Journal of Fluorine Chemistry 76 (1996) 121–124

Reaction of methanol with perfluorotetracyclobuta-1,3,5,7-cyclooctatetraene

William R. Cullen [a,*], Steven J. Rettig [a], Alice E. Moore [b], Robert L. Soulen [b]
[a] Chemistry Department, University of British Columbia, Vancouver, B.C, V6T 1Z1 Canada
[b] Chemistry Department, Southwestern University, Georgetown, TX 78626, USA

Received 5 January 1995; accepted 13 September 1995

Abstract

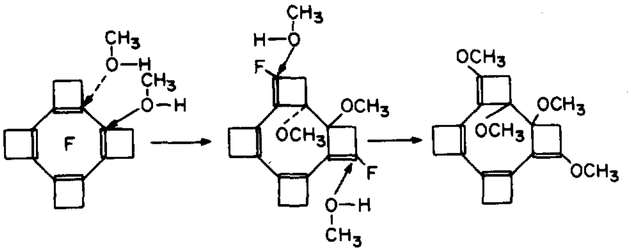
Perfluorotetracyclobuteno-1,3,5,7-cyclooctatetraene (PCOT) is a planar and centrosymmetric molecule which possesses an extraordinary electron affinity due to the planarity of the eight π-electron system and the cumulative electron-withdrawing effects of the 16 fluorine atoms. An improved method for the synthesis of PCOT and the product resulting from the spontaneous reaction of PCOT with excess alcohol is reported. Crystal structures of the methyl (**1**) and ethyl (**2**) derivatives are described.

Keywords: Methanol; Perfluorotetracyclobutacyclo-octatetraene; Reaction; Crystal structure; NMR spectroscopy; Mass spectrometry; IR spectroscopy

1. Introduction

The structure [1] and some of the unusual physical properties [2–4] of perfluorotetracyclobuteno-1,3,5,7-cyclooctatetraene (PCOT) have been reported previously. Reports on the chemical reactions of PCOT have been slow in appearing because of the complex nature of the reactions and the lengthy process required to prepare small quantities of the starting compound.

The rapid reaction of PCOT with normal laboratory solvents is readily apparent whenever one rinses out glassware containing even trace amounts of the perfluorocarbon. Intense colours develop which quickly fade to a yellow–brown solution. In this study we report on the structure of the products obtained from the reaction of anhydrous methanol or ethanol with PCOT (Scheme 1). A single product has been isolated following evaporation of the excess alcohol and vacuum sublimation of the residues. Mass spectral data of the products indicate that the starting material has lost four fluorine atoms and gained four alkoxy groups. Proton NMR spectroscopy suggests that two of the alkoxy substituents are bonded to an sp^2 carbon and the other two are bonded to an sp^3 carbon. Additional information about the structure of the product has come from X-ray crystal analysis.



Scheme 1.

2. Results and discussion

The structure of the methoxy derivative is shown in Fig. 1. There are two *trans*-alkoxy groups attached to the eight-membered ring, raising several questions concerning the mechanism of this reaction, especially the first step. Upon addition of alcohol to PCOT an intense blue colour forms which rapidly changes within a few seconds through red to a bright yellow. Similar charge-transfer complexes are also observed with aromatic derivatives and are not unexpected because of the unusual electron affinity of PCOT (est. 3.37 eV from charge-transfer spectra). For comparison, we have found the λ_{max} value for the charge-transfer complex PCOT–naphthalene to be 690 nm versus the reported value of 548 nm for tetracyanoethylene–naphthalene [5]. Thus it is reasonable to suggest that the initially formed charge-transfer complex between the oxygen non-bonding electron pair and the eight electron π-system collapses to form the RO–C σ-

---

* Corresponding author.

SSDI 0022-1139(95)03368-8

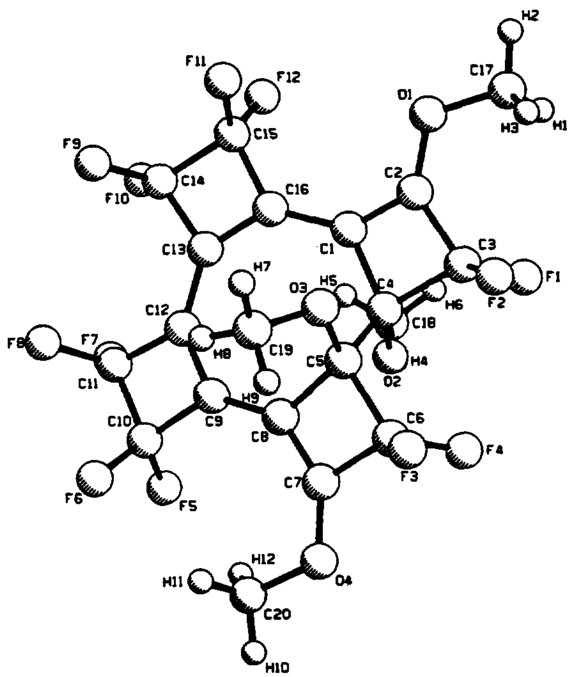


Fig. 1. PLUTO drawing of 1.

bond with concurrent elimination of an allylic fluorine atom. Subsequent attack by alcohol to displace the vinylic fluorine and produce the alkyl vinyl ether follows well-established reaction patterns for perfluorocycloalkenes [6,7]. The fact that the two alkoxyl groups are joined *trans* to the eight-membered ring further suggests that the charge-transfer complex forms from two solvent molecules in closest approach from opposite sides of the ring.

The rapid reaction of PCOT with neutral alcohol is in striking contrast to other perfluorocycloalkene fused systems. For example, tri(perfluorocyclobuteno)benzene, tri(perfluorocyclopenteno)benzene or tetra(perfluorocyclopenteno)cyclo-octatetraene require refluxing alcoholic KOH to initiate substitution of the fluorine atom [8]. These molecules do not form coloured charge-transfer complexes with alcohol. In the benzene derivatives, there is no deviation in the bond distances and thus the fully aromatic character is preserved in the central ring (see Ref. [1] and references quoted therein). Unlike PCOT, tetra(perfluorocyclopenteno)cyclo-octatetraene does not possess sufficient exocyclic ring strain to force the central eight-membered ring flat and the anti-aromatic eight π-electron system is avoided. PCOT, which is planar, shows an alternating short–long bond difference of only 0.07 Å versus 0.14 Å for the non-planar cyclopenteno derivative. Thus the rapid reaction of PCOT with alcohol may be rationalized as a means of avoiding the imposed *anti*-aromatic state by coordination with oxygen and simultaneous movement of one double bond to an exocyclic position.

The structures of the methoxy (**1**) and ethoxy (**2**) derivatives are essentially the same, so only the PLUTO diagram for **1** is shown in Fig. 1. Selected distances and angles for this molecule are listed in Table 1. The most significant differences between the structure of **1** and **2** are seen in the lengths of the chemically equivalent bonds C(2)–C(3) [1.487(5) Å] and C(6)–C(7) [1.475(6) Å] in molecule **1** and the corresponding bonds in molecule **2**, 1.503(4) Å and 1.505(4) Å, respectively. The origin of this effect, if real, is not obvious.

The planar eight-membered ring system of the starting material PCOT is distorted in the reaction products which now have endocyclic and exocyclic double bonds, with the former, e.g. C(13)–C(16) of length 1.350(5) Å, being longer than the latter, e.g. C(1)–C(2) of length 1.331(5) Å. The single bonds in the ring are of course longer: C(12)–C(13), 1.441(5) Å; C(8)–C(9), 1.430(5) Å; C(4)–C(5) which is situated between two sp^3-hybridized carbon atoms is the longest at 1.539(5) Å.

The bonds around the eight-membered ring of PCOT are alternately short [av. 1.353(10) Å] and long [av. 1.425(14) Å], so that breaking the cyclic conjugation of PCOT does not have a major effect on these distances apart from that noted above for C(4)–C(5).

Table 1
Selected bond lengths (Å) and angles (°) for 1 with estimated standard deviations in parentheses

Atom	Atom	Distance	Atom	Atom	Atom	Angle
C1	C2	1.331(5)	C1	C2	C3	94.5(3)
C1	C16	1.417(5)	C2	C3	C4	86.7(3)
C1	C4	1.519(5)	C1	C4	C3	84.5(3)
C2	C3	1.487(5)	C2	C1	C4	94.3(3)
C3	C4	1.563(5)	C2	O1	C17	117.1(4)
C4	C5	1.539(5)	C7	O4	C20	117.7(4)
C5	C8	1.517(5)	C2	C1	C16	136.3(4)
C5	C6	1.555(6)	C4	C1	C16	129.1(3)
C6	C7	1.475(6)	C4	O2	C18	119.5(3)
C7	C8	1.344(5)				
C8	C9	1.430(5)				
C9	C12	1.364(5)				
C12	C13	1.441(5)				
C13	C16	1.350(5)				

The dihedral angle between the planes C(13)C(16)-C(14)C(15) and C(1)C(2)C(3)C(4) is 6.14° which is similar to that between the planes C(5)C(6)C(7)C(8) and C(9)C(10)C(11)C(12), but is less than that between planes C(9)C(10)C(11)C(12) and C(13)C(14)C(15)C(16), 13.72°. On this basis, the structure of **1** can be described as two bi(cyclobuten-1-yl) moieties with transoid double bonds joined at C(13)–C(12) and C(4)–C(5). The only other structures determined to date that contain these units are tetracarbonyl-[2,2′-bis(cyclohexylphosphino)-octafluorobi(1-cyclobuten-1-yl)molybdenum] [9] and 1,1′-bi(3,3,4,4-tetrafluoro-2-diphenylphosphinocyclobutene) [10].

In the molybdenum complex, the double bonds are cisoid and of lengths 1.359(12) and 1.335(10) Å, joined by a carbon–carbon bond of length 1.451(12) Å. In the ditertiary phosphine, the double bonds, length 1.358(3) Å and 1.359(3) Å, are again in the cisoid configuration with the connecting carbon–carbon bond being of the usual length, i.e. 1.439(3) Å.

A cobalt carbonyl cluster containing a related ditertiary arsine has been structurally characterized but, in this case, the double bonds are involved in bonding to cobalt atoms and are lengthened to 1.40(4) Å: the connecting single bond is shortened to 1.34(6) Å [11].

3. Experimental details

Methanol and ethanol were dried by distillation from calcium hydride. Reagent grade DMF was used without further purification. Activated copper powder was prepared by a modification of the Brewster method [12]. Powdered zinc was added to a concentrated solution of copper sulfate containing a few drops of sulfuric acid until the aqueous layer was decolourized. The precipitated copper was filtered and quickly washed successively with water, acetone and ether, and then vacuum-dried. Exposure of the copper powder to air was held to a minimum during all stages of preparation. The powder thus prepared is a light brown colour and about one-third the density of commercial copper metal powder. Infrared spectra were obtained on a Perkin-Elmer 1430 spectrophotometer using KBr pellets. Mass spectral data were obtained from a Finnegan TSQ-70 instrument. The ^{19}F and ^{13}C NMR spectra of PCOT in C_6D_6 were obtained on a Brucker WH-90 instrument. The ^{1}H and ^{19}F NMR spectra of methoxy PCOT was obtained in $CDCl_3$ using TMS and F-11 as reference standards.

3.1. Preparation of tetrakis(tetrafluorocyclobuta)cyclooctatetraene (PCOT)

In an inert atmosphere, a small sublimation apparatus was charged with 2.54 g, 40 mmol of the copper powder followed by 1.85 g, 4.9 mmol of 1,2-diiodotetrafluorocyclobutene when the apparatus was sealed from air by means of a rubber stopper. After 24 h at room temperature, the lower part of the sublimation apparatus was heated to 90 °C for 24 h then to 135 °C for an additional 30 h. The crude product (0.65 g) was separated and washed with 5 ml of hot heptane to remove the colourless cyclic trimer. The dark red crystals were vacuum-sealed in a 700 mm × 10 mm glass tube and heated (100 °C hot end) in a thermal gradient sublimation apparatus. The purified PCOT crystals (0.38 g, 62% yield) were clear deep-red cubic-shaped crystals, m.p. 201.0–201.5 °C (sealed tube). IR (KBr) (cm^{-1}): 1637 (weak). ^{19}F NMR ϕ: −119.5 (broad singlet) ppm. ^{13}C NMR (^{19}F decoupled) δ: 115.1; 142.5 ppm.

3.2. Preparation of trans-4,4,7,7,11,11,12,12,15,15,16,16-dodecafluoro-3,5,6,8-tetramethoxypentacyclo-[12.2.0.0^{2,5}.0^{6,9}.0^{10,13}]hexadeca-1(14),2,8,10(13)-tetraene (1)

PCOT (15 mg, 0.03 mmol) was placed into a small vial followed by 500 ml of dry methanol. After a few minutes the excess methanol was evaporated by means of a nitrogen stream to leave 15.1 mg (92%) of a yellow–broad residue. Sublimation of the crude product in a thermal gradient sublimation apparatus (0.01 mmHg vac./64 °C hot end) gave large bright yellow crystals, m.p. 138–139 °C. IR (KBr) (cm^{-1}): 1675; 1645; 1390; 1320; 1125; 1100; 1000. ^{1}H NMR ($CDCl_3$) δ: 3.35 (s, 6H); 4.00 (s, 6H) ppm. ^{19}F NMR ϕ: −108.3 (m); −110.8 (s); −112.1 (s); −112.3 (m); −112.7 (t); −114.7 (br,s) ppm. MS (m/e): 544 (88%, M^+); 529 (100%, $M^+ - CH_3$); 513 (34%, M^+OCH_3); 467 (49%, $M^+ - 2CH_3O, CH_3$); 405 (59%, $M^+ - 4CH_3O, CF$).

3.3. Preparation of trans-4,4,7,7,11,11,12,12,15,15,16,16-dodecafluoro-3,5,6,8-tetra-ethoxypentacyclo-[12.2.0.0^{2,5}.0^{6,9}0.^{10,13}]hexadeca-1(14),2,8,10(13)-tetraene (2)

This compound was prepared in the same way as **1** by using excess ethanol.

3.4. X-Ray crystallographic analyses

Crystallographic data for both compounds are listed in Table 2. The final unit-cell parameters were obtained by least-squares analysis of the setting angles for 25 reflections with $2\theta = 60.6$–$74.6°$ for **1** and 29.1–38.9° for **2**. The intensities of three standard reflections, measured every 150 reflections throughout the data collections, showed only small random fluctuations. The data were processed [1] and corrected for Lorentz and polarization effects, and for absorption (empirical, based on azimuthal scans for four reflections).

---

[1] TEXSAN/TEXRAY structure analysis package which includes versions of the following: MITHRAL, integrated direct methods, by C.J. Gilmore; DIRDIR, direct methods for difference structures, by P.T. Beurskens; ORFLS, full-matrix least-squares and ORTFE, functions and errors, by W.R. Busing, K.O. Martin and H.A. Levy; ORTEP II, illustrations by C.K. Johnson.

Table 2
Crystallographic data [a]

Compound	1	2
Formula	$C_{20}H_{12}F_{12}O_4$	$C_{24}H_{20}F_{12}O_4$
Formula weight	544.29	600.40
Crystal colour, habit	yellow needle	yellow prism
Crystal size (mm)	0.10×0.12×0.42	0.25×0.30×0.40
Crystal system	orthorhombic	triclinic
Space group	*Pbca*	$P\bar{1}$
a (Å)	14.750(2)	9.618(2)
b (Å)	25.056(3)	15.917(4)
c (Å)	11.4732(9)	9.382(2)
α (°)	90	94.14(2)
β (°)	90	112.52(2)
γ (°)	90	94.24(2)
V (Å^3)	4240.2(6)	1315.3(5)
Z	8	2
ρ_{calc} (g cm^{-3})	1.71	1.52
$F(000)$	2176	608
Radiation	Cu	Mo
Wavelength (Å)	1.54178	0.71069
μ (cm^{-1})	16.79	1.51
Transmission factors	0.964–1.00	0.977–1.00
Scan type	ω–2θ	ω–2θ
Scan range (deg in ω)	$0.94+0.30 \tan\theta$	$1.26+0.35 \tan\theta$
Scan speed (deg min^{-1})	16	16
Data collected	$+h, +k, +l$	$+h, \pm k, \pm l$
$2\theta_{max}$ (°)	155.3	60.0
Crystal decay	negligible	negligible
Total No. of reflections	4710	7938
No. of unique reflections	4710	7680
R_{merge}	–	0.024
No. of reflections with $I \geqslant 3\sigma(I)$	1860	2837
No. of variables	326	361
R	0.042	0.043
R_w	0.049	0.054
GOF	1.83	2.00
Max Δ/σ (final cycle)	0.005	0.01
Residual density e Å^3	0.35	0.23

[a] Temperature, 294 K; Rigaku AFC6S diffractometer; graphite monochromator; takeoff angle, 6.0°; aperture, 6.0×6.0 mm at a distance of 285 mm from the crystal; stationary background counts at each end of the scan (scan/background time ratio, 2:1); $\sigma^2(F^2) = [S^2(C+4B) + (pF^2)^2]/Lp^2$ (S = scan rate, C = scan count, B = normalized background count, $p = 0.030$ for **1** and 0.035 for **2**); function minimized $\Sigma w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \Sigma \| F_p| - |F_c \| / \Sigma |F_o|$, $R_w = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2)^{1/2}$, and GOF $= [\Sigma(|F_o| - |F_c|)^2 (m-n)]^{1/2}$. Values given for R, R_w and GOF are based on those reflections with $I \geqslant 3\sigma(I)$.

The structure analysis of **2** was initiated in the centrosymmetric space group $P\bar{1}$, the choice being confirmed by the subsequent successful solution and refinement of the structure. Both structures were solved by direct methods, the coordinates of all non-hydrogen atoms being determined from E-maps. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in idealized positions ($d_{C\text{–}H} = 0.98$ Å, $B_H = 1.2\ B_{\text{bonded atom}}$, methyl groups staggered). Neutral atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for X-Ray Crystallography* [14]. Selected bond lengths and angles are given in Table 1.

4. Supplementary material available

Stereoviews of both compounds, tables of final atomic coordinates, equivalent isotopic thermal parameters, bond lengths, bond angles, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, least-squares planes, and measured and calculated structure factor amplitudes for both compounds are available from the authors.

Acknowledgements

We are grateful to the Natural Sciences and Engineering Research Council of Canada (W.R.C. and S.I.R.) and the Welch Foundation (A.E.M. and R.L.S.) for support of this work.

References

[1] F.W.B. Einstein, A.C. Willis, W.R. Cullen and R.L. Soulen, *J. Chem. Soc., Chem. Commun.*, (1981) 526.

[2] M.A. Fox, K.A. Colapret, J.R. Hurst, R.L. Soulen, R. Maldonado and L. Echegoyen, *J. Org. Chem.*, *57* (1992) 3728.

[3] W.E. Britton, J.P. Ferraris and R.L. Soulen, *J. Am. Chem. Soc.*, *104* (1982) 5322.

[4] E. Heilbronner, J. Wirz and R.L. Soulen, *Helv. Chim. Acta*, *67* (1984) 47.

[5] L.E. Lyons and L.D. Palmer, *Aust. J. Chem.*, *29* (1976) 1919.

[6] J.D. Park, R.J. McMurtry and J.H. Adams, *Fluorine Chem. Rev.*, *2* (1968) 55.

[7] Q.-C. Mir and J. Shreeve, *J. Fluorine Chem.*, *68* (1994) 269.

[8] G. Gamaggi, *J. Chem. Soc. C* (1971) 2382.

[9] W.R. Cullen, M. Williams, F.W.B. Einstein and C.-H. Huang, *J. Fluorine Chem.*, *11* (1978) 365.

[10] S.J. Rettig and J. Trotter, *Can. J. Chem.*, *55* (1977) 3065.

[11] F.W.B. Einstein and R.D.G. Jones, *J. Chem. Soc., Dalton Trans.*, (1972) 2568.

[12] R.Q. Brewster and T. Groening, *Org. Synth.*, *2* (1943) 445.

[13] *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, UK (present distributor, Kluwer Academic Publishers, Dordrecht, The Netherlands), 1974, Vol. IV, pp. 99–102 and p. 149.