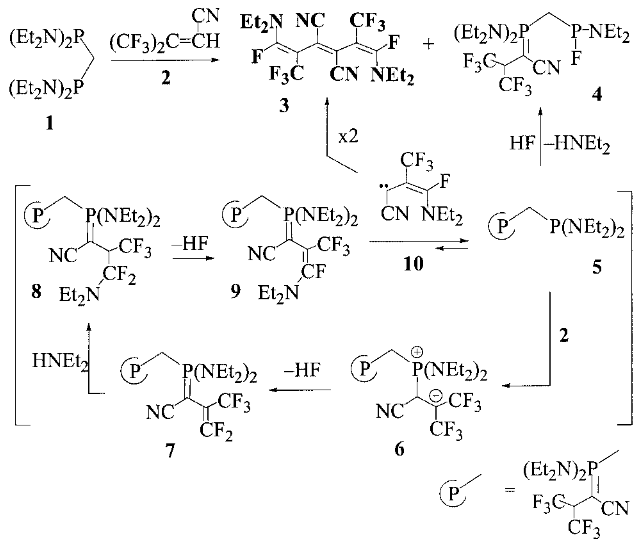
Bis[bis(dialkylamino)phosphanyl]methane (**1**) and 4,4,4-trifluoro-3-(trifluoromethyl)-2-butenenitrile (**2**) unexpectedly gave triene **3**. According to the X-ray structure analysis compound **3** exists in the solid state exclusively as one isomer.

Among known compounds containing three conjugated C=C double bonds, there are only two fluorine substituted examples: perfluoro-1,3,5-hexatriene[1−5] and 1,6-dichlorohexafluoro-1,3,5-hexatriene.[6] Here we wish to report on an unusual reaction of bis[bis(dimethylamino)phosphanyl]methane (**1**) with 4,4,4-trifluoro-3-(trifluoromethyl)-2-butenenitrile (**2**) which, unexpectedly, gave the triene **3**. The second product of this reaction was identified as the fluorine-substituted ylide **4** (Scheme 1).



Scheme 1

It is interesting to note that one of the trifluoromethyl groups of the starting acrylonitrile **2** loses two fluorine atoms and adds one of the diethylamino groups which was initially connected to a trivalent phosphorus atom of **1**. The mechanism of this reaction includes the intermediate formation of the ylide **5**, which was detected in the ^{31}P NMR spectrum of the reaction mixture as two characteristic doublets at δ = 73.78 and 67.18 ppm ($^{2}J_{P,P}$ = 102.4 Hz). These signals decrease slowly in intensity during the course of the reaction and the two doublets of the final product **4** appear. Intermediate **5** can react further with **2** to give the unstable betaine **6**, which decomposes into compound **7** and HF. The hydrogen fluoride thus formed cleaves the P−N bond of the trivalent phosphorus atom of **5** immediately to give **4** and diethylamine. This amine then adds across the C=C double bond of **7**, yielding the intermediate compound **8**, which splits off hydrogen fluoride and gives the unsymmetrical double ylide **9**. These considerations are supported by the fact that the reaction mixture contains a certain amount of diethylammonium fluoride.

The most probable route of formation of the symmetric molecule **3** is the dimerization of carbene **10**. This carbene can be formed during the disintegration of **9** into **5**; the cleavage of the ylidic bond in compound **9** is probably reversible. Of course, some aspects of the detailed mechanism shown in Scheme 1 may differ slightly; for example, some of the proposed steps may be concerted. However, the general concept of an exchange between a fluorine atom and a diethylamino group probably does not differ considerably from the proposed scheme, as a similar process has been observed recently.[7]

The triene **3** was isolated as a slightly yellow crystalline product. The structure of a single crystal was determined by X-ray analysis (Figure 1).

The three double bonds are not conjugated as they are not coplanar. The diethylamino and trifluoromethyl groups at the terminal double bonds, and the central double bond, have a *trans*-configuration. It is interesting to note that no

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[a] Institute of Bioorganic Chemistry,
Murmanskaya Street 1, 02094 Kiev, Ukraine
Fax: (internat.) +38-044/573-2552
E-mail: ishev@bpci.kiev.ua
[b] Institute of Inorganic and Physical Chemistry, Universität Bremen, NW2, C2350,
Leobener Str, 28334 Bremen, Germany
Fax: (internat.) +49-(0)421/218-4267
E-mail: gvr@chemie.uni-bremen.de

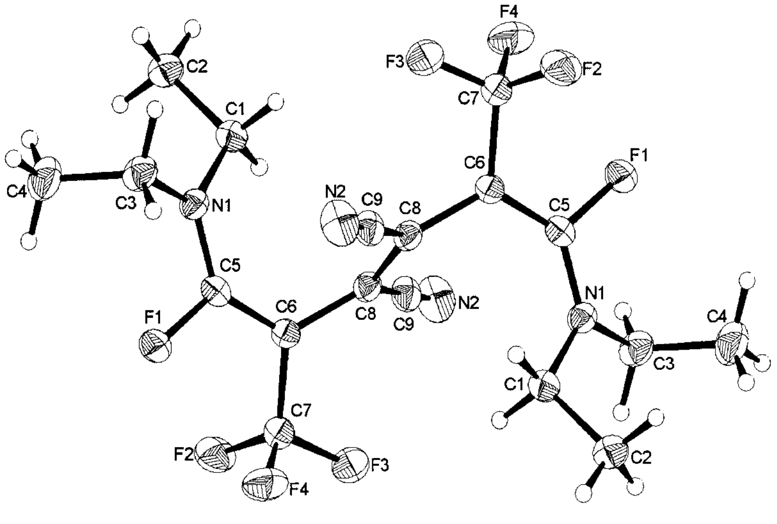
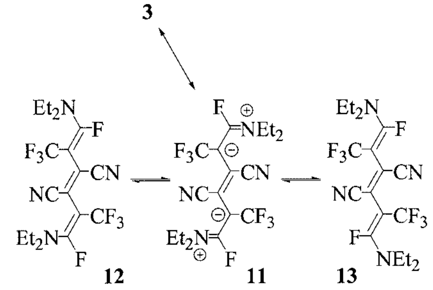


Figure 1. Selected bond lengths [Å] and angles [°]: N(1)−C(5) 1.3296(19), C(5)−F(1) 1.3523(17), C(5)−C(6) 1.361(2), C(6)−C(7) 1.496(2), C(6)−C(8) 1.470(2), C(8)−C(8) 1.365(3); N(1)−C(5)−F(1) 111.85(12), N(1)−C(5)−C(6) 132.27(14), F(1)−C(5)−C(6) 115.88(12), C(8)−C(6)−C(7) 119.23(13), C(9)−C(8)−C(6) 117.98(12), C(8)−C(8)−C(9) 117.35(17)

other possible steric isomers have been found in the crystalline form. An explanation for this phenomenon can be found in the NMR spectra, where a fast interconversion between the isomers in solution at room temperature can be seen. The ^{19}F NMR spectrum displays a doublet for the CF_3 groups ($\delta = -56.6$ ppm, $^4J_{F,F} = 18$ Hz) and a broad unresolved signal for the CF fluorine atoms ($\delta = -66.2$ ppm). At +60 °C the rate of interconversion substantially exceeds the NMR detection limit and the broad signal transforms into a quadruplet with the same coupling constant. An analysis of the low temperature spectra leads to several conclusions. Interconversion between the isomers proceeds rather easily as the other isomers begin to appear at −25 °C. At −60 °C the spectrum shows three isomers in the proportion 1:1:3 indicating that one of the isomers is more stable than the other two. The appearance of only three isomers indicates that the rotation occurs only at terminal double bonds, whereas the central C=C bond retains its *trans*-configuration (otherwise the number of isomers would be larger[4]). The relatively easy rotation around the terminal double bonds is probably accounted for by the π-electron donating ability of the diethylamino groups and the electron-accepting ability of the trifluoromethyl groups, leading to the conjugation of the free electron-pairs of the nitrogen atoms with the adjacent double bonds and formation of the betainic structure **11** (Scheme 2).

Although the lengths of all the C=C double bonds are equal, the influence of **11** should be rather large. The C(5)−N(1) bond is substantially shorter than the other two bonds to nitrogen (132.96 vs. 148.56 pm) and the diethylamino groups have an almost ideal flat conformation. Thus, rotation can occur via the resonance structure **11** to give the two other possible isomers **12** and **13**.



Scheme 2

Experimental Section

General Remarks: All operations were performed under nitrogen in a dry box. The solvents were dried by the usual procedures. NMR: Spectrometer Bruker AC-200 (^1H at 200.1 MHz, ^{13}C at 50.3 MHz, ^{31}P at 81.3 MHz); reference substances were $SiMe_4$ (TMS) ext. (^1H, ^{13}C), and 85% H_3PO_4 ext. (^{31}P). MS: Spectrometer Finnigan MAT 8430; E.I. at 70 eV. Materials: Compound **1** was obtained from methylenebis(dichlorophosphane) and diethyl(trimethylsilyl)amine in petroleum ether at 0 °C (yield 70%; b.p. 108−110 °C, 0.07 Torr). Compound **2** was obtained by adding gaseous hexafluoroacetone to (triphenylphosphoranylidene)acetonitrile without solvent at 20 °C (yield 90%; b.p. 88−90 °C) .

Compound 3: Compound **2** (140 mg, 0.74 mmol) was added to **1** (120 mg, 0.33 mmol) without solvent at 20 °C. After completion of the slightly exothermic reaction the mixture was heated to 50 °C for 15 min. Dichloromethane (2 mL) was then added followed by addition of diethyl ether (0.5 mL) and the mixture left at −15 °C for 2−3 days. The crystals of **3** that formed were isolated, washed with diethyl ether (2 × 2 mL) and dried in vacuo (0.05 mm). Yield 36 mg (49%), m.p. 78−80 °C. ^{1}H NMR ($CDCl_3$): $\delta = 1.26$ (t, $^3J_{H,H} = 7.0$ Hz, 12 H, CH_2CH_3), 3.32 (dq, $^3J_{H,H} = 7.0$, $^3J_{F,H} = 3.2$ Hz, 8 H, CH_2CH_3) ppm. ^{19}F NMR ($CDCl_3$): $\delta = -56.6$ (d, $^4J_{F,F} = 18$ Hz, 6 F), −66.2 (broad, 2 F) ppm. MS (EI): $M_{calcd.} = 444.37$; $M_{exp.} = 444$. $C_{18}H_{20}F_8N_4$ (444.4): calcd. C 48.65, H 4.54, N 12.61; found C 48.64, H 4.51, N 12.56.

Compound 4: The solvent was evaporated from the mother liquor remaining after crystallisation of **3** and the resulting oil was extracted with hexane (4 × 10 mL). The extracts were combined and concentrated to a volume of 5 mL. In order to dissolve the precipitated oil the mixture was heated to boiling point, cooled to room temperature and left to stand for 30 min and then cooled to −15 °C for 3−4 days. The crystals formed were separated from the mother liquor and dried in vacuo (0.05 mm). Yield 82 mg (49%). M.p. 90−91 °C. ^{1}H NMR ($CDCl_3$): $\delta = 1.14$ (t, $^3J_{H,H} = 7.03$ Hz, 6 H, NCH_2CH_3), 1.16 (t, $^3J_{H,H} = 7.03$ Hz, 12 H, NCH_2CH_3), 2.3−2.7 (m, 2 H, P-CH_2-P), 2.9−3.4 [m, 12 H, NCH_2CH_3, 1 H, $CH(CF_3)_2$] ppm. ^{13}C NMR ($CDCl_3$): $\delta = 12.68$ (dm, $J_{P,C} = 238.9$ Hz, 1 C, PCCN), 13.48 (m, 4 C, NCH_2CH_3), 15.13 (m, 2 C, NCH_2CH_3), 34.26 (ddd, $^1J_{P,C} = 19.5$, $^1J_{P,C} = 87.8$, $^2J_{F,C} = 48.8$ Hz, PCP), 39.36 (m, 4 C, NCH_2CH_3), 42.89 (d, $^3J_{F,C} = 18.5$ Hz, 2 C, NCH_2CH_3), 47.44 [m, 1 C, $CH(CF_3)_2$], 124.16 [q, $^1J_{F,C} = 281.8$ Hz, 2 (CF_3)], 124.90 (d, $^2J_{P,C} = 12.6$ Hz, CN) ppm. ^{19}F NMR ($CDCl_3$): $\delta = -67.04$ (dd, $^3J_{H,F} = 7.8$, $^3J_{P,F} = 3.6$ Hz, 6 F) ppm. ^{31}P NMR ($CDCl_3$): $\delta = 62.23$ (dd, $^2J_{P,P} = 68.2$, $^3J_{P,F} = 17.1$ Hz,), 155.05 (dd, $^2J_{P,P} = 68.2$, $^1J_{F,P} = 958.1$ Hz) ppm. $C_{18}H_{33}F_7N_4P_2$ (500.42): calcd. C 43.20, H 6.64, N 11.20; found C 44.39, H 6.98, N 12.20.

X-ray Crystallographic Study: Empirical formula $C_{18}H_{20}F_8N_4$; formula weight 444.38; monoclinic; crystal dimensions 0.70 × 0.50 × 0.50 mm; space group $P2_1/n$; $a = 1002.40(10)$, $b = 897.50(10)$, $c = 1165.1(2)$ nm, $\beta = 108.620(10)°$, $V = 0.9933(2)$ nm^3, $Z = 2$; $D_{calcd.} = 1.486$ mg/mm^3; $F_{000} = 456$; $2\theta_{max} = 27.50°$; reflections collected 3031; independent reflections 2269 [R(int) = 0.0209]; completeness to theta (27.50°) = 99.2%; refinement method: full-matrix least-squares on F^2; data/restraints/parameters: 2269/0/141; goodness-of-fit on $F^2 = 1.041$; final R indices [$I > 2\sigma(I)$] $R1 = 0.0385$, $wR2 = 0.0930$; R indices (all data) $R1 = 0.0576$, $wR2 = 0.1031$; extinction coefficient 0.019(3). CCDC-174595 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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