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FORMATION OF 1,1′-BI-1H-PYRROLO[3,2-c]PYRIDINES BY THE DEOXYGENATION OF 4-NITRO-3-STYRYLPYRIDINE 1-OXIDES WITH TERVALENT PHOSPHORUS COMPOUNDS[1]

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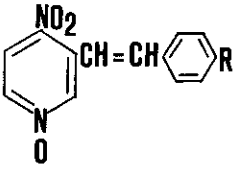
Abstract- The deoxygenation reaction of 4-nitro-3-styrylpyridine 1-oxides with triethyl phosphite or, more favourably, with hexaalkylphosphorous triamide afforded 1,1′-bi-1H-pyrrolo[3,2-c]pyridines instead of a monomeric product.

The N-N bonded dimers of pyrroles,[2] indoles,[3] and carbazoles[4] have been prepared by the oxidation reaction of the corresponding heterocycles. We wish to report that the deoxygenation reaction of 4-nitro-3-styrylpyridine 1-oxides with tervalent phosphorus compounds produces the N-N bonded dimers in moderate yields. This appears to be a rare instance in the deoxygenation reactions of nitro-arenes.[5]

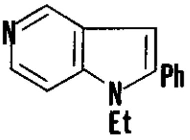
Whereas 4-nitro-3-styrylpyridine 1-oxide[6] (1a), when heated in a large excess of triethyl phosphite, gave 1-ethyl-2-phenyl-1H-pyrrolo[3,2-c]pyridine (2) [mp 198-199°, 29 % yield], heating of (1a) with 6 moles of triethyl phosphite in benzene for 7 days (the conditions reported to yield 2-phenyl-1H-pyrrolo[3,2-c]pyridine from (1a)[7]) afforded a compound $C_{26}H_{18}N_4$ [mp 266-268° (decomp.), 6 % yield].

^{1}H Nmr spectrum of this compound displays aromatic protons only whose chemical shifts and coupling constants are in keeping with those recorded for pyrrolo[3,2-c] pyridines[8] and the spectral pattern did not change after the addition of deuterium oxide, indicating the absence of protons exchangeable with deuteriums. This is further supported by the absence of a ν(NH) absorption in its ir spectrum, which contains bands characteristic of pyrrolo[3,2-c]pyridine.[9] From these observations the structure of 2,2′-diphenyl-1,1′-pyrrolo[3,2-c]pyridine (3a) was assigned.

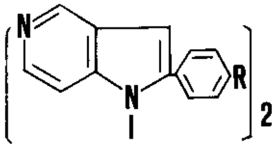
The synthesis could be advantageously improved when (1a) was heated with 6 moles of hexamethyl- or hexaethyl-phosphorous triamide in tert.-butylbenzene or xylene at 130° in nitrogen for a few hours (a vigorous reaction took place at



(1)



(2)



(3)

(1), (3): a; R=H b; R=MeO c; R=Cl d; R=Me_2N e; R=Me

ca. 110° and the temperature of the mixture rose rapidly). By this procedure the following 2,2'-diaryl-1,1'-bi-1H-pyrrolo[3,2-c]pyridines[10] were prepared: [(3a); 47 %]; [(3b); mp 278-279° (decomp.), 38 %)]; [(3c); mp 290° (decomp.), 54 %]; [(3d); mp 280° (decomp.), 32 %]; [(3e); mp 272° (decomp.), 49 %].

Table 1. Spectral Data of 2,2'-Diaryl-1,1'-1H-pyrrolo[3,2-c]pyridines (3a-e)

Compd.	$\lambda_{max.}$ nm (log ε) (EtOH)	Ir Bands (cm^{-1}) (Nujol)
(3a)[a]	242 (4.48), 248 (4.49), 304 (4.42)	1320, 910
(3b)[b]	253 (4.44), 260 (4.43), 309 (4.43)	1320, 910
(3c)[c]	244 (4.55), 251 (4.56), 309 (4.55)	1315, 910
(3d)[c]	225 (4.53), 279 (4.22), 334 (4.74)	1300, 910
(3e)[c]	250 (4.73), 306 (4.61)	1320, 910

[a] $\delta[(CD_3)_2SO]$ 7.04 (s, 2H), 7.46 (m, 8H), 7.92 (m, 4H), 8.18 (d, J=6 Hz, 2H), 8.82 (s, 2H). [b] $\delta[(CD_3)_2SO]$ 3.80 (s, 6H), 6.90 (s, 2H), 7.07 (d, J=9 Hz, 4H), 7.34 (d, J=6 Hz, 2H), 7.84 (d, J=9 Hz, 4H), 8.15 (d, J=6 Hz, 2H), 8.78 (s, 2H). [c] Low solubilities of (3c-e) prevented nmr spectral determinations.

References and Notes

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[10] Recrystallized from methanol. Satisfactory micro-analyses have been obtained.

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