Synthesis of the *N*-Unsubstituted Dewar Pyrrole 1,2,3,4-Tetrakistrifluoromethyl-5-azabicyclo[2.1.0]pent-2-ene

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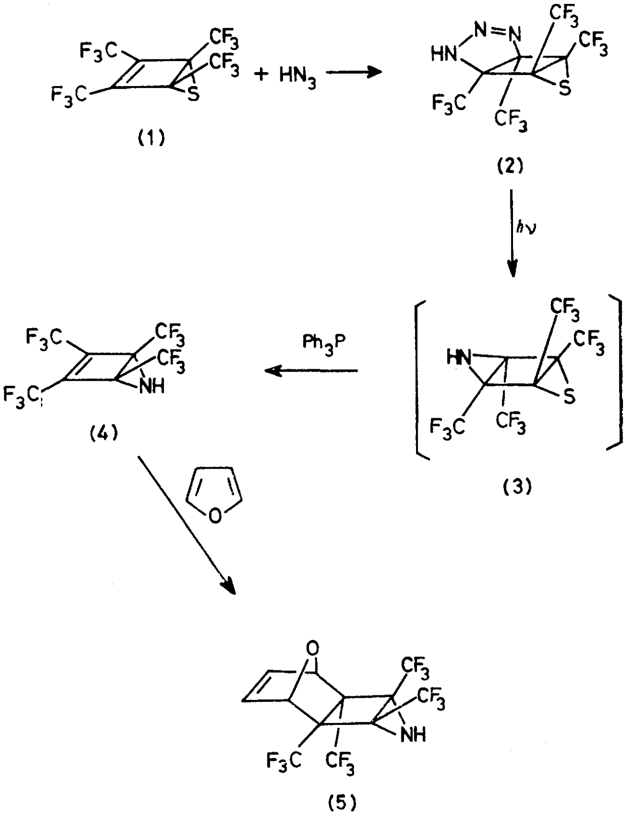
Summary The *N*-unsubstituted Dewar pyrrole, 1,2,3,4-tetrakis(trifluoromethyl)-5-azabicyclo[2.1.0]pent-2-ene, was synthesized by the reaction of 1,2,3,4-tetrakis(trifluoromethyl)-5-thiabicyclo[2.1.0]pent-2-ene with hydrogen azide followed by photochemical denitrogenation and desulphurization with triphenylphosphine.

In a previous paper, we reported the synthesis of *N*-substituted tetrakis(trifluoromethyl) Dewar pyrroles,[1] the first example of valence bond isomers of pyrrole derivatives. The question of whether or not such a ring system without a substituent on the nitrogen atom could exist aroused our interest since the N–H bond might accelerate the isomerization of such a hindered ring system through prototropy. We here report the synthesis of the *N*-unsubstituted Dewar pyrrole (**4**).

Hydrogen azide is a much less reactive 1,3-dipole than alkyl or aryl azides and its 1,3-dipolar reactions with olefins have not been reported, although reaction with highly reactive acetylenes is known to take place.[2] However, the Dewar thiophen (**1**) was found to be a sufficiently reactive dipolarophile to react with hydrogen azide, the triazoline derivative (**2**)† being obtained in chloroform in 90% yield, m.p. 140—144 °C (decomp.); i.r. (KBr) 3140 cm^{-1} (>NH); ^{1}H n.m.r. $[(CD_{32})CO]$‡ δ 3·77 (>NH); ^{19}F n.m.r. (Et_2O) $-3{\cdot}2$ and 5·6 p.p.m.§ (br. s, intensity ratio, 1 : 1); *m/e* 371 ($M^+ - N_2$). Photoreaction of (**2**) in ether caused elimination of nitrogen; the ^{19}F n.m.r. singlets, due to (**2**) disappeared and two new singlets ($-1{\cdot}0$ and 3·2 p.p.m.) ascribable to (**3**) appeared.¶ Compound (**3**) was not isolated from the reaction mixture. When the solution containing (**3**) was treated with triphenylphosphine, triphenylphosphine sulphide was precipitated; the two ^{19}F n.m.r. singlets due to (**3**) disappeared and two new singlets appeared. Work-up gave the Dewar pyrrole (**4**),¶ whose structure was determined from the following spectral data and its Diels–Alder reaction with furan. Compound (**4**), although stable at room temperature, is highly volatile and could not be isolated free from ether. Thus, spectral data for (**4**) were obtained in the presence of a small amount of ether: i.r. (CCl_4) 3300 (>NH) and 1700 cm^{-1} (C=C); ^{1}H n.m.r. (CCl_4) δ 6·16 (>NH); ^{19}F n.m.r. (CCl_4) 1·6 and 2·4 p.p.m. (intensity ratio, 1 : 1).

Reaction of (**4**) with furan gave the Diels–Alder adduct (**5**), m.p. 61—64 °C.¶ The structure of (**5**) was determined from the following spectral data, and its stereochemistry was assumed, as shown in the Scheme, by analogy with the reaction of (**1**) with furan; i.r. (CCl_4) 3370 (>NH), 1160, and 1135 cm^{-1} (C–F); ^{1}H n.m.r. (CCl_4) δ 6·62 (=CH–), 5·35 (>CH–O–), and 3·72 (>NH); ^{19}F n.m.r. (CCl_4) $-0{\cdot}6$ and 2·6 p.p.m. (intensity ratio, 1 : 1); *m/e* 387 (M^+ — HF), 339 (M^+ — furan), and 68 (furan). The i.r. spectrum of (**5**) showed no absorption near 1700 cm^{-1} which could be ascribed to a cyclobutene double bond. Thus the cyclobutene double bond of (**4**) is acting as a dienophile.[3]



Scheme

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† The stereochemistry of (**2**) was assumed by analogy with the reaction of the Dewar thiophen (**1**) with furan.

‡ Compound (**2**) was desulphurized slowly in $(CD_3)_2CO$.

§ Benzotrifluoride (0 p.p.m.) as an internal standard.

¶ The yield based on the ^{19}F n.m.r. spectrum was quantitative.

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[3] Y. Kobayashi, I. Kumadaki, A. Ohsawa, Y. Sekine, and A. Ando, *J.C.S. Perkin I*, 1977, **2355**; Y. Kobayashi, A. Onsawa, Y. Sekine, and H. Mochizuki, *Chem. and Pharm. Bull.* (*Japan*), 1975, **23**, 2773.