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STUDIES OF HETEROAROMATICITY-LXVII.[1] SYNTHESES OF N-VINYLIMINOPYRIDINIUM YLIDES AND THEIR INTERMOLECULAR REACTIONS WITH ACETYLENIC COMPOUNDS

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N-Vinyliminopyridinium ylides, readily obtainable from pyridinium N-imines and vinylhalide in the presence of alkali, show a remarkable 1,5-dipolar character and the resulting cyclization reactions[2,3,4] are a useful method for the preparation of nitrogen-bridged heteroaromatics and their dihydro-compounds.

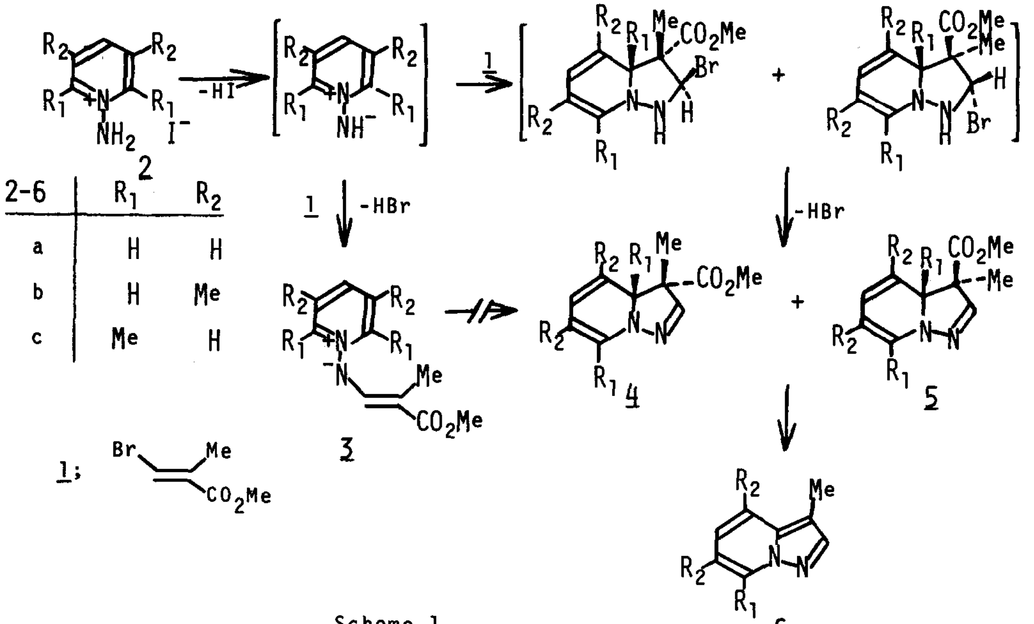
On the other hand, intermolecular reaction of such ylides has been scarcely investigated because of their highly reactivity in the cyclization reactions. Recently, we have reported that 3'-substituent in N-(*trans*-2',3'-dimethoxycarbonylethenyl)iminopyridinium ylide derivative hinders the cyclization but its *cis*-isomer cyclizes with facility to give the dihydro-bicyclo-adduct.[2] Related to this substituent effect, we attempted to prepare the N-vinyliminopyridinium ylides with 3',3'-disubstituents and some reactions of their ylides.

We wish to report here the preparation and the intermolecular reaction with acetylenic compound of N-(3'-methyl-3'-methoxycarbonylethenyl)iminopyridinium ylides.

Treatment of pyridinium N-imine hydriodide 2a with methyl β-bromomethacrylate 1 in the presence of excess potassium carbonate in chloroform at room temperature gave the corresponding ylide 3a(21%), m.p. 85-87°, $\nu^{KBr}_{C=O}$ 1540cm^{-1}, accompanied with two kinds of bicyclic compounds(57%), dihydropyrazolopyridine derivatives 4a and 5a as unstable pale yellow oils, $\delta(CCl_4)$, *inter alia*, 1.31 and 1.48(each 3H, s, CH_3), 3.56 and 3.68(each 3H, s, OCH_3), 4.33 and 4.84(each

1H, br s, 3a-H) ppm, and 3-methylpyrazolopyridine 6a, m.p.(picrate) 116-119°, $\delta(CCl_4)$, 2.26(3H, s, CH_3), 6.50(1H, br t, J=7.0, 7.0Hz, 6-H), 6.86(1H, br t, J=7.0, 8.0Hz, 5-H), 7.28(1H, dd, J=8.0, 1.5Hz, 4-H), 7.55(1H, s, 2-H), and 8.26 (1H, dd, 7.0, 1.5Hz, 7-H) ppm. From similar treatments of 2b and 2c and 1, products, 3b(25%, m.p. 145-148°), 4b, 5b and 6b(59%), and 3c(77%, m.p. 140-143°), were obtained, but in the case of the reaction of 2c with 1,4c and 5c were not produced. Grossly similar nmr spectra among N-vinyliminopyridinium ylide, dihydropyrazolopyridine and pyrazolopyridine supported those proposed structures in comparison with analogous compounds as previously reported by us.[2]

That of these ylides, as might be expected, did not cyclize under the same reaction conditions suggested these bicyclic compounds were produced *via* the 1,3-dipolar cycloaddition reactions[5] of pyridinium N-imines with 1, followed by elimination of hydrogen bromide from the primary cycloadducts. By contrast, the dihydro-compounds 4a and 5a, and 4b and 5b, were aromatized readily even at room temperature to give the corresponding 3-metylpyrazolopyridine derivatives, 6a and 6b, in good yields, respectively. These are summarized in Scheme 1.



2-6	R_1	R_2
a	H	H
b	H	Me
c	Me	H

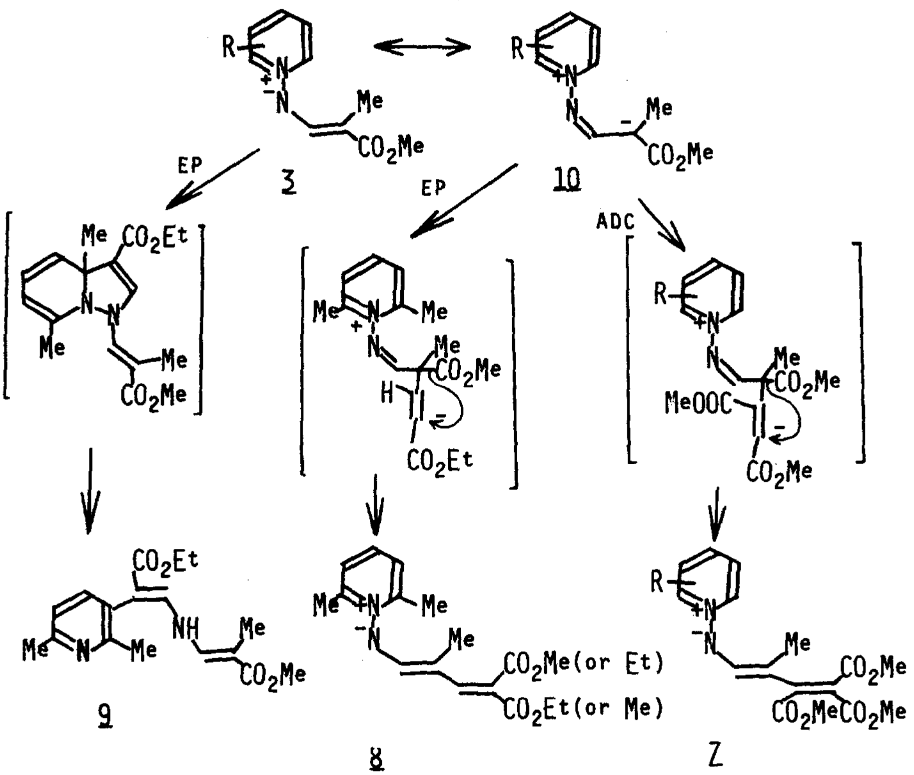
Scheme 1.

Reactions of the ylides 3a, 3b and 3c with dimethyl acetylenedicarboxylate in benzene at room temperature gave the corresponding N-dienyliminopyridinium ylides, 7a(30%) as amorphous powders, 7b(53%, m.p. 105-108°), and 7c(80%, m.p. 124-126°). Furthermore, in the reaction of 3c and ethyl propiolate, ylide 8(28%, m.p. 147-150°), and 3-vinylpyridine derivative 9(51%, m.p. 123-125°) were obtained; 9; $\delta(CDCl_3)$, 1.30(3H, t, J=7.0Hz, $OCH_2\underline{CH_3}$), 1.62(3H, d, J=1.5Hz, CH_3), 3.78(3H, s, OCH_3), 4.27(2H, q, J=7.0Hz, $O\underline{CH_2}CH_3$), 6.05(1H, br, NH), 7.06 (1H, d, J=8.0Hz, 5-H), 7.37(1H, d, J=8.0Hz, 4-H), 7.47(1H, br d, J=12.0Hz, NH$\underline{CH}$=), and 7.73(1H, d, J=13.0Hz, =$\underline{CH}$NH). Structural elucidation of the N-dienyliminopyridinium ylides 7a, 7b, 7c and 8 was accomplished on the basis of physical and spectral analyses; their nmr spectra showed strongly to have common ylide structure as shown in Table 1.

Table 1. NMR Data of N-Ylides

Compd.	C-2	C-3	C-4	C-5	C-6	C-2'	C-3'	$OCH_3(OCH_2CH_3)$			
3a	8.23		7.37		8.23	8.19	1.94	3.67			
	m		m		m	s	s	s			
3b	7.95	2.33	6.94	2.33	7.75	8.10	1.89	3.65			
	s	s	s	s	s	s	s	s			
3c	2.65	7.43	7.71	7.40	2.65	7.61	1.88	3.60	J=9.0, 6.0Hz		
	s	d	q	d	s	s	s	s			
7a	8.39		7.65		8.39	8.35	1.98	3.67	3.73	3.76	
	m		m		m	s	s	s	s	s	
7b	8.12	2.40	7.37	2.40	8.12	8.40	1.95	3.64	3.69	3.72	
	s	s	s	s	s	s	s	s	s	s	
7c	2.64	7.45	7.79	7.43	2.64	7.69	2.03	3.58	3.71(6H)	J=8.0, 6.0Hz	
	s	d	q	d	s	s	s	s	s		
8	2.66	7.43	7.76	7.42	2.66	7.66	1.96	3.70	4.12	1.26	J=8.0, 6.0
	s	d	q	d	s	s	d	s	q	t	Hz

The formation of the ylides may be considered as a result of cationotropic rearrangement of methoxycarbonyl group[6] after Michael-type addition of the carbanion (10) in N-vinyliminopyridinium ylide molecule on dimethyl acetylenedicarboxylate. Interestingly, similar rearrangement in the reaction of pyridinium methylide with same reagent has been reported recently by Leonte and Zugravescu.[7] On the other hand, the rearranged compound 9 was similar to that of the 1,3-dipolar cycloaddition reaction of N-acyliminopyridinium ylide with acetylenic compound.[8,9] These results are summarized in Scheme 2.



EP; $\equiv\!-CO_2Et$, ADC; $MeOOC\!-\!\equiv\!-COOMe$

Scheme 2.

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