PROBLEM 15

[SUPPL Problem 15 # 1]

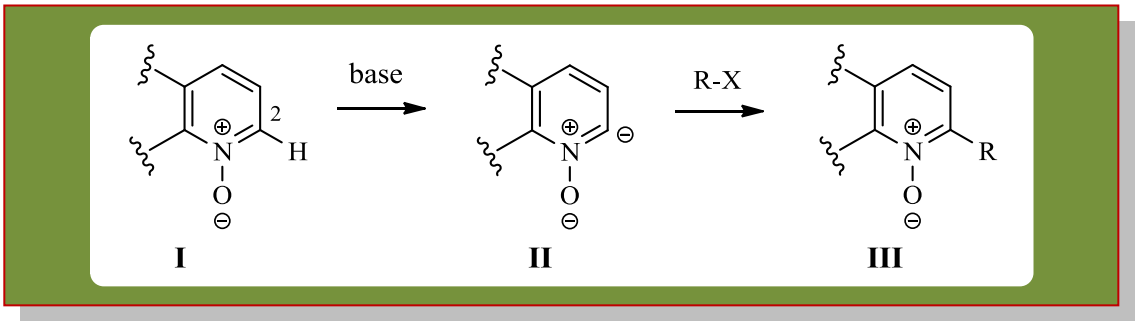
Arabic compound numbers in TAPSOC,
Roman numerals in Supplementary material

In Perspective

Having so many products of the reaction crude dripping out of the chromatography column is the sort of reaction you hate to come across in a synthesis laboratory, and yet a delightful one if your interests revolve around mechanism.

Professor Masamoto Hamana and his coworkers at Fukuoka University in Japan observed a host of unexpected products **2 – 6** (TAPSOC Scheme 15.1) while studying the deprotonation of quinoline N-oxides and the various reactions open to the predictable nucleophilic anionic intermediate. Pyridine N-oxide behaved likewise.

Their initial plan was based on the logical presumption that the formal positive charge on N in **1** imparts acidic properties to the proton on C^2 (Scheme SP15.1.1), a long-held concept in pyridine N-oxide models [1]. Once the vinyl carbanion was formed in strong base, straightforward alkylations and acylations would occur chiefly at this site. However, compound **1** had a different plan, opening the lid of what seemed the Pandora's box to a plethora of byproducts.



SCHEME SP15.1.1

For a more thorough treatment of this problem consider the following experimental evidence. Also, when ^{18}O-labeled benzoyl chloride was used, product **2** displayed almost a 1:1 ratio of ^{18}O on benzoyl and acyl group.

TABLE SP15.1 Compound distribution in Scheme 15.1 (TAPSOC) depending on base used.

	% yield				
REAGENT	**2**	**3**	**4**	**5**	**6**
TMP	30	22	10	12	47
Et_3N	21	18	9	11	51
t-BuOK, NaOEt, DBU, piperidine	0	0	0	0	0

REFERENCE

[1] Abramovitch RA, Saha M, Smith EM, Coutts RT. J. Am. Chem. Soc. 1967;84:1537-1538.