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New cycloaddition reactions of perfluoro-1,3,4-oxadiazoles

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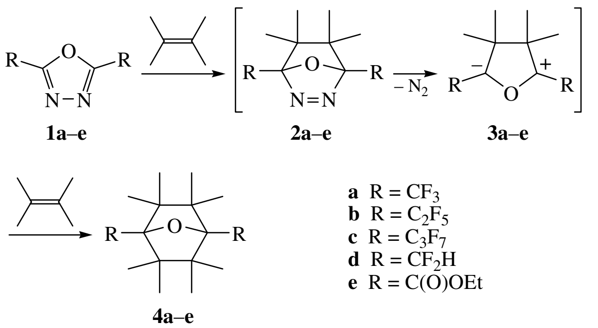
Butadiene, cycloocta-1,5-diene and cycloheptatriene were found to form cycloaddition products with 2,5-bis(perfluoroalkyl)-1,3,4-oxadiazoles: 3-oxatricyclo[2.2.1.$0^{2,6}$]heptane, 7-oxatetracyclo[6.3.0.$0^{2,6}$.$0^{5,9}$]undecane and 6-oxatetracyclo[5.3.0.$0^{2,5}$.$0^{4,8}$]dec-9-ene, respectively. The structure of the last compound was confirmed by single crystal X-ray diffraction.

The cycloaddition of 2,5-bis(trifluoromethyl)-1,3,4-oxadiazole **1a** to olefins[1] was first reported in 1987. This reaction was extended to other oxadiazoles,[2] as well as 2,5-bis(methoxycarbonyl)-1,3,4-oxadiazole.[3] The cycloaddition reaction proceeds as a two-stage process. The first stage involves [2 + 4]-cycloaddition to form unstable 2,3-diazabicyclo[2.2.1]hept-2-ene **2** (Scheme 1). The low stability of this intermediate results from extremely easy and thermally allowed retro [2 + 3]-cycloaddition resulting in the extrusion of nitrogen and formation of carbonylylide **3**. Intermediate **3** can further undergo [2 + 3]-cycloaddition with the second olefin molecule resulting in the stereoselective formation of 7-oxabicyclo[2.2.1]heptane **4**[4,5] (Scheme 1).



a R = CF_3
b R = C_2F_5
c R = C_3F_7
d R = CF_2H
e R = C(O)OEt

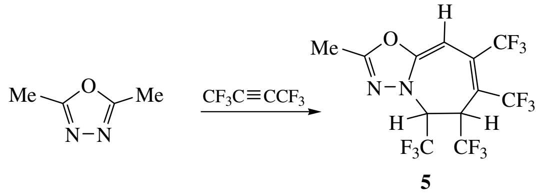
Scheme 1

In general, this reaction can be characterised as a concerted process controlled by the LUMO of oxadiazole. This conclusion is consistent with the relatively low values of calculated energies of LUMO and HOMO of fluorinated oxadiazoles and also low experimental values of ionization potentials of oxadiazoles.[6]

Interestingly, similar reactions for donor-type oxadiazoles are unknown.[7] For example, electron-rich 2,5-dimethyl-1,3,4-oxadiazole does not react with the majority of electron-deficient dienophiles, and the reaction of perfluorobut-2-yne leads to adduct **5**[8] (Scheme 2).

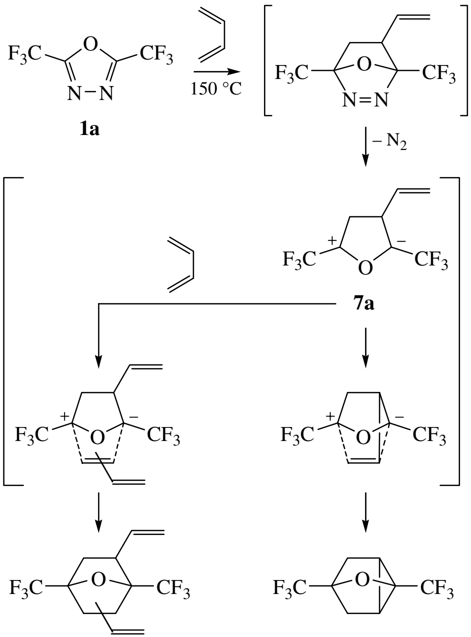
We studied the cycloaddition of fluorinated oxadiazoles: the reactions of oxadiazoles **1a**,**c** with dienes such as butadiene and cycloocta-1,5-diene, as well as with cycloheptatriene, were investigated.

The reaction of norbornadiene and **1a** results in the formation of an adduct of double cycloaddition.[4] Note that the reaction



Scheme 2

of oxadiazole **1a** with butadiene under similar conditions (120→150 °C) proceeds with the formation of product **6** (three major isomers) and volative oxatricycloheptane **7**, as confirmed by NMR spectra.† Compounds **6** and **7** result from the cycloaddition of carbonylylide intermediate **7a** (Scheme 3). It is believed that oxabicycloheptane **6** formed by the interaction



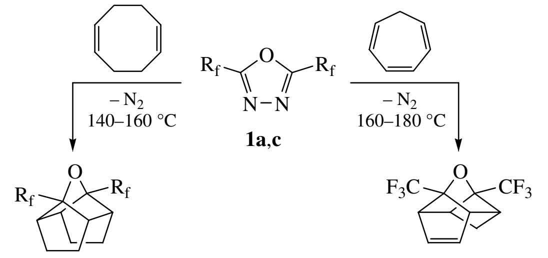
Scheme 3

of **7a** with the second butadiene molecule, but the formation of oxatricycloheptane **7** is the result of intramolecular cyclization of carbonylylide **7a** (Scheme 3).

Surprisingly, oxadiazoles **1a** and **1c** react with cycloocta-1,5-diene at 150–160 °C with the selective formation of products **8** and **9** isolated in 58 and 61% yields, respectively (Scheme 4). Note that the formation of 1:2 adducts was not observed in these reactions.

The reaction of oxadiazole **1a** with cycloheptatriene proceeds at higher temperatures (≥ 170 °C) with the selective formation of tetracyclodecene **10** (isolated yield 62%, Scheme 4); however, oxadiazole **1c** is unreactive towards cycloheptatriene even at a higher temperature.

Product **10** isolated by the distillation of a crude reaction mixture contained impurities (~20%) of four unidentified compounds, isomeric to **10** (GC/MS). Pure product **10** was isolated after multiple vacuum fractionations, and its structure was confirmed by NMR spectroscopy and single crystal X-ray diffraction (Figure 1).



1a,**c**

8 R$_f$ = CF$_3$ (58%)
9 R$_f$ = C$_3$F$_7$ (61%)

10 (62%)

Scheme 4

The molecule of **10** in a crystal has approximate C_s symmetry with the torsion angles O(6)C(7)C(11)F(1) and O(6)C(5)C(12)F(4) equal to 178.9 and 178.8°, respectively.[‡] The geometry of a tetracyclic skeleton in **10** is close to that of tetracyclo[5.3.0.0^{2,5}.0^{4,8}]dec-9-en-3-yl 3,5-dinitrobenzoate.[9] The five-membered rings C(4)C(5)O(6)C(7)C(8), C(2)C(1)C(7)O(6)C(5) and C(1)C(5)–C(8)C(9)C(10) are characterised by the envelope conformation with the deviation of the O(6) and C(7) atoms by ~0.7 Å. The bent angle for the four-membered ring C(2)C(3)C(4)C(5) is equal to 36.9°.

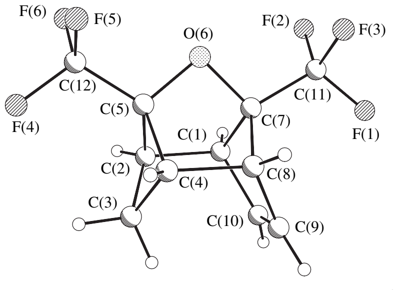
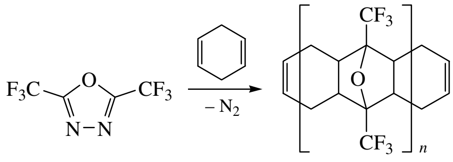


Figure 1 The general view of **10**. Selected bond lengths (Å): C(1)–C(10) 1.508(2), C(1)–C(7) 1.548(2), C(1)–C(2) 1.582(2), C(2)–C(3) 1.539(2), C(2)–C(5) 1.560(2), C(3)–C(4) 1.539(2), C(4)–C(5) 1.556(2), C(4)–C(8) 1.582(2), C(5)–O(6) 1.408(2), O(6)–C(7) 1.414(2), C(7)–C(8) 1.548(2), C(8)–C(9) 1.506(2), C(9)–C(10) 1.327(3).

The formation of cycloaddition products in the reactions of fluorinated oxadiazoles with cycloocta-1,5-diene and cycloheptatriene could be a result of a favourable transition state. However, it was found that cyclohexa-1,4-diene reacts with oxadiazole **1a** with the formation of compounds **11a**,**b** only at ≥ 200 °C. The absence of products similar to **8**–**10** in the last reaction is unclear since the transition state for the reaction of hexa-1,4-diene with **1a** does not look more strained compared to the transition state in the reactions of cycloocta-1,5-diene and cycloheptatriene.



1a

11a,**b**

Scheme 5

[†] ^{1}H NMR spectra were recorded in CDCl$_3$ on a Bruker AC-300 spectrometer at 300.1 MHz, ^{19}F NMR spectra (CDCl$_3$) were measured on a Bruker WP-200 SY spectrometer at 188.31 MHz. ^{1}H ^{19}F NMR spectra were recorded in CDCl$_3$ on a Bruker DRX-500 spectrometer at 500.1 and 470.6 MHz for ^{1}H or ^{19}F, respectively; TMS or CFCl$_3$ was an internal standard for ^{1}H or ^{19}F, respectively. IR spectra were recorded on a Hitachi 127-30 instrument in a liquid film (KBr). The mass spectra were obtained on a GC–MS instrument based on an HP 5890 II Series gas chromatograph equipped with an HP 5972A MSD mass-selective detector. Commercial reagents and solvents used in the study were prepared according to known recommendations.[10]

Typical procedure. A mixture of oxadiazoles **1a** or **1c** (19.4 mmol) and a corresponding diene (19.4 mmol) was heated in a sealed Pyrex tube and then fractionated in a vacuum.

In the IR spectra of all new compounds, a band at 2950–2980 cm^{-1} was present; the spectra of compounds **6** and **10** exhibited a low-intensity band at ~1620 cm^{-1}.

Compound **6** (mixture of three isomers): bp 82–84 °C (18 Torr). ^{1}H NMR δ: 1.7–2.5 (m, 4H, CH$_2$), 2.8 and 3.3 (m, 2H, CH), 5.1, 5.4 and 5.6 (m, 2H, =CH). ^{19}F NMR, δ: –78.0 (s), –76.5 (s), –76.1 (s), –72.8 (s), –70.7 (s).

2,4-Bis(trifluoromethyl)-3-oxatricyclo[2.2.1.0^{2,6}]heptane **7**: bp 43 °C (18 Torr), n_D^{20} 1.3565. ^{1}H NMR, δ: 1.7 (d, 2H, 2CH$_2$, J_{AB} 23.5 Hz), 1.8 (d, 2H, 2CH$_2$, J_{AB} 23.5 Hz), 2.15 (s, 2H, 2CH). ^{19}F NMR, δ: –69.6 (s, 3F, CF$_3$), –74.6 (s, 3F, CF$_3$).

6,8-Bis(trifluoromethyl)-7-oxatetracyclo[6.3.0.0^{2,6}.0^{5,9}]undecane **8**: bp 101 °C (17 Torr), mp 83–85 °C. ^{1}H NMR, δ: 1.85 (br. s, 8H, 4CH$_2$), 2.53 (br. s, 4H, 4CH). ^{19}F NMR, δ: –75.1 (s, CF$_3$).

*6,8-Bis(*n*-heptafluoropropyl)-7-oxatetracyclo[6.3.0.0^{2,6}.0^{5,9}]undecane* **9**: bp 78 °C (2 Torr), mp 45 °C. ^{1}H NMR, δ: 1.85 (br. s, 8H, 4CH$_2$), 2.65 (br. s, 4H, 4CH). ^{19}F NMR, δ: –81.0 (br. s, 6F, 2CF$_3$), –117.3 (br. s, 4F, 2CF$_2$), –125.6 (br. s, 4F, 2CF$_2$).

5,7-Bis(trifluoromethyl)-6-oxatetracyclo[5.3.0.0^{2,5}.0^{4,8}]dec-9-ene **10**: bp 77 °C (10 Torr), mp 45–47 °C. ^{1}H NMR, δ: 1.35 (d, 1H, CH$_2$, J 12.1 Hz), 2.15 (dt, 1H, CH$_2$, J 12.1 and 7.3 Hz), 2.66 (dd, 2H, 2CH, J 7.3 and 6.8 Hz), 2.98 (br. d, 2H, 2CH, J 6.8 Hz), 6.08 (br. s, 2H, CH=CH). ^{19}F NMR, δ: –75.4 (s, 3F, CF$_3$), –74.2 (s, 3F, CF$_3$). ^{13}C NMR, δ: 130.5 (s, =C), 130.5 (s, =C), 123.1 (q, CF$_3$, J 1077.5 Hz), 122.8 (q, CF$_3$, J 1100.5 Hz), 102.3 (q, CCF$_3$, J 120.0 Hz), 91.9 (q, CCF$_3$, J 120.0 Hz), 49.4 (s, CH), 41.1 (s, CH), 21.1 (s, CH$_2$).

For **11a**,**b**: two fractions were obtained after the removal of volatiles from the reaction mixture at 10 Torr. Product **11a** was sublimed at 2 Torr and 110→130 °C, mp 192–213 °C and contained ~60% compound **11a** with $n = 1$. ^{1}H NMR, δ: 1.5–2.5 (m), 1.7–1.85 (m), 2.0–2.3 (m), 2.55 (s), 2.75 (m), 2.95 (m), 5.95 (s), 6.0 (br. s).

Product **11b**, sublimed, mp 280–310 °C, contained compounds $n \geq 2$, 3. ^{1}H NMR, δ: 1.5–1.7 (m), 2.0–2.3 (m), 2.8–3.0 (m), 5.95 (s), 6.0–6.85 (m).

[‡] *Crystallographic data*. Crystals of **10** (C$_{11}$H$_8$F$_6$O, $M = 270.17$) are monoclinic, space group $P2_1/n$, at 120 K: $a = 9.0803(8)$, $b = 11.156(1)$ and $c = 10.2771(9)$ Å, $\beta = 98.201(5)°$, $V = 1030.4(2)$ Å^3, $Z = 4$ ($Z' = 1$), $d_{calc} = 1.742$ g cm^{-3}, μ(MoKα) = 1.84 cm^{-1}, $F(000) = 544$. Intensities of 7281 reflections were measured with a Smart 1000 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans with a 0.3° step in ω, $2\theta < 59°$] and 2859 independent reflections ($R_{int} = 0.0193$) were used in a further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Hydrogen atoms were located from the Fourier synthesis of electron density and refined in the isotropic approximation. The refinement converged to $wR_2 = 0.1106$ and GOF = 1.057 for all independent reflections [$R_1 = 0.0465$ was calculated against F for 2309 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 611932. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2006.

Table 1 Cycloaddition conditions and yields of compounds **6–10**.

Compound	*T*/°C	*t*/h	Yield[a] (%)
6, **7**	150	20	25 (**6**), 24 (**7**)
8	140–150	25	58
9	160	80	61
10	160–180	80	62

[a] The ratio of addends was 1:1; the yields were calculated based on the amount of diene.

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