

REACTION OF N-p-TOLUENESULFONYLDIPHENYLCYCLO-
PROPENIMINE WITH PYRIDINIUM N-IMINES

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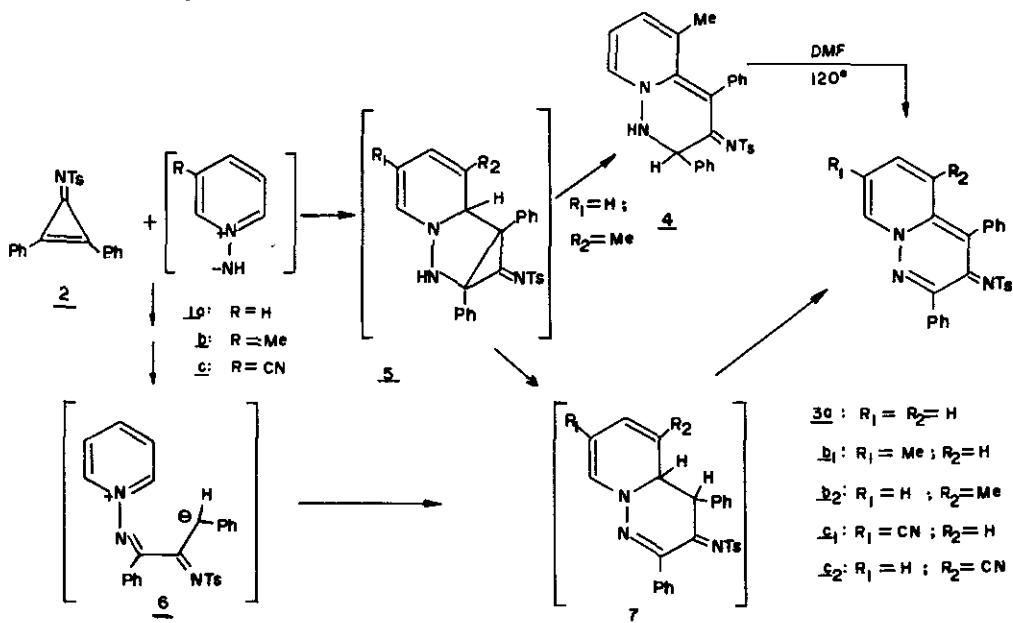
Abstract — Pyridinium N-imines (1) react with N-p-toluene-sulfonyldiphenylcyclopropenimine (2) to afford pyridopyridazinimines (3).

A variety of pyridinium N-imines [N-substituted¹ and N-unsubstituted (1a)²] have been reported to react with diphenylcyclopropenone, the products in all cases being consistent with a pathway involving initial nucleophilic attack on the cyclopropenone ring with subsequent elimination of pyridine. Recently, we observed³ a similar behavior for N-p-toluenesulfonyldiphenylcyclopropenimine (2) upon reaction with pyridinium N-carboethoxyimine. Our interest in evaluating the dipolarophilic character of small ring systems in reactions with pyridinium ylides prompted a study of the reactivity of 2 with pyridinium N-imines (1). Reaction of 2 with 1a (formed in situ from the hydriodide and triethylamine)² in methanol or methylene chloride was complete within 24 h at room temperature to yield a cycloadduct assigned structure 3a (see Table). Support for this assignment was obtained from the reaction of 1b in methylene chloride (2 days) which afforded as the major product a stable intermediate, 4, corresponding to the more sterically hindered regioisomer, in addition to 3b₁. The pmr spectrum (DMSO-d₆) of 4 was particularly informative, containing two broadened 1H singlets at δ 6.13 and 8.66. The latter absorption was D₂O exchangeable, while the former sharpened in the process. Dehydrogenation of 4 to 3b₂ was observed in DMF at 120°C (65% conversion after 1 day). The C-5 methyls of both 4 and 3b₂ showed the expected diamagnetic anisotropic shielding effect of the C-4 phenyls. Predominant cycloaddition at the more hindered site on a 3-substituted pyridinium N-imine has been observed as a general phenomenon in reactions of ethyl propiolate, regardless of the electron-donating or electron-withdrawing character of the

TABLE

Cmpd	Yield (%) ^{a, b} mp (°C)	IR (KBr, cm ⁻¹)	¹ H-NMR (TMS _{int.} , δ)	UV λ _{max} nm(ε)
<u>3a</u>	65 226-227	1638(w), 1540, 1490, 1453, 1430	^c 2.28 (s, 3H), 6.9-7.8 (m, 17H), 8.37 (d, J=7Hz, H-8)	^f 369 (19880) 269 (19670)
<u>3b₁</u>	32 230-232	1642(w), 1535, 1492, 1456, 1430	^c 2.24 (s, 3H), 2.30 (s, 3H), 6.9-7.9 (m, 16H), 8.28 (s, H-8)	^f 371 (22690) 269 (23260)
<u>3b₂</u>	quant. from <u>4</u> 225-226	1643(w), 1550, 1495, 1463, 1430	^c 1.75 (s, 3H), 2.28 (s, 3H), 6.8-8.1 (m, 16H), 8.45 (d, J=7Hz, H-8)	^f 370 (21540) 273 (23050)
<u>3c₁</u>	55 252-253	2230, 1640, 1540, 1495, 1450	^c 2.32 (s, 3H), 6.9-7.9 (m, 16H), 8.63 (s, H-8)	^g 390 (19430) 258 (14820)
<u>3c₂</u>	10 301-302	2230, 1635 (w), 1562, 1500, 1455	^d 2.43 (s, 3H), 7.1-7.9 (m, 14H), 8.30 (t, H-7), 8.90 (d, H-6), 9.60 (d, H-8) (all J=7Hz)	^g 376 (16560) 286 (11674)
<u>4</u>	64 222-224	3060 (br), 1615, 1490, 1465, 1445, 1420	^e 1.43 (s, 3H), 2.28 (s, 3H), 6.13 (s, br, H-2), 6.7-7.6 (m, 16H), 8.06 (d, J=7Hz, H-8), 8.66 (s, br, H-1)	^f 349 (20576) 297 (13112)

a) All products were isolated by means of column chromatography on silica gel: elution with CH₂Cl₂ (3) and 40% ether-CH₂Cl₂ (4). b) All compounds gave satisfactory elemental analyses (± 0.3%). c) CDCl₃. d) CF₃CO₂H. e) DMSO-d₆. f) EtOH. g) CH₃CN.



substituent.⁴ In the case of 2, reaction with 1c (formed in situ from the mesitylenesulfonate and potassium carbonate)⁴ in methylene chloride (12 days) produced both 3c₁ and 3c₂, with a large preference for the former. Such inverse orientation to the sterically less hindered position has been observed in the reaction of 1c with 2-phenylazirine.⁵

The formation of 4 provides direct evidence for the participation of 5. However, since a 1,2-dihydro intermediate was isolated in one case only, an alternative pathway to other 3 involving inverse hydrogen transfer in 5 or a step-wise process with participation of 6 to produce a 4,4a-dihydro intermediate (7) cannot be excluded. In fact, an intermediate analogous to 7, which was observed⁶ in the reaction of 1a with methylphenylcyclopropenone, suffered dehydrogenation under mild conditions.

The results of the present study demonstrate the continuing utility of pyridinium N-imines 1 as probes for dipolarophilic character of unsaturations contained within small ring systems.

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