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PRELIMINARY NOTE

Reactions of N-Iminopyridinium Ylide with Dipolarophiles of the Fluorocarbon Class : Synthesis of Fluorinated 3-Azaindolizines

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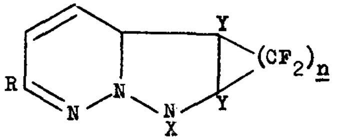
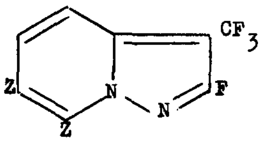
The recent claim [1] that 1:1 cycloadducts (I) can be obtained by treating 1,2-dibromodifluorocyclopropene or 1,2-dichlorotetrafluorocyclobutene with N-substituted iminopyridazinium ylides prompts us to disclose preliminary results of an investigation of reactions between N-iminopyridinium ylide and potential dipolarophiles of the fluorocarbon class [2,3].



(I) $n = 1$: R = H, Ph; X = COMe; Y = Br
$n = 2$: R = H, Ph; X = COMe, CO_2Et;
Y = Cl



(II) Z = H
(III) Z,Z =

Perfluoropropene reacts with N-iminopyridinium ylide in dichloromethane at room temperature to yield 2-fluoro-3-(trifluoromethyl)pyrazolo[1,5-a]-pyridine (II; 65%). The same 3-azaindolizine is formed when the ylide is treated with 2H-pentafluoropropene, aromatization of the possible cycloadducts (see the Scheme) formed initially in this case involving elimination of hydrogen – a not uncommon feature in this area of heterocyclic chemistry [4]. Attack of N-iminoquinolinium ylide (generated *in situ* from its dimer [4]) on perfluoropropene in hot (75 °C) DMF provides a benzo-analogue (III; 39% yield) of the 3-azaindolizine II.

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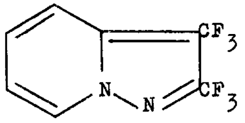
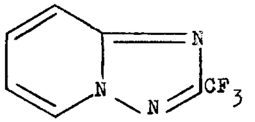
2,3-Bis(trifluoromethyl)pyrazolo[1,5-a]pyridine (IV; 77% yield) can be prepared from perfluorobut-2-ene (E,Z-mixture) and N-iminopyridinium ylide in dichloromethane at ambient temperature, or, predictably [5], from perfluorobut-2-yne and the ylide (18% yield at 20 °C). Not unexpectedly also [5], trifluoroacetonitrile partakes in a 1,3-dipolar cycloaddition with N-iminopyridinium ylide; this proceeds regiospecifically at room temperature in dichloromethane to give (40% yield) an inseparable 3:1 mixture of the triazolo[1,5-a]pyridine V and a dihydro-analogue, shown by ^{1}H n.m.r. spectroscopy to possess either structure VI or VII, with the latter preferred. The triazolopyridine (V) is best prepared by heating 1,2-diaminopyridinium iodide with trifluoroacetic anhydride (>50% yield).



(IV)



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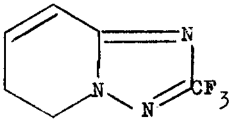

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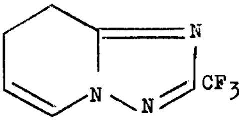

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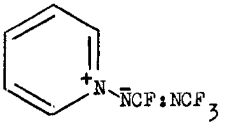

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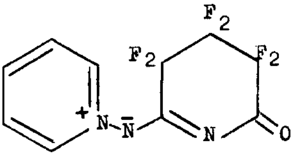
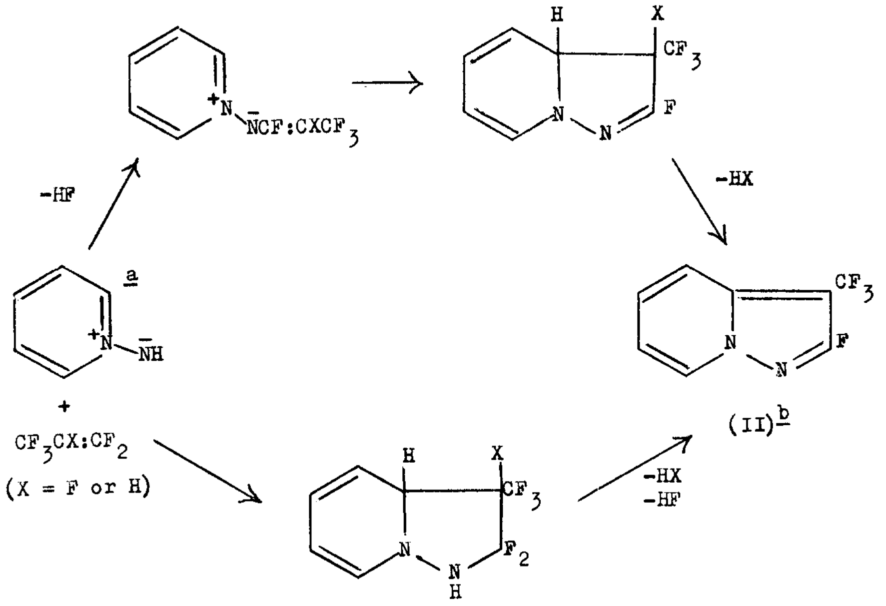


(IX)

Currently, the action of N-iminopyridinium ylide on perfluorinated imines and nitroso-compounds is under investigation. No cycloadducts have been isolated yet. Perfluoro-2-azapropene yields a complex mixture believed from n.m.r. data to contain the N-substituted ylide VIII, and perfluoro-1-azacyclohexene is transformed into ylide IX, which derives its carbonyl group from water produced during generation of N-iminopyridinium ylide (see the Scheme). Mechanisms for these conversions, the question of concerted versus stepwise formation of bicyclic products from heteroaromatic N-imines and fluorinated dipolarophiles, and the source of dihydropyridine material in the reaction involving trifluoroacetonitrile will be discussed in full papers; so will work still in progress on the synthesis of fluorinated pyrazoles *via* oxidation of azaindolizines II and IV.



Scheme

[a] Generated *in situ* from *N*-aminopyridinium iodide and K_2CO_3 in CH_2Cl_2 [3].

[b] Isolated by column chromatography and purified finally by sublimation to give material melting at 62-63 °C.

Correct elemental analyses (C,H,F and N in every case) and consistent spectroscopic data [i.r., mass, and n.m.r. (including ^{13}C and ^{15}N for compound II)] were obtained for new compounds II-V and IX.

REFERENCES

1 A. Ohsawa, I. Wada, H. Igeta, T, Akimoto, A. Tsuji, and Y. Iitaka, Tetrahedron Letters, (1978) 4121.

2 This investigation was initiated in October 1976 (S. M. Hitchen, M.Sc. Qualifying Thesis, UMIST, 1977).

3 See R. E. Banks and S. M. Hitchen, J. Fluorine Chem., 12 (1978) 159 for the results of work involving fluoroaromatic substrates.

4 H.-J. Timpe, Adv. Heterocyclic Chem., 17 (1974) 213.

5 T. Uchida and K. Matsumoto, Synthesis, (1976) 209.