Perfluoroalkyl-Induced Dimerization of Allylic Azides

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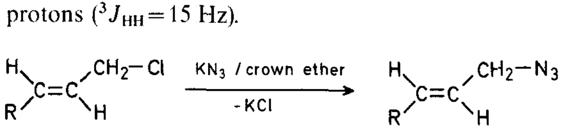
Although allyl azide and its dimer[1] have been known since 1908, it was not recognized until much later[2,3] that the dimer forms via an intermolecular cycloaddition. Since, apparently, no analogues of this cycloadduct have been described so far, we have prepared some new allylic azides by the phase transfer-catalyzed method and have investigated the tendency of these allylic azides having substituents in the 1-position to undergo a similar self-cyclization.

The chloroalkenes **1** were transformed into the azido derivatives **2** by a crown ether-catalyzed displacement reaction[4] which proceeded with retention of configuration at the C=C bond according to Scheme **A**. The *E*-configuration of starting materials as well as products is derived from the N.M.R. observation of a typical *trans* coupling between vinylic protons ($^3J_{HH} = 15$ Hz).



1 **2**

	R
a	C_2F_5
b	C_6F_{13}
c	C_6H_5
d	C_2H_5

Scheme **A**

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Table. Spectral and Physical Data of Alkenes **2** and Bis-triazolo-pyrazines **3**

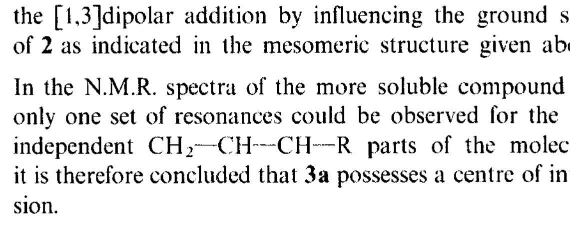
Compound	Yield [%]	b.p./torr or m.p.	Molecular formula[a]	I.R. ν_{max} [cm^{-1}]	^{1}H-N.M.R. [CCl_4, 60 MHz, TMS (int.)] δ [ppm]	^{19}F-N.M.R. [CCl_4, 56.4 MHz, CF_3COOH (ext.)] δ [ppm]
2a	71	60°/50	$C_5H_4F_5N_3$ (201.1)	2116 (N_3), 1684 (C=C)	3.93 (d, 2H); 5.85 (dt, 1H, $^3J_{HH}$ = 15.1 Hz, $^3J_{HF}$ = 10.5 Hz); 6.33 (dtt, 1H)	7.5 (s, 3F); 37.4 (d, 2F)
2b	75	73°/10	$C_9H_4F_{13}N_3$ (401.1)	2114 (N_3), 1681 (C=C)	4.02 (d, 2H); 5.96 (dt, 1H); 6.40 (dtt, 1H)	
2c	70		$C_9H_9N_3$ (159.2)	2100 (N_3), 1652 (C=C)	3.73 (d, 2H); 6.04 (dt, 1H, $^3J_{HH}$ = 15.2 Hz); 6.47 (d, 1H); 7.20 (m, 5H)	—
3a	(100)	186° (dec.)	$C_{10}H_8F_{10}N_6$ (402.2)	—	3.60 (dd, 1H, $^2J_{HH}$ = 12.0 Hz, $^3J_{HH}$ = 4.4 Hz; 4.08 (pseudoseptett, 1H); 4.56 (dd, $^3J_{HH}$ = 10.2 Hz); 5.03 (pseudoseptett, 1H, $^3J_{HF}$ = 10.5 and 18.0 Hz)[b]	5.4 (s, 3F); 40.7 (dd, 1F, $^2J_{FF}$ = 282 Hz); 46.9 (dd, 1F)[b]
3b	(100)	201° (dec.)	$C_{18}H_8F_{26}N_6$ (802.2)	—	—	—

[a] All products gave correct microanalyses (C ±0,1 %, H ±0.1 %, F ±0.3 %, N ±0.1 %); analyses were performed by our microlab.

[b] Acetone-d_6 solution.

However, reaction of 1-chloropent-3-ene (**1d**) gave a mixture (b.p. 25–40°/25 torr) consisting of **2d** (R = C_2H_5, $\nu_{C=C}$ = 1667 cm^{-1}) and of 3-azidopent-1-ene ($\nu_{C=C}$ = 1642 cm^{-1}). The ratio of the two isomers, at 25°, was determined to be 52:48 by G.L.C. (2.5 m × 4 mm column of 10 % trifluoropropyl silicone on "Embacel®"). This finding confirms an earlier study[5] in which rapid vinylogous attack accompanied by double bond shift has been observed in the reactions of methyl-substituted chloroalkenes with the azide ion.

While neither cinnamyl azide (**2c**) nor the mixture containing **2d** showed any change during a period of some months, **2a** and **b** slowly deposited colourless prism-shaped crystals of the dimers **3** (Scheme **B**). At 23°, the half life was found to be 211 days for C_2F_5 and 180 days for C_6F_{13}, respectively.



Scheme **B**

Assuming similar steric requirements for alkyl and *F*-alkyl groups, it is likely that the *F*-alkyl substituent facilitates the [1,3]dipolar addition by influencing the ground state of **2** as indicated in the mesomeric structure given above.

In the N.M.R. spectra of the more soluble compound **3a**, only one set of resonances could be observed for the two independent CH_2—CH—CH—R parts of the molecule; it is therefore concluded that **3a** possesses a centre of inversion.

Preparation of Azido Alkenes 2a–c:

To a mixture of potassium azide (40.6 g, 0.5 mol), water (1 ml), and dicyclohexano-18-crown-6 (1.0 g), the corresponding chloride **1** (0.35 mol) is added under nitrogen. The mixture is vigorously stirred at 70° for 5 h and then cooled to 20°. The solids are filtered off and washed with diethyl ether (50 ml). The combined filtrates are dried over sodium sulfate. Products **2a**, **b** are isolated by distillation in vacuo as colourless liquids. Since **2c** shows some decomposition on attempting distillation, it is purified by passing its ether solution through a column of neutral alumina (30 × 1.5 cm), followed by removal of the solvent under reduced pressure.

Caution: Although the azides **2a–c** *proved non-hazardous in our experiments, it is strongly recommended to use thick-meshed wire gauze and safety screens as protective measures.*

1,5a,6,10a-Tetrahydro-5,10-bis(*F*-alkyl)-bis-*v*-triazolo-[1,5-a:1′,5′-d]pyrazines (3a, b):

Samples of the azides **2a**, **b** (0.1 mol) are stored in stoppered flasks for 6 months in the dark. After cooling to 0° for 3 h, the crystalline dimers are separated by filtration, washed with low boiling petroleum ether (20 ml) and dried under vacuum (**3a**: 8.4 g, **3b**: 19.8 g). The unreacted azide is set aside for further use. Refluxing **2** in benzene solution accelerates the formation of **3** but leads to less pure materials.

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