

1,8-Diazabicyclo[5.4.0]undec-7-ene as a Difunctional Nucleophile

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DBU **1** reacts as a (1,3) difunctional nucleophile with 2-H heptafluorobut-2-ene **2**, giving the unusual product **8**; a mechanism for the formation of **8** is proposed and an X-ray crystal structure of **8** is described.

DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) **1** is widely used as a so-called 'non-nucleophilic base' in organic chemistry,¹ although we are aware of reports describing DBU acting as a nucleophile to form a nitrogen–phosphorus bond,² a nitrogen–carbon bond³ and acting as a difunctional nucleophile.⁴ We now report a further remarkable reaction in which DBU acts as a difunctional nucleophile, forming a fused pyrrole derivative **8** through concomitant formation of new nitrogen–carbon and carbon–carbon bonds.

In the process of exploring the chemistry of 2-H heptafluorobut-2-ene **2**, we studied the effect of various bases on the elimination of hydrogen fluoride, for the synthesis of hexafluorobut-2-yne. DBU was stirred with **2** (4:1 ratio), in n-hexane solution, at room temp. for two days in a sealed

system. Colourless crystals were obtained (85% yield) and, to our surprise, mass spectrometry indicated that this product resulted from elimination of two equivalents of hydrogen fluoride between DBU and **2**. After recrystallisation (n-hexane) elemental analysis confirmed this finding. Furthermore, ¹⁹F NMR indicated both –CF₃ and –CF₂H groups contained in the product.

We have now established this unusual structure **8** by a single-crystal X-ray diffraction study,[†] as shown in Fig. 1, and this fully supported our deductions. Formation of **8** probably begins with nucleophilic attack by DBU on **2**, (see Scheme 1) leading to vinylic displacement of fluoride ion followed by proton loss to give **4**. The further loss of fluoride ion obviously must occur from trifluoromethyl and it is reasonable to suggest step **4** to **5**. Indeed, we have demonstrated other examples of loss of fluorine from systems closely related to **4**. Then the cyclisation step arises from generation of the anion **6a**, no doubt facilitated by the adjacent positively charged nitrogen, doubt facilitated by the adjacent positively charged nitrogen, followed by cyclisation to **7** via nucleophilic attack of the ketimine on the difluoroallene **6b**. Proton transfer to the anion **7** provides the CF₂H group in **8**, together with the pyrrole structure, which would be extremely difficult to account for, other than by the process shown.

We also find that DBU reacts with other fluorinated alkenes but, so far, each of the additional cases that we have investigated gave a complex product mixture, except for the reaction between DBU and hexafluorobut-2-yne which also gave product **8** (64% yield). This raises the possibility, which at this stage we cannot exclude, that the formation of **8** occurs via initial formation of hexafluorobut-2-yne and further reaction. However, we did not observe any hexafluorobut-2-yne in recovered **2**, and the reaction proceeds more efficiently with **2** than hexafluorobut-2-yne. Furthermore, the general reactivity with fluorinated alkenes demonstrates that nucleophilic displacement of vinylic fluorine occurs readily.

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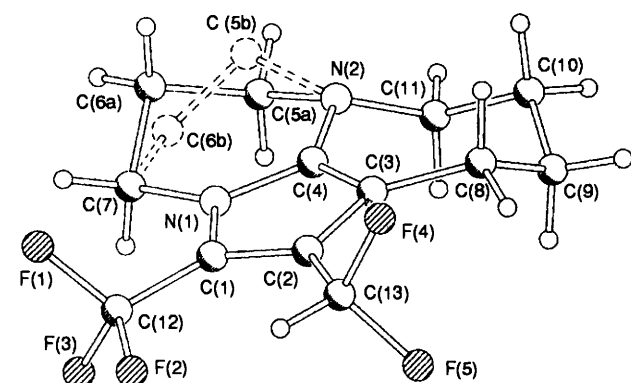
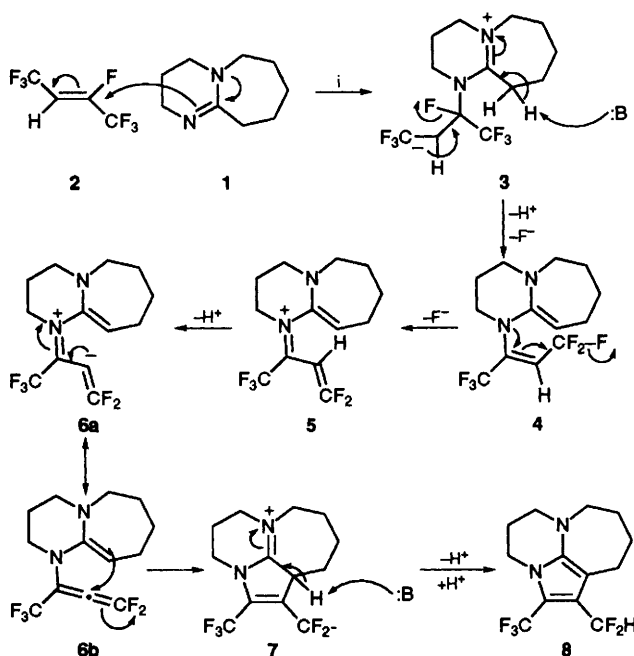


Fig. 1 Molecular structure of **8**. Five-membered ring is planar, seven-membered ring adopts a distorted chair conformation, and six-membered ring has a non-symmetrical twist conformation. The C(5) and C(6) atoms are disordered over two positions with occupancies of 75% (a) and 25% (b), dashed, H atoms omitted.



Scheme 1 Reagents and conditions: i, DBU:2 = 4:1, hexane, sealed tube, room temp., 2 days

Footnote

† Crystal data for **8**: C₁₃H₁₅F₅N₂, *M* = 294.27, monoclinic, space group *P*2₁/*c*, *a* = 8.752(2), *b* = 15.637(6), *c* = 9.559(4) Å, β = 102.15(3)°, *V* = 1278.9(8) Å³ (at 150 K, from 2θ reflections with 12.7 < θ < 15.0°), *Z* = 4, *F*(000) = 608, μ(Mo-Kα) = 1.42 cm⁻¹, *D*_c = 1.53 g cm⁻³, crystal size 0.11 × 0.38 × 0.50 mm. 1754 total (1629 independent) reflections were collected on a Rigaku AFC6S diffractometer at 150 K (graphite-monochromated Mo-Kα radiation, λ̄ = 0.71073 Å, 2θ/ω scan mode, 2θ ≤ 45°). The structure was solved by direct methods (using SHELXS-86 programs) and refined by full-matrix least squares analysis (using SHELXL-93 programs) in the anisotropic approximation (176 variables, H atoms in riding model) on *F*² of 1628 reflections with Chebyshev weighting scheme to *R*(*F*) = 0.052 and *wR*(*F*²) = 0.102 for all data, with maximum residual peak in the final Fourier difference synthesis of 0.25 e Å⁻³. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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