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REACTION OF N-p-TOLUENESULFONYLDIPHENYLCYCLOPROPENIMINE WITH PYRIDINIUM N-IMINES

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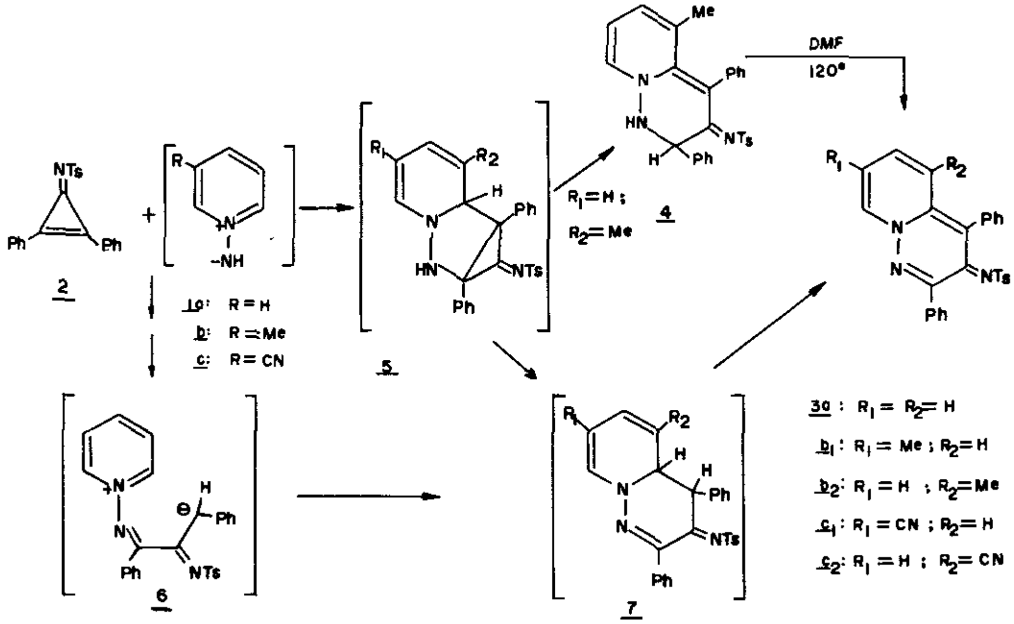
Abstract — Pyridinium N-imines (1) react with N-p-toluenesulfonyldiphenylcyclopropenimine (2) to afford pyridopyridazinimines (3).

A variety of pyridinium N-imines |N-substituted[1] 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 observed[3] 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 $3b_1$. The pmr spectrum (DMSO-d_6) of 4 was particularly informative, containing two broadened 1H singlets at δ 6.13 and 8.66. The latter absorption was D_2O exchangeable, while the former sharpened in the process. Dehydrogenation of 4 to $3b_2$ was observed in DMF at 120°C (65% conversion after 1 day). The C-5 methyls of both 4 and $3b_2$ 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 (^{o}C)	IR (KBr, cm^{-1})	^{1}H-NMR (TMS$_{int.}$, δ)	UV|λ$_{max}$ nm(ε)|
3a	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)
3b$_1$	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)
3b$_2$	quant. from 4 225-226	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)
3c$_1$	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)
3c$_2$	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)
4	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 CH_2Cl_2 (3) and 40% ether-CH_2Cl_2 (4). b) All compounds gave satisfactory elemental analyses (± 0.3%). c) $CDCl_3$. d) CF_3CO_2H. e) DMSO-d_6. f) EtOH. g) CH_3CN.



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 $3c_1$ and $3c_2$, 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 observed[6] 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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