The Photolysis of Schneider's 1-Phenyliminopyridinium Ylides

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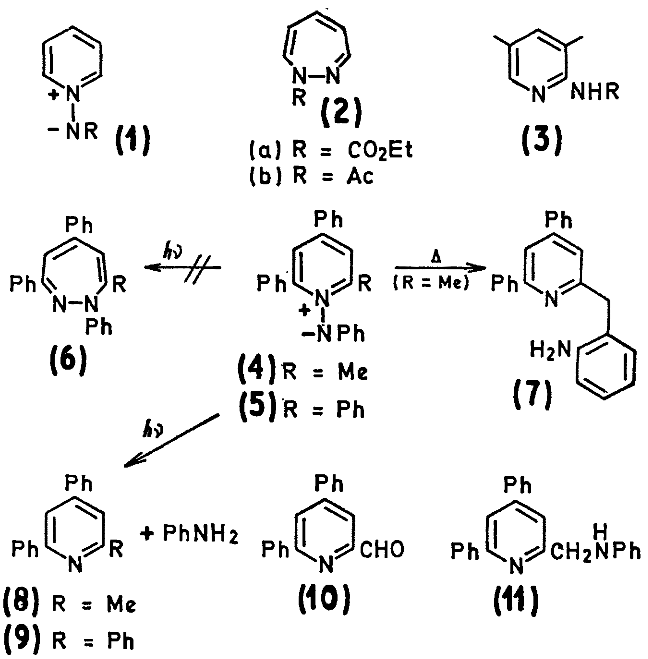
Summary Photolysis of the pyridinium ylides (**4**) and (**5**) produces, besides high yields of aniline and (**8**) and (**9**) respectively, the additional products (**10**) [from (**4**) in benzene] and (**12**) [from (**5**) in diethylamine] which suggest a phenyl nitrene intermediate in these reactions.

RECENT investigations in the field of 1-iminopyridinium actions: (i) ring expansion to 1(1*H*),2-diazepines [(**1**) → ylide photochemistry has uncovered three types of re- (**2**)];[1–3] (ii) rearrangement to 2-amino-pyridines [3,5-dimethyl-(**1a**) → (**3a**)];[3b] and (iii) photo-Curtius rearrangement [(**1b**) → pyridine + MeCNO].[3a] We now report on the photolysis of the 1-phenylpyridinium ylides (**4**) and (**5**), two of the first known examples of this class of compounds.[4,5] Our work offers new information on some structural and mechanistic aspects of N–N ylide photochemistry, provides a new method for the generation of phenyl nitrene and thereby an alternate mechanistic probe with which to study the nature of its electronic state,[6] and presents the first opportunity for direct comparison of the less complicated photochemical behaviour of an N–N ylide (**5**) with that of a similarly substituted, isoelectronic *N*-oxide (2,4,6-triphenylpyridine *N*-oxide).[7]



Photolysis of 1-aryliminopyridinium ylides[a]

Compound	Reaction conditions		Solvent[b]	Products, % yield[c]			
				(8)	$PhNH_2$	(**10**)	(**12**)
(**4**)	0—5°,	17 hr.	CH_2Cl_2	16·5	17[d]		
	0—5°,	18 hr.	Et_2NH	33	35·5		
	5—10°,	18 hr.[e]	C_6H_6	12	59	24	
				(9)			
(**5**)	8—12°,	2 hr.	CH_2Cl_2	79	12·5[d]		
	8—12°,	2 hr., N_2	Et_2NH	73	89		2
	8—12°,	2 hr., O_2	Et_2NH	70	91·5		2
	8—12°,	4 hr.	C_6H_6	79	24		

[a] Irradiations (40 ml) were conducted in a Rayonet Reactor using 3500 Å lamps in a Pyrex vessel similar to the one described by G. T. Tisue, S. Linke, and W. Lwowski, *J. Amer. Chem. Soc.*, 1967, **89**, 6303. Concentrations were *ca.* $2·5 \times 10^{-3}$M in starting ylides.

[b] All solvents were dried and distilled before use.

[c] Compounds (**8**) and (**9**) were obtained by preparative thick-layer or column chromatography (silica gel) and were characterized by comparison with authentic samples: (**8**);[15] (**9**).[+d] Yields of aniline and (**12**) were determined by g.l.c. analysis using naphthalene as an internal standard on a 6 ft. × ¼ in. column of 25% Carbowax 20 M and 3% KOH on Chromosorb W60 × 80 mesh. For the purpose of direct comparison of retention times, compound (**12**) was prepared by the known procedure.[13]

[d] The low yield is due to formation of aniline hydrochloride in this solvent.

[e] A higher temperature was required to avoid freezing the benzene solution. Under these conditions, thermal rearrangement could not be prevented and 10·5% of (**7**) was isolated.

The ylide (**4**) was known to undergo a Sommelet-type rearrangement[8] in many solvents at ambient temperatures to yield the pyridine derivative (**7**).[4b,5] This thermal dark reaction [†] was completely avoided by carrying out the photolysis at 0—5°. The Table summarizes the results obtained from the photolysis of (**4**) in several solvents.[‡] Rather than ring expanding to a 1-aryl-1(1*H*), 2-diazepine (**6**),[9] compound (**4**) undergoes fragmentation in methylene chloride or diethylamine solution to yield 2-methyl-4,6-diphenylpyridine (**8**) and aniline as the only isolable products. In benzene solution, an additional product, the aldehyde (**10**) [m.p. 110—113°; i.r. ($CHCl_3$) 1695 cm^{-1} (C=O); n.m.r. ($CDCl_3$) τ −0·1 (s, 1H, C*H*O), 2·3 (m, 2H, pyridine protons), 1·9—2·5 (m, 10H, aromatic protons)] is

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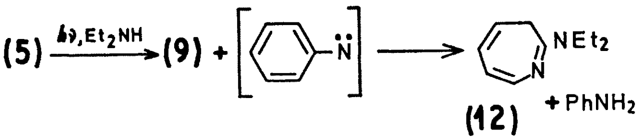
[†] For example, ylide (**4**) on standing in methylene chloride at room temperature in the dark gave 44% yield of (**7**). The n.m.r. spectrum ($CDCl_3$) of (**7**) [τ 1·60 (m, 2H, pyridine protons), 1·88—3·18 (m, 14H, aromatic protons), 5·11 (br s, 2H, exchanged with D_2O, NH_2), 5·67 (s, 2H, $PhCH_2$–] confirmed Schneider's original far-sighted assignment.[4b]

[‡] The fact that (**4**) is light-sensitive had received brief comment (see ref. 5).

produced.[§] By analogy with our observations[3a] on the ylide (**1b**), a reasonable mechanism for the decomposition of (**4**) is *via* heterolytic N–N bond cleavage to produce (**8**) and phenyl nitrene. In agreement with reactions characteristic of aryl nitrenes,[10] the formation of aniline and aldehyde (**10**) is observed. The latter product presumably arises *via* C–H insertion of singlet phenyl nitrene [6a,11] to form (**11**) followed by hydrogen abstraction and hydrolysis of the resulting Schiff base on chromatography.[12] That the formation of (**10**) may involve a cage mechanism receives support from the observation that the photolysis of a mixture of (**8**) and phenyl azide does not yield (**10**). Further evidence for the intermediacy of phenyl nitrene was obtained from the much cleaner photochemical breakdown of ylide (**5**).

As seen from the Table, the photolysis[¶] of ylide (**5**) also results in fragmentation to 2,4,6-triphenylpyridine (**9**) in high yield while the amounts of aniline obtained are again strongly dependent on solvent. Furthermore, irradiation in diethylamine under nitrogen produced minor but reproducible amounts of 2-diethylamino-3*H*-azepine (**12**) indicative of the intermediacy of phenyl nitrene.[13,14] Photofragmentation was not quenched and (**12**) was still produced when the irradiation was carried out under oxygen. Although attempts to sensitize the reaction have been complicated by the intense absorption of ylide (**5**) in the u.v. and visible region, the above results are suggestive of the reaction proceeding *via* an excited singlet ylide and singlet phenyl nitrene species. Comparative evidence which points to the involvement of singlet phenyl azide and singlet phenyl nitrene in the photolysis of phenyl azide is available.[6a,14] The failure to detect triplet phenyl nitrene in the photolysis of (**5**) at 77°K in methylene chloride–Fluorolube by e.s.r. measurements supports our tentative conclusions.



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[§] The structure of (**10**) was established by oxidation to the known 4,6-diphenylpyridine-2-carboxylic acid: C. Gastaldi, *Gazzetta*, 1922, **52**, 174.

[¶] In contrast to ylide (**4**), (**5**) was found to be stable in all solvents at room temperature in the dark.

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[14] J.-S. Splitter and M. Calvin, *Tetrahedron Letters*, 1968, 1445.

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