Diels–Alder reactions of 1,1,4,4-tetrafluorobutatriene†

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At low temperature 1,1,4,4-tetrafluorobutatriene undergoes Diels–Alder reaction with various dienes; the structure of one product and its isomerisation derivative has been elucidated by X-ray crystallography.

Honoured in 1950 with the Nobel prize, the Diels–Alder reaction is still one of the most remarkable organic reactions.[1] We studied the scope of tetrafluorobutatriene in this type of reaction by subjecting it to various dienes and enes. Although tetrafluorobutatriene (**1**) was synthesized and characterized by IR- and ^{19}F-NMR spectroscopy by Martin and Sharkey as early as 1959, its chemistry remained almost unexplored due to the compound's extreme instability: it polymerizes even at −85 °C and is said to explode violently on warming to −5 °C or on contact with air.[2]

This limited the known chemistry of **1** to a few derivatives also reported by Martin and Sharkey using addition of bromine and chlorine, and oxidation. Later, Raman- and PE-spectroscopic data were added[3] and its structure and experimental charge density were elucidated by high-resolution X-ray diffraction.[4]

Compound **1** decomposes even in anhydrous solvents under vacuum or inert atmosphere within a few hours forming numerous unstable decomposition products which could not be characterized thus far. Nevertheless it was possible to synthesize two of its transition metal complexes, $[M(\eta^2\text{-}C_4F_4)(CO)(PPh_3)_2Cl]$ (M = Ir, Rh).[5]

After the development of a more efficient synthesis of 1,1,4,4-tetrafluorobutatriene (**1**) we were able to further examine its chemistry.

Once prepared, it can only be transferred by condensation at reduced pressure and must be stored at −196 °C. This method has so far prevented explosions and polymerization.

Herein we report on the Diels–Alder reaction of **1** with various dienes **2a–k** of different reactivity as outlined in Scheme 1. Due to the instability of the triene all reactions have to be performed at or below ambient temperature. Depending on the reactivity and solubility of **2a–k** the yields of **3a–k** range from quantitative to almost zero.‡

No product could be detected with 9,10-dimethylanthracene, α-terpinene, fullerene-C_{60}, various thiophene derivatives, 1,1-difluorobut-1-en-3-yne, hexachlorocyclopentadiene, pyrene, methyl methacrylate, acrylonitrile, octafluoro-1,2-dimethylene-cyclobutane, tetraphenylcyclopentadienone, 2,5-dimethyl-1,3,4-thiadiazole, trimethylsilylazide, *N*-methylpyrrole, 1-methoxynaphthalene, tetraphenylfurane and pentaphenyl-cyclopentadiene, respectively. Most likely this is a result of either insufficient solubility of the diene, steric hindrance (*e.g.* pentaphenylcyclopentadiene for both reasons) or insufficient reactivity. Interestingly, fluorine NMR indicates in some cases (*e.g.* thiophene derivatives) an increased decomposition rate of the triene.

Tetrafluorobutatriene reacts solely as an ene component in the Diels–Alder reaction. The perfect linear shape of the three cumulated double bonds is most likely the reason for that since for the diene the s-*cis* configuration is required for sufficient reactivity.[6] Employing the inverse electron demand hexachloro-cyclopentadiene or octafluoro-1,2-dimethylene-cyclobutane did not lead to reaction at the terminal double bonds. Since the reaction with electron rich dienes is restricted to the central double bond well defined products result. Almost quantitative reactions were observed with **2a–f** and single crystals of the reaction product **3a** with 1,3-diphenylisobenzofurane could be obtained. However, **3a** also isomerized during the crystallization forming a few crystals of the naphthalene derivative **4**. Similar rearrangement reactions have been observed previously.[7]

The structures of **3a** and **4** were determined by X-ray crystallography. As depicted in Fig. 1 the asymmetric unit of **3a** consists of two molecules which are connected by H–F contacts. The crystal packing of the molecules is dominated by numerous H–F interactions[8] rather than by fluorine segregation.[9] The two phenyl substituents are twisted against each other by 70.5° and 82.1° probably due to intra-molecular H–F contacts shown in red. The conjugated cisoid double bonds are non-planar (C1–C2–C11–C12 −27.6°/−31.5°) to minimize the repulsion of the fluorine atoms F2 and F4.

Several short H–F contacts can be found in the rearranged naphthalene derivative **4** depicted in Fig. 2 but again no fluorine segregation can be observed.

We tried to enforce the isomerisation of **3a** to **4** by heating in toluene to 160 °C, bubbling air through a hexane solution of **3a**, addition of either potassium hydroxide or sodium fluoride to a THF/water solution of **3a**. The Diels–Alder product remains stable under all these conditions and not even a trace of **4** could be detected (Scheme 2).

All compounds presented exhibit a characteristic AA′BB′-type ^{19}F-NMR spectrum. We were able to perform the synthesis of **3a–c** in such a manner that no purification of the product was necessary and all NMR-spectroscopic data could be taken. In all other cases we could not isolate the product from the excess diene since starting material and

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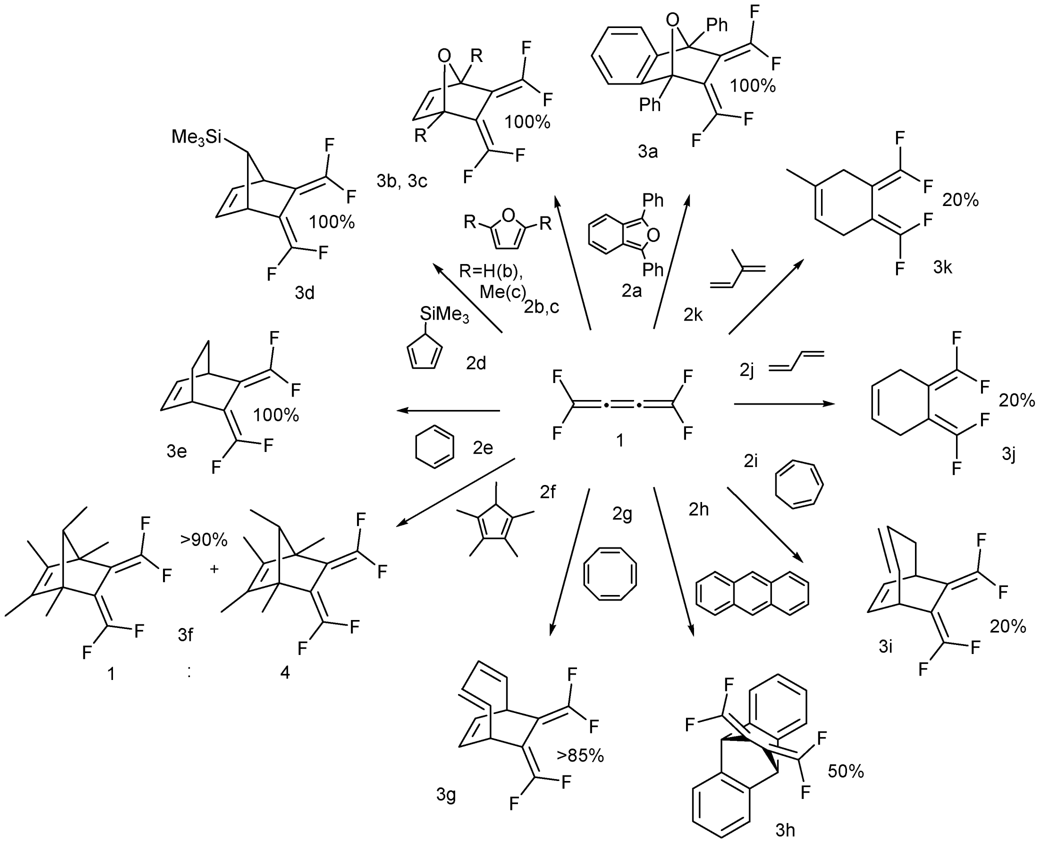
† Electronic supplementary information (ESI) available: NMR data for compounds **3b–k** and crystallographic data of **3a** and **4**. CCDC 752618 and 752619. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b922424f



Scheme 1 Diels–Alder reactions of tetrafluorobutatriene, conversion determined by ^{19}F-NMR-spectroscopy, reaction time 1 minute (furane) up to 14 days (anthracene), solvent: CH_2Cl_2 (anthracene and diphenylisobenzofurane), all others in substance.

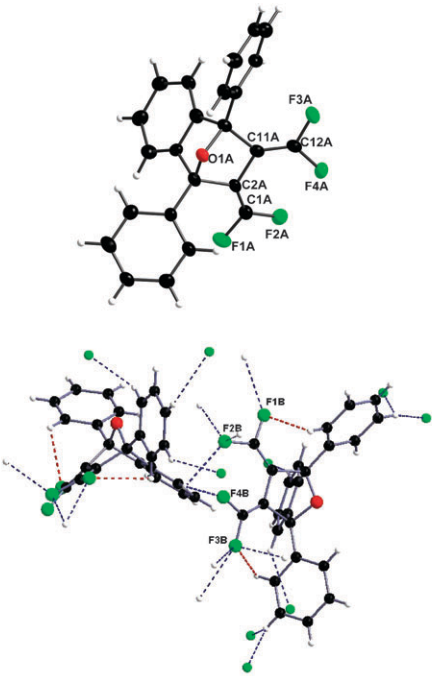


Fig. 1 Molecular structure (DIAMOND[12]) of **3a** (top). Inter- and intra-molecular H–F contacts between the molecules are symbolized by blue and red dashed lines, respectively (bottom). Fluorine atoms of neighbouring molecules are drawn as smaller balls.

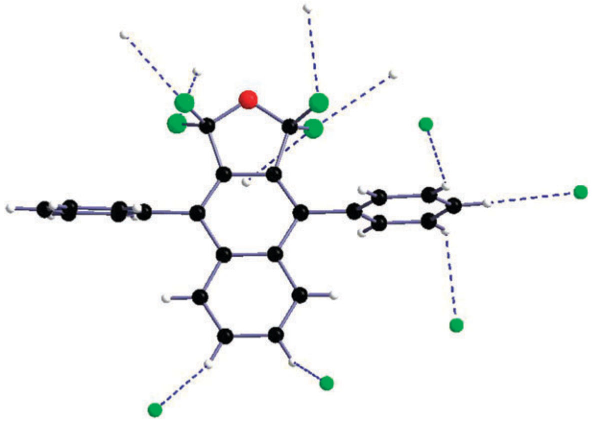
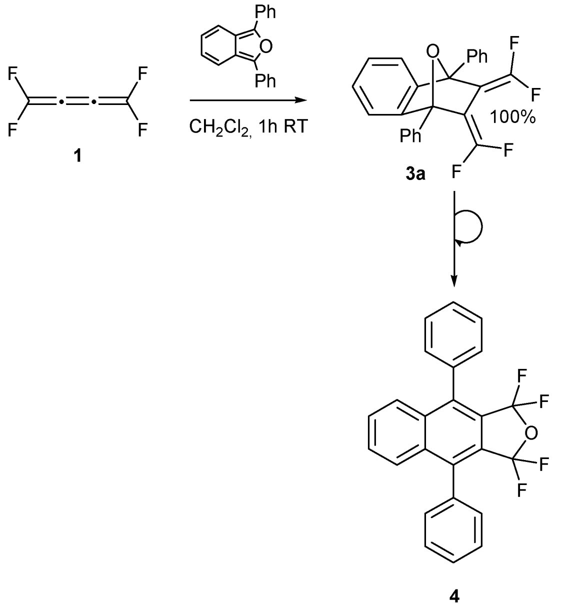


Fig. 2 Molecular structure (DIAMOND[12]) of **4**.

product co-elute and have a comparable volatility. We analysed the AA′BB′-type ^{19}F-NMR spectrum for compound **3a** with the gNMR program.[10] The geminal fluorine–fluorine coupling and 2 of the 3 ^{5}J-couplings exhibit normal values with 38.1 Hz, 16.3 Hz and 8.9 Hz, respectively. In contrast, the coupling constant of the two fluorine atoms standing face-to-face together shows a large ^{5}J through space coupling, resulting in a coupling constant of 62.9 Hz.

The enormous reactivity of 1,1,4,4-tetrafluorobutatriene is best displayed by a comparison to its tetrabromo-derivative.



Scheme 2 Rearrangement of the Diels–Alder product **3a**.

While the Diels–Alder reaction with furane in the latter case needs 48 h for completion, in the former case the reaction is complete after 1 minute at room temperature.[11]

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Notes and references

‡ *Preparation of* **3a–k**: all manipulations of air and moisture-sensitive substance were carried out in an atmosphere of dry argon or under vacuum. All glassware were carefully dried prior to use. Solvents were dried with the appropriate drying agents and distilled onto molecular sieves before use. **1** was prepared as described earlier[4] and purified by fractional condensation. The amount of **1** was determined by pVT techniques. With the exception of the anthracene and 1,3-diphenylisobenzofurane all reactions were carried out in 4 mm-Duran-glass tubes. Tetrafluorobutatriene (0.1 mmol) was condensed onto the liquid nitrogen cooled diene (0.2 mL) and the tube was flame sealed and rapidly warmed to room temperature. The reaction was monitored by ^{19}F-NMR spectroscopy until all of the triene was consumed. In case of anthracene (0.25 mmol) high dilution conditions (100 ml) (dichloromethane or pentane) were used while in case of 1,3-diphenylisobenzofurane 10 ml dichloromethane was used as solvent. In both cases the same amount of tetrafluorobutatriene was added. The reaction with 1,3-diphenylisobenzofurane is finished in 2 h when the yellow solution turns colourless. *Spectroscopic data for* **3a**: δ_F (C_6D_6, $CFCl_3$ ref.): −78.5 (4F, 62.9, 38.1, 16.3, 8.9 Hz); δ_H (C_6D_6): 7.80 (4H, m), 7.38 (1H, d, 5.5), 7.37 (1H, d, 5.5), 7.21 (6H, m), 7.03 (1H, d, 5.5), 7.02 (1H, d, 5.5), δ_C (C_6D_6): 151.5 (2C, m, CF2), 146.4 (2C), 133.7 (2C), 130.0 (2C), 129.1 (2C), 128.9 (2C), 128.2 (2C), 121.4 (2C), 95.5 (2C, m, C=CF$_2$), 89.7 (2C). *Spectroscopic data for* **3h**: δ_F ($CDCl_3$, $CFCl_3$ ref.): −81.4 (2F, m), −87.4 (2F, m); δ_H ($CDCl_3$): 7.36 (4H, m), 7.20 (4H, m), 5.08 (2H, m, 5.5), δ_C ($CDCl_3$): 152.5 (2C, m, CF$_2$), 141.6 (4C), 125.3 (4C), 123.9 (4C), 88.7 (2C, m, C=CF$_2$), 45.2 (2C, m, bridging Cs).

Crystal structure analysis:

a suitable crystal was selected using a microscope, mounted onto glass fiber using silicon grease, and transferred into the cold gas stream of a diffractometer. BRUKER-AXS, SMART CCD, $Mo_{K\alpha}$, λ = 0.71073 Å, T = 133 K.

Crystal data for **3a** *and* **4**:

3a: $C_{24}H_{14}F_4O$, M = 394.35, monoclinic, a = 14.810(6) Å, b = 8.927(3) Å, c = 26.933(10) Å, β = 91.120(10)°, V = 3560(2) Å^3, T = 133(2) K, space group $P2_1/n$, Z = 8, 21 334 reflections measured, 5070 independent reflections (R_{int} = 0.1449) of which 2944 have $F_o > 2\sigma(F_o)$. Empirical absorption correction (SADABS[13]), least squares refinement (SHELXL-97[14]), anisotropic temperature factors, H atoms isotropic on calculated positions. The final R_1 values were 0.0971 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.2684 (all data). The goodness of fit on F^2 was 0.987. **4**: $C_{24}H_{14}F_4O$, M = 394.35, orthorhombic, a = 14.189(5) Å, b = 7.746(3) Å, c = 16.523(5) Å, V = 1816.2(10) Å^3, T = 123(2) K, space group $Pna2_1$, Z = 4, 26 842 reflections measured, 2857 independent reflections (R_{int} = 0.0410, Friedel opposites merged) of which 2601 have $F_o > 2\sigma(F_o)$. The final R_1 values were 0.0486 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.1315 (all data). The goodness of fit on F^2 was 1.062.

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