Journal of Fluorine Chemistry 88 (1998) 191–194

Carbene reactions with pentafluorophenol

Gerald M. Brooke *, Julian A. Cooper, Judith A.K. Howard, Dmitri S. Yufit
Chemistry Department, Science Laboratories, South Road, Durham DH1 3LE, UK

Received 17 July 1997; accepted 22 October 1997

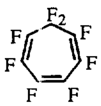
Abstract

Pentafluorophenol reacts with sodium trichloroacetate in monoglyme in a Reimer–Tiemann reaction to give not only pentafluorophenyl orthoformate (**6**) but also a previously unknown 'abnormal' type of product, tetra*kis*(pentafluorophenoxy)ethene (**5**), *one* possible formation of which could be by dimerisation of an intermediate carbene.

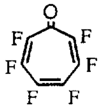
Keywords: Reimer–Tiemann; Pentafluorophenol; Alkene formation

1. Introduction

Highly fluorinated unsaturated 7-membered ring compounds are relatively rare in organic chemistry because the number of synthetic routes to them is limited. The synthesis of octafluorotropilidene (**1**) has been accomplished via multistage processes [1,2] and hydrolysed to hexafluorotropone (**2**), but a more direct route to the ring system shown in (**3**) involved pyrolysis of easily accessible pentafluorophenyl propynoate [3].



(1)



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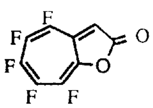


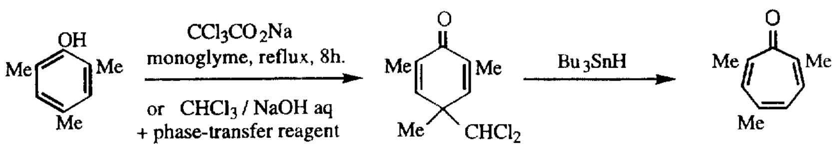
(3)

In 1984, D.H.R. Barton [4] published a simple synthesis of tropones from suitably substituted phenols via reduction of intermediate dichloromethanecyclohexadiene derivatives with tri-butyltin hydride, e.g., Scheme 1 [for the 2,5-cyclohexadienone (**4**)].

The intermediate (**4**), unable to aromatise because of the three methyl groups (i.e., *not* hydrogen) at *ortho* and *para* positions, suggested an analogous experiment with pentafluorophenol. The use of sodium trichloroacetate was the method of choice since NaOH as a nucleophile would substitute fluorine *β* to a carbonyl group in the polyfluorocyclohexadiene intermediate(s) with great ease [5]. Russian workers have studied the reaction of pentafluorophenol under conventional Reimer–Tiemann reaction conditions ($CHCl_3$ with aqueous NaOH) and isolated pentafluorophenyl orthoformate (**6**), below [6].

2. Results and discussion

The heterogeneous mixture of pentafluorophenol with excess sodium trichloroacetate in monoglyme at reflux temperature began to darken after 10 min, and after 1 h, chromatography of the chocolate coloured mixture produced two compounds, **A** and **B**. Compound **A** was examined by NMR spectroscopy: the ^1H NMR spectrum contained *no* hydrogen; there were three magnetically different fluorine atoms present in the ratio 2:1:2, characteristic of a C_6F_5 group in the ^{19}F NMR spectrum; and the non-decoupled ^{13}C spectrum showed five magnetically different atoms, four of which were multiplets due to carbon in the aromatic ring (128–143 ppm) while



Scheme 1.

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* Corresponding author.

PII S0022-1139(98)00120-1

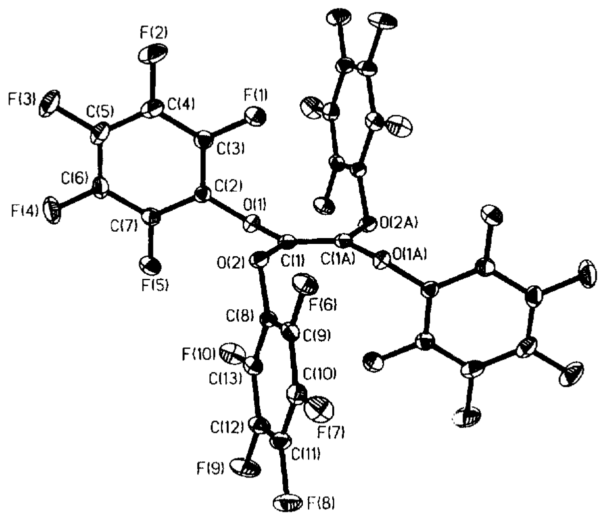
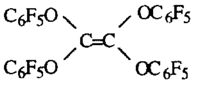


Fig. 1. The molecular structure and labelling scheme for (5). Ellipsoids are shown at 50% probability level.

the fifth was a singlet at 137.6 ppm. X-ray crystallography showed that the structure of **A** was tetra*kis*(pentafluorophenyl)ethene (**5**), Fig. 1, which explained not only the NMR data, but also the mass spectrum (parent ion M$^+$ at 756) and the elemental analysis.



$(C_6F_5O)_3CH$

(5) (6)

The second compound isolated, **B**, showed a singlet in the ^{1}H NMR spectrum; there was a C_6F_5 group in the ^{19}F NMR spectrum; and the ^{13}C showed five magnetically different atoms, four of which were multiplets due to carbon in the aromatic ring (126–142 ppm) while the fifth was a singlet at 113.8 ppm. Mass spectrometry revealed an intense peak M$^+$ at 379, characteristic of $(C_6F_5O)_2CH^+$ (M-C_6F_5OH) and a small peak at 561 $(C_6F_5O)_3C^+$ (M − 1). All the spectroscopic data were consistent with compound (**6**), and this was confirmed by repeating the Russian experiment [6] and finding identical physical data. We also examined the crude product from this reaction and found *no evidence* for the presence of any of the alkene (**5**).

The Reimer–Tiemann reaction involves the attack of a carbene, e.g., Cl_2C: at a *nucleophilic carbon* under normal circumstances in phenolic substrates [7,8], but recent work with phenol using $CHCl_3$ with KF as the base produced $(C_6H_5O)_3CH$ as 'the major product' accompanied by $C_6H_5OCF_2H$ (16%) [9]. The formation of the products (**5**) and (**6**) in the present work can be rationalised by invoking an initial insertion reaction between the dichlorocarbene and the O–H bond in the phenol to form (**7**); thereafter, other carbenes (**8**) and (**9**) may be involved, as well as possible 'solvolysis' reactions, as shown in Scheme 2.[1]

To our knowledge there is no precedent in the literature for the formation of an *alkene* product of type (**5**) in the Reimer–Tiemann reaction [7,8]. Consequently, the present work adds yet another type of 'abnormal' product to the others which may be formed in this well-known reaction.

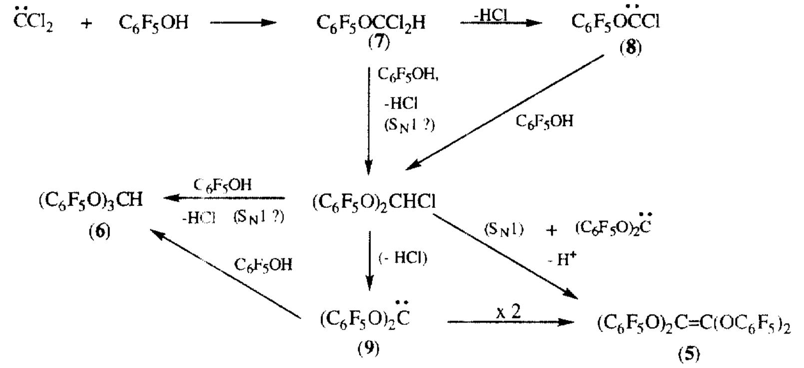
Nevertheless, the intended formation of a 4-dichloromethylpentafluoro-cyclohexa-2,5-dienone derivative had failed, presumably because of the reduced nucleophilicity of the *para* (and *ortho*) carbon in the fluorinated ring towards the incoming carbene. We are currently exploring other possible routes to related polyfluorinated precursors amenable to Barton's ring expansion reaction, based on the known 2,3,4,5,6-pentafluoro-4-allyl-2,5-cyclohexadieneone [10].

3. Experimental

NMR spectra were obtained with a Varian VXR 400 S [^{1}H(399.952 MHz), ^{19}F(376.289 MHz) and ^{13}C(100.577 MHz)] and a Varian Gemini 200 [^{13}C(50.289 MHz)]. Mass spectroscopy data were obtained with a VG 7070 E instrument. Molecular ions M$^+$ are quoted for electron ionisation unless chemical ionisation (CI) is stated.

3.1. Reaction of pentafluorophenol with sodium trichloroacetate

Pentafluorophenol (3.07 g), sodium trichloroacetate (7.41 g) and anhydrous monoglyme (20 ml) were heated together



Scheme 2.

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[1] We thank a referee for helpful comments.

under reflux for 1 h, and the chocolate brown mixture washed through a short column of silica with chloroform to remove insoluble material. Evaporation of the solvent in vacuo at 40° and careful chromatography of the residue (2.54 g) on silica using light petroleum [bp 40–60°] gave two fractions both containing compound (**5**) (faster moving component) and compound (**6**); the ^{19}F NMR spectra of these fractions enabled the yields of these products to be determined as (**5**) (0.467 g, 15%) and (**6**) (0.393 g, 13%). Fractional recrystallisation of these mixtures enabled pure samples of both compounds to be obtained: tetra*kis*(pentafluorophenyl)-ethene (nc) (**5**) mp 143.0–144.0°C [from light petroleum (bp 60–80°)]. (Analysis: Found: 41.62; H, 0.00%; M^+ 756. $C_{26}F_{20}O_4$ requires: C, 41.07; H, 0.00%; M, 756). ^{19}F NMR ($CDCl_3$) δ: -156.2 (d, 2-F, 6-F); -158.0 (t, 4-F); -161.0 (t, 3-F, 5-F) ppm; $J_{2\text{-F},3\text{-F}} = 20.3$; $J_{3\text{-F},4\text{-F}} = 21.8$ Hz. ^{13}C NMR ($CDCl_3$) δ: 141.0 (dd, 2-C, 6-C); 139.2 (dt, 4-C); 138.0 (dt, 3-C, 5-C); 128.6 (broad, 1-C); 137.6 (s, alkenic C) ppm; all $J_{C\text{–}F} = 254$ Hz.; and pentafluorophenyl orthoformate (**6**) mp 82–82.5° ([6], 82.7–83.3°). (Analysis: Found: 40.69; H, 0.15%; M^+ 562. $C_{19}H_1F_{15}O_3$ requires: C, 40.59; H, 0.18%; M, 562). ^{19}F NMR ($CDCl_3$) δ: -153.4 (d, 2-F, 6-F); -157.4 (t, 4-F); -161.3 (t, 3-F, 5-F) ppm; $J_{2\text{-F},3\text{-F}} = 19.6$; $J_{3\text{-F},4\text{-F}} = 21.4$ Hz. ^{1}H NMR ($CDCl_3$) δ: 6.63 (s, C–H). ^{13}C NMR ($CDCl_3$) δ: 141.9 (dd, 2-C, 6-C); 139.5 (dt, 4-C); 138.0 (dt, 3-C, 5-C); 126.8 (t, 1-C); 113.8 (s, alkyl C) ppm; all $J_{C\text{–}F} = 250$ Hz. The infrared was identical with authentic compound prepared below [6].

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **5**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U(eq)
F(1)	12 049(1)	−5467(1)	1990(1)	28(1)
F(2)	14 268(1)	−4455(1)	3170(1)	36(1)
F(3)	16 144(1)	−2899(1)	2321(1)	39(1)
F(4)	15 852(1)	−2442(1)	281(1)	37(1)
F(5)	13 674(1)	−3487(1)	−889(1)	27(1)
F(6)	8539(1)	−1528(1)	1133(1)	24(1)
F(7)	6999(1)	485(1)	8(1)	[illegible]
F(8)	7304(1)	913(1)	−1966(1)	[illegible]
F(9)	9198(1)	−641(1)	−2808(1)	32(1)
F(10)	10 778(1)	−2609(1)	−1675(1)	27(1)
O(1)	11 757(1)	−5060(1)	−100(1)	17(1)
O(2)	10 475(1)	−3086(1)	354(1)	17(1)
C(1)	10 519(2)	−4549(2)	52(1)	15(1)
C(2)	12 824(2)	−4489(2)	534(1)	17(1)
C(3)	12 988(2)	−4726(2)	1572(1)	20(1)
C(4)	14 106(2)	−4200(2)	2173(1)	24(1)
C(5)	15 068(2)	−3418(2)	1741(1)	25(1)
C(6)	14 919(2)	−3178(2)	710(1)	23(1)
C(7)	13 801(2)	−3713(2)	109(1)	20(1)
C(8)	9656(2)	−2136(2)	−263(1)	15(1)
C(9)	8696(2)	−1333(2)	163(1)	18(1)
C(10)	7909(2)	−300(2)	−411(1)	20(1)
C(11)	8076(2)	−70(2)	−1411(1)	[illegible]
C(12)	9034(2)	−862(2)	−1842(1)	20(1)
C(13)	9828(2)	−1875(2)	−1263(1)	18(1)

3.2. Reaction of pentafluorophenol with chloroform/sodium hydroxide

This reaction [6] was repeated using tetrahydrofuran as the co-solvent and the crude product was separated by chromatography as before to give pentafluorophenyl orthoformate (**6**) (54%) mp 82–83°. Thin layer chromatographic analysis of earlier fractions failed to detect any of the alkenic compound (**5**).

3.3. Crystal data for (5)

$C_{26}F_{20}O_4$, M = 726.26, monoclinic, space group $P2_1/c$, $Z = 4$, at 120 K. $a = 10.112(3)$, $b = 8.999(2)$, $c = 13.344(3)$ Å, $\beta = 97.38(3)°$, $V = 1204.2(4)$ Å^3, $D_{calc} = 2.086$ g/cm^3, μ(Mo Kα) = 0.242 mm^{-1}, $F(000) = 736$. Data were collected from a transparent prism of size 0.2 × 0.2 × 0.3 mm on a Rigaku AFC6S diffractometer (λ Mo Kα, graphite mono-

Table 2
Bond lengths [Å] and angles [°] for **5**

F(1)–C(3)	1.339(2)	C(1)–C(1)*	1.320(3)
F(2)–C(4)	1.339(2)	C(2)–C(7)	1.388(2)
F(3)–C(5)	1.336(2)	C(2)–C(3)	1.390(2)
F(4)–C(6)	1.340(2)	C(3)–C(4)	1.383(2)
F(5)–C(7)	1.338(2)	C(4)–C(5)	1.385(3)
F(6)–C(9)	1.335(2)	C(5)–C(6)	1.382(3)
F(7)–C(10)	1.338(2)	C(6)–C(7)	1.386(2)
F(8)–C(11)	1.339(2)	C(8)–C(9)	1.389(2)
F(9)–C(12)	1.335(2)	C(8)–C(13)	1.388(2)
F(10)–C(13)	1.341(2)	C(9)–C(10)	1.389(2)
O(1)–C(1)	1.373(2)	C(10)–C(11)	1.382(2)
O(1)–C(2)	1.382(2)	C(11)–C(12)	1.386(2)
O(2)–C(1)	1.379(2)	C(12)–C(13)	1.383(2)
O(2)–C(8)	1.385(2)		
C(1)–O(1)–C(2)	116.11(12)	F(5)–C(7)–C(2)	120.10(14)
C(1)–O(2)–C(8)	117.05(11)	C(6)–C(7)–C(2)	120.6(2)
C(1)*–C(1)–O(1)	120.4(2)	O(2)–C(8)–C(9)	118.31(13)
C(1)*–C(1)–O(2)	124.2(2)	O(2)–C(8)–C(13)	122.40(14)
O(1)–C(1)–O(2)	115.27(13)	C(9)–C(8)–C(13)	119.10(14)
O(1)–C(2)–C(7)	118.49(14)	F(6)–C(9)–C(8)	120.33(14)
O(1)–C(2)–C(3)	122.46(14)	F(6)–C(9)–C(10)	119.41(14)
C(7)–C(2)–C(3)	118.97(14)	C(8)–C(9)–C(10)	120.25(14)
F(1)–C(3)–C(4)	120.0(2)	F(7)–C(10)–C(11)	120.1(2)
F(1)–C(3)–C(2)	119.41(14)	F(7)–C(10)–C(9)	119.9(2)
C(4)–C(3)–C(2)	120.6(2)	C(11)–C(10)–C(9)	120.0(2)
F(2)–C(4)–C(3)	120.3(2)	F(8)–C(11)–C(10)	119.9(2)
F(2)–C(4)–C(5)	119.9(2)	F(8)–C(11)–C(12)	120.0(2)
C(3)–C(4)–C(5)	119.9(2)	C(10)–C(11)–C(12)	120.2(2)
F(3)–C(5)–C(6)	119.9(2)	F(9)–C(12)–C(13)	120.2(2)
F(3)–C(5)–C(4)	120.0(2)	F(9)–C(12)–C(11)	120.2(2)
C(6)–C(5)–C(4)	120.1(2)	C(13)–C(12)–C(11)	119.6(2)
F(4)–C(6)–C(5)	120.7(2)	F(10)–C(13)–C(12)	119.33(14)
F(4)–C(6)–C(7)	119.4(2)	F(10)–C(13)–C(8)	119.78(14)
C(5)–C(6)–C(7)	119.9(2)	C(12)–C(13)–C(8)	120.9(2)
F(5)–C(7)–C(6)	119.3(2)		

Symmetry transformations used to generate equivalent atoms: * $-x+2, -y-1, -z$.

Table 3
Anisotropic displacement parameters ($Å^2 \times 10^4$), for 5. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F(1)	27(1)	36(1)	21(1)	7(1)	4(1)	−4(1)
F(2)	44(1)	41(1)	19(1)	−2(1)	−9(1)	2(1)
F(3)	29(1)	30(1)	50(1)	−5(1)	−18(1)	−5(1)
F(4)	25(1)	32(1)	55(1)	7(1)	7(1)	−11(1)
F(5)	29(1)	30(1)	23(1)	7(1)	7(1)	−2(1)
F(6)	32(1)	25(1)	18(1)	2(1)	9(1)	1(1)
F(7)	32(1)	24(1)	39(1)	2(1)	13(1)	11(1)
F(8)	37(1)	23(1)	31(1)	8(1)	−5(1)	10(1)
F(9)	55(1)	26(1)	14(1)	4(1)	4(1)	5(1)
F(10)	35(1)	24(1)	23(1)	0(1)	12(1)	8(1)
O(1)	15(1)	19(1)	18(1)	−2(1)	0(1)	0(1)
O(2)	20(1)	12(1)	18(1)	−1(1)	−3(1)	1(1)
C(1)	18(1)	13(1)	14(1)	1(1)	−1(1)	1(1)
C(2)	16(1)	14(1)	19(1)	0(1)	−1(1)	1(1)
C(3)	20(1)	19(1)	20(1)	1(1)	2(1)	1(1)
C(4)	28(1)	22(1)	20(1)	−2(1)	−5(1)	4(1)
C(5)	21(1)	19(1)	34(1)	−4(1)	−8(1)	2(1)
C(6)	17(1)	17(1)	36(1)	2(1)	2(1)	−1(1)
C(7)	21(1)	16(1)	22(1)	2(1)	2(1)	2(1)
C(8)	18(1)	11(1)	16(1)	1(1)	−2(1)	−1(1)
C(9)	20(1)	16(1)	17(1)	1(1)	3(1)	−3(1)
C(10)	19(1)	16(1)	25(1)	−1(1)	3(1)	1(1)
C(11)	24(1)	15(1)	23(1)	3(1)	−4(1)	1(1)
C(12)	30(1)	16(1)	14(1)	1(1)	0(1)	−2(1)
C(13)	22(1)	14(1)	18(1)	−2(1)	4(1)	0(1)

chromator, $\omega/2\theta$-scan mode at 120 K. A total of 3675 reflections were collected with $0 \leq h \leq 14$, $0 \leq k \leq 12$, $-18 \leq l \leq 18$. The structure was solved by direct methods [11] and refined anisotropically by full-matrix least-squares against F^2 [12]. No absorption or extinction corrections were applied. The refinement converged to $R = 0.0355$ [for 2442 reflections with $F \geq 4\sigma(F_{obs})$], $wR = 0.115$ for all reflections, $S = 1.027$.

The molecular geometry of (**5**) and atomic labelling scheme are given in Tables 1 and 2. Anisotropic displacement parameters are listed in Table 3.

Acknowledgements

One of us (DSY) thanks the Royal Society for financial assistance.

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