

tets have been interpreted as arising from H-3, the hydrogen β to the nitro, and the two magnetically nonequivalent methylene protons α to the nitro group in 3-nitromethylphthalide. The nonequivalence results from unequal time average population of rotamers. The quartet at δ 6.29 results from the coupling of H-3 to the α protons by 7.8 and 3.0 Hz. Geminal coupling between the two nonequivalent α hydrogens is 14.3 Hz. Of these two, that which is downfield is then coupled to H-3 by 3.0 Hz and that which is upfield is coupled to H-3 by 7.8 Hz. The difference in coupling constants results from unequal average dihedral angles because of unequal time average populations of rotamers.

In an attempt to isolate the β -nitrostyrene, the work of Hashimoto and Nagase² was repeated for the synthesis of their reported *o*-(2-nitrovinyl)benzanilide. The product from the condensation of 3-nitromethylphthalide and aniline was recovered as a white, colorless solid. Its nmr displayed no vinylic or amide hydrogen signals and its ir lacked the amide NH stretching band. The same general nmr signal pattern was observed for this derivative in acetonitrile as was seen in the case of 3-nitromethylphthalide, and it has been concluded that the correct structure of this compound is 2-phenyl-3-nitromethylphthalimidine. Once again the α -methylene protons are magnetically nonequivalent being separated by ~ 0.27 ppm. They give two slightly overlapping quartets centered at δ 4.76 and 5.03 resulting from a geminal coupling of 13.5 Hz, and from a coupling of the α proton at lower field to H-3 by 4.3 Hz and that at higher field to H-3 by 4.6 Hz. The methine H-3 gives a triplet-like pattern at δ 5.83 resulting from coupling with the α hydrogens. The aromatic protons are observed as a complex multiplet centered at δ 7.56. Partial deuterium exchange of the α protons employing deuterium oxide and a catalytic amount of anhydrous potassium carbonate results in collapsing the signal attributed to H-3 to a singlet and in virtually eliminating the signal of the two α hydrogens. This confirms the assignment of the α -methylene hydrogens and the five-membered ring lactam. The result of the deuterium exchange on II also substantiates the structure of I because of the similarity in chemical shifts and multiplicities of the signals of the methine and methylene hydrogens in the two compounds.

Experimental Section⁵

3-Nitromethylphthalide.²—To a solution of 176.3 g (1.175 mol) of *o*-phthalaldehydic acid,⁶ 72.4 g (1.18 mol) of nitromethane, and 885 ml of methanol cooled to -15° was added dropwise and with stirring a solution of 112 g (2.78 mol) of sodium hydroxide in 400 ml of distilled water. After addition of the base, the solution was allowed to warm to 25° and stirred for 2.5 hr. The solution was then poured into 710 ml of 5 *N* hydrochloric acid with stirring. The product crystallized and was filtered and washed with distilled water. Additional cooling of the reaction mixture resulted in more crystalline material. The combined product was dissolved in 2-propanol and recrystallized to give 140.4 g (61%) of white crystals: mp 129 – 131° (Fisher-Johns) (lit. mp 129 – 130° ,² 130° ,³ 130 – 131°); ir (KBr) 1560 (NO_2), 1755 (lactone C=O), 2980 (aliphatic CH), and 3040 cm^{-1} (aromatic CH).

(5) All nmr spectra were recorded on a Varian A-60 spectrometer at operating temperature of about 37° utilizing $\sim 20\%$ solutions of compound with tetramethylsilane (TMS) as the internal reference. Infrared spectra were determined using a Beckman IR 5-A infrared spectrophotometer. All melting points are uncorrected.

(6) R. L. Shriner and F. J. Wolf, "Organic Syntheses," Col. Vol. III, Wiley, New York, N. Y., 1955, p 737.

2-Phenyl-3-nitromethylphthalimidine.²—A solution of 5.0 g (26.0 mmol) of 3-nitromethylphthalide and 4.65 g (50.0 mmol) of aniline was refluxed in 10 ml of anhydrous toluene for 18 hr. The reaction mixture was diluted with benzene and extracted three times with 0.6 *N* hydrochloric acid. After washing the organic layer with distilled water to pH 5.5 and drying over anhydrous sodium sulfate, the solvents were evaporated and the remaining oil dissolved in 2-propanol. Repeated recrystallization gave 4.6 g (66%) of white crystals: mp 158.0 – 159.0° (Kofler) (lit.² mp 151 – 153°); ir (KBr) 1380 and 1540 (NO_2), 1685 (lactam C=O), 2920 (aliphatic CH), and 3060 cm^{-1} (aromatic CH).

Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_3$: C, 67.16; H, 4.51; N, 10.44. Found: C, 67.03; H, 4.38; N, 10.64.

Registry No.—I, 3598-68-3; II, 25097-57-8.

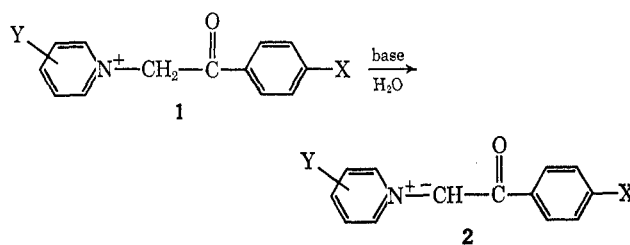
Basicity of N-Ylides¹

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Received March 5, 1970

Although nitrogen ylides were isolated and characterized by Krohnke² over 30 years ago, no systematic study of the basicities of these ylides has been reported. The basicity trends are significant in that they suggest to some extent the expected nucleophilic reactivity and delineate the factors which are important in this respect in ylide structures. Also nitrogen ylides are unique in that they can derive no stabilization by d-orbital carbanion delocalization, a usually important factor in the better known sulfur and phosphorus ylides. We have determined the $\text{p}K_a$'s of a number of pyridinium (1) and ammonium salts in order to determine to some extent the significant factors affecting the stability and reactivity of the corresponding ylide (2).



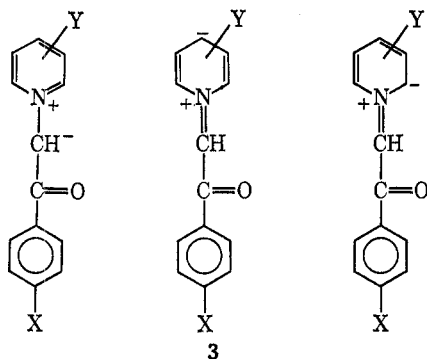
The $\text{p}K_a$'s of a number of pyridinium salts are listed in Table I. In cases where the pyridinium salt was not acidic enough to conveniently titrate with aqueous sodium hydroxide solution, the $\text{p}K_a$ was determined by titrating the isolated ylide with aqueous hydrochloric acid. In preparative runs, the ylides were isolated by employing sodium carbonate as the base (see Table II).

Table III summarizes the results of the $\sigma\rho$ treatments of the $\text{p}K_a$'s. When the phenacyl substituent X is held at H, NO_2 , or halogen and the pyridine substituent Y is varied, ρ is fairly constant and equals an average of 2.9. This indicates that electron-withdrawing substituents on the pyridine nucleus tend to stabilize the ylide. An inductive effect is certainly one reason for the moderately high ρ value. An additional

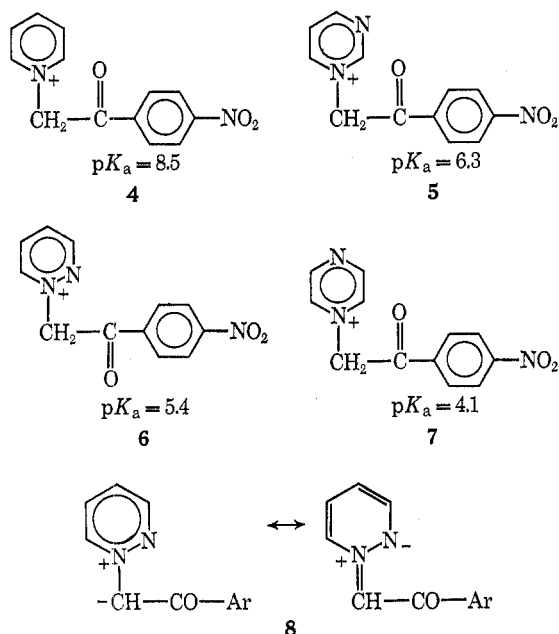
(1) For a previous paper in this series, see W. G. Phillips and K. W. Ratts, *Tetrahedron Lett.*, 1383 (1969).

(2) F. Krohnke, *Chem. Ber.*, **68**, 1177 (1935).

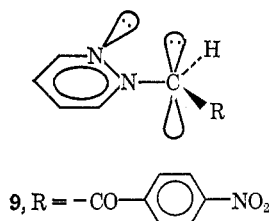
explanation involves the resonance stabilization shown below in which the negative charge is delocalized into the pyridine ring.



The pK_a 's of pyrimidinium, pyridazinium, and pyrazinium salts (5, 6, and 7) are less than that for the pyridinium salt (4). Accordingly, the replacement of carbon with a nitrogen atom in the aromatic ring is a stabilizing factor since nitrogen is more electronegative than carbon (8). However, the comparative order of basicities for 5, 6, and 7 involves more complicating

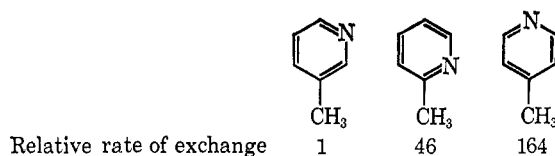


factors. Those ylides where the negative charge can be resonance delocalized on nitrogen (6 and 7) are more stable than the pyrimidinium ylide where this possibility does not exist. The fact that 7 has a lower pK_a than 6 may indicate that repulsion between the electron pairs as depicted in 9 raises the ground-state energy of 8.³



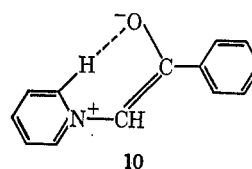
(3) We are indebted to Professor P. Beak for making this suggestion.

In this connection the relative rates of exchange of the isomeric picolines are noteworthy.⁴ Results in the



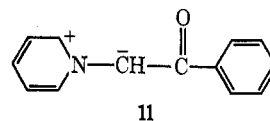
analogous benzene series suggest that the relative rates reflect the relative acidities of hydrocarbons.⁵ Since 4-picoline exchanges faster than 2-picoline, this same type of steric effect may be operative here.

As seen in Tables I and II, the α -protons of the pyridine ring in the ylide are shifted downfield as compared to the α -protons of the pyridine ring in the starting salt. An attractive explanation involves deshielding of the α -hydrogens by the carbonyl function as depicted in 10.



Here a six-membered ring is formed and the α -hydrogen is partially polarized in a resonance structure possessing considerable electron density at oxygen. Evidence for the carbonyl possessing considerable electron density was obtained by Henrick^{6a} who noted that pyridinium ylides showed strong carbonyl absorption at low frequency.

Henrick^{6b} in a recent paper has noted a similar nmr effect but prefers to attribute this to a deshielding of the α -proton resulting from resonance structure 11. In light of our basicity studies, this explanation now appears unlikely.⁷



In additional pK_a studies of structure 1, when Y is held constant and X is varied, $\rho = +2.3$. Thus it is clear that substituents on the phenacyl aromatic ring which are electron withdrawing tend to stabilize the nitrogen ylide 2 by inductive effects. This value is consistent with similar ρ values obtained for sulfur and phosphorus salts. Ratts and Yao⁸ found ρ to be +2.1

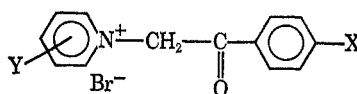
(4) N. N. Zatssepina, I. F. Tupitsyn, and L. S. Efros, *Zh. Obshch. Khim.*, **33**, 2705 (1963); *Dokl. Akad. Nauk SSSR*, **154**, 148 (1964).

(5) A. Streitwieser and D. E. Van Sickle, *J. Amer. Chem. Soc.*, **84**, 249 (1962).

(6) (a) C. A. Henrick, E. Ritchie, and W. C. Taylor, *Aust. J. Chem.*, **20**, 2455 (1967); (b) *ibid.*, 2441 (1967).

(7) An additional explanation involves an electric-field effect. Buckingham has reported calculations which show that a C-H proton is deshielded by the electric field of a nearby charge: A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

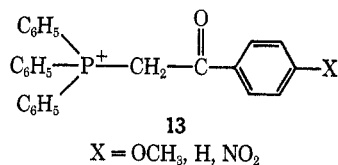
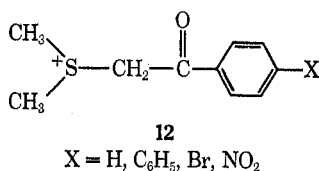
(8) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966).

TABLE I
 N-PHENACYLPYRIDINIUM SALTS^a


Y ^b	X	Registry no.	Mp, °C, dec	% yield	pK _a	Nmr (SO ₂ solvent, τ, ^c multiplicity ^d)				Y	X
						α-Pyridine	β- + γ-pyridine	Methylene	Aromatic		
H	H	a	194.5-197	64	9.7	s, 1.2	m, 2.0	s, 3.6	m, 2.0		
H	Br	b	242-243 ^e	75	9.4						
CH ₃	H	c	159-161	92	10.5	d, 1.4	m, 2.0	s, 3.7	m, 2.0	s, 7.1	
CN	H	d	236-237	60	7.0	d, 0.9	d, 1.5	s, 3.4	m, 2.1		
C ₂ H ₅	H	e	236-238	93	10.3	d, 1.4	m, 2.1	s, 3.7	m, 2.1	q, 6.9	
CN	NO ₂	f	220-222	99	5.1	d, 0.8	m, 2.1	s, 3.2	m, 1.4		t, 8.6
CN	Cl	g	259-261	26	6.45	d, 0.9	d, 1.4	s, 3.4	q, 2.2		
H	NO ₂	h	255-257	65	8.5	d, 1.0	m, 1.5	s, 3.3	m, 1.5		
CH ₃	NO ₂	i	242-243	89	8.8	d, 1.4	d, 2.0	s, 3.6	s, 1.7	s, 7.2	
CH ₃	Cl	j	242-243	65	9.9	d, 1.4	d, 2.4	s, 3.7	m, 2.0	s, 7.1	
<i>t</i> -C ₄ H ₉	H	k	247-248	84	10.4	d, 1.4	d, 2.3	s, 3.8	m, 1.9	s, 8.5	
CH ₃ CO	H	l	214-215	25	8.3	d, 0.9	d, 1.3	s, 3.6	m, 1.9	s, 7.1	
H	OCH ₃	m	208-210	78	10.8	m, 1.2-3.0'	m, 1.2-3.0	s, 3.6	q, 2.4		s, 6.1
CN	OCH ₃	n	230-231	55	7.5	d, 1.1	d, 1.5	s, 3.6	q, 2.5		s, 6.1
3-CN	H	o	195-196	43	7.7	m, 1.6	m, 1.6	s, 3.5	m, 1.6		
3-Br	H	p	114-117	28	9.15	m, 1.0-2.6'	m, 1.0-2.6	s, 3.5	m, 1.0-2.6		

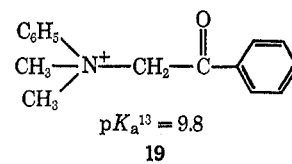
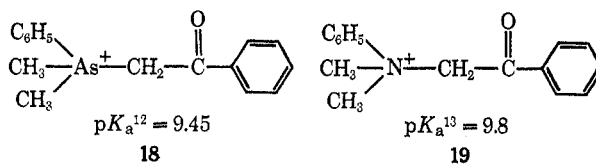
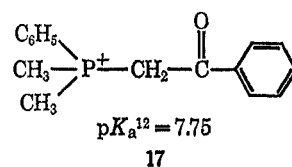
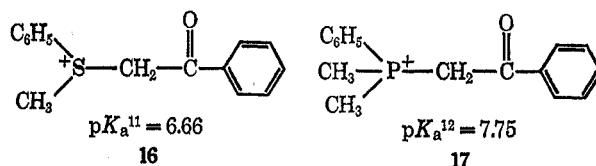
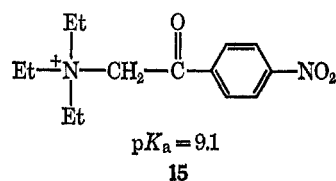
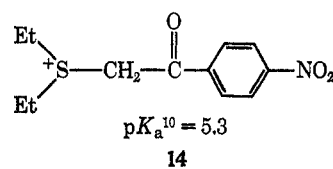
^a Satisfactory analyses ($\pm 0.35\%$ for C and H) were reported for all compounds except the salt with Y = CN, X = NO₂, which tended to decompose upon standing. Ed. ^b The substituent is in the 4 position unless indicated otherwise. ^c Internal TMS. ^d s = singlet, d = doublet, m = unresolved multiplet, q = quartet, t = triplet; all integrations were in accord with theory. ^e Lit. mp 235°: F. Krohnke, *Ber. Deut. Chem. Ges.*, 68, 177 (1935). ^f The phenyl and pyridine protons were not well resolved here.

for series 12. Fliszar, Hudson, and Salvadori⁹ found ρ to be +2.3 for series 13.



An examination of pK_a's of 14 through 19 reveals that nitrogen ylides are more basic than corresponding sulfur, phosphorus, or arsenic ylides. Thus sulfur, phosphorus, and arsenic ylides have a stabilizing factor which is deprived from nitrogen ylides. Since electronegativity differences and bond length differences favor the stability of N-ylides, one can conclude that back donation of electrons in d orbitals accounts for the increase in stability of phosphorus, sulfur, and arsenic ylides over nitrogen ylides. No conclusions regarding

the degrees of d-orbital participation in 16, 17, and 18 can be made since electronegativity differences and bond length differences can equally as well explain the pK_a trends.



(9) S. Fliszar, R. F. Hudson, and G. Salvadori, *Helv. Chim. Acta*, 1580 (1963).

(10) Since the 4-Br analog was more accessible, its pK_a was determined and found to be 6.44. The value of 5.3 shown was calculated by using a ρ of +2.1.

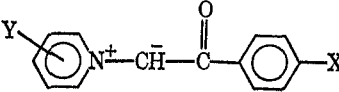
(11) A. W. Johnson and R. T. Amel, *Can. J. Chem.*, 46, 461 (1968).

(12) G. Aksnes and J. Sonstad, *Acta Chem. Scand.*, 18, 655 (1964).

(13) Since the 4-Br analog was more accessible, its pK_a was determined and found to be 9.3. The value of 9.8 shown was calculated by using a ρ of +2.3. It also should be noted that different solvents were used.

Experimental Section

Synthesis of Pyridinium Salts.—The pyridinium salts employed were synthesized by the action of the appropriate pyridine on the appropriate phenacyl bromide in benzene. The results are summarized in Table I.

TABLE II
PYRIDINIUM YLIDES


Y	X	Registry no.	Mp, °C, dec	% yield	Nmr (CDCl ₃ solvent, τ, multiplicity ^d)					
					Y	α-Pyridine	β- + γ-pyridine	Methine	Aromatic	Neut equiv ^e
H	H	a	89-92 ^a	85		m, 0.4	m, 2.2	Not seen	m, 2.7	212 (197)
H	Br	b	133-136 ^b	93		m, 0.9	m, 2.2	Not seen	m, 2.2	
CH ₃	H	c	110-113		s, 7.3	d, 0.3	m, 2.1	s, 3.2	m, 3.3	214 (211)
CN	H	d	114-118	Quant		d, 0.6 ^f	m, 2.0	s, 3.2	m, 2.0	216 (222)
C ₂ H ₅	H	e	103-106	83	q, 7.4 t, 8.8	d, 0.5	m, 2.0	s, 3.2	m, 2.7	
CN	NO ₂	f	187-189		g					
CN	Cl	g	148-150	32		d, 0.9 ^f	m, 2.2	d, 3.3	m, 2.2	265 (257)
H	NO ₂	h	Slow dec	Quant		m, 0.3	m, 2.5	s, 3.2	q, 1.9	239 (242)
CH ₃	NO ₂	i	Slow dec	95	s, 7.5	d, 0.5	m, 2.7	Not seen	q, 1.9	236 (256)
CH ₃	Cl	j	86-89	87	s, 7.6	d, 0.6	d, 2.3	s, 3.4	m, 2.8	262 (246)
<i>t</i> -C ₄ H ₉	H	k	155-162		s, 8.7	d, 0.5	m, 2.2	s, 3.2	m, 2.6	
CH ₃ CO	H	l	93-98		g					
H	OCH ₃ ^h	m	103-107	56		m, 0.4	m, 2.8	Not seen	q, 2.6	233 (227)
CN	OCH ₃ ⁱ	n	128-131	Quant		d, 1.0 ^f	d, 2.9	s, 3.4	m, 1.8	260 (252)
3-CN	H	o	143-147	82		m, 1.8-2.9 ^j	m, 1.8-2.9		m, 1.8-2.0	
3-Br	H	p	118-120	88		s, 0.0 d, 1.0	m, 2.2	Not seen	m, 2.8	274 (276)

^a Lit.² mp 93-96°. ^b Lit.² mp 135-136°. ^c Internal TMS. ^d m = unresolved multiplet (the integrations were all consistent with theory), d = doublet, s = singlet, q = quartet, t = triplet. ^e Theoretical values are in parentheses. ^f SO₂ was solvent here. ^g A nmr spectrum was not obtained because of solubility difficulties. ^h The methoxy gives raise to a nmr absorption at τ 6.2 (s). ⁱ The methoxy gives raise to a nmr absorption at τ 6.1 (s). ^j The phenyl and pyridine protons overlapped here.

TABLE III
RESULTS OF $\sigma\rho$ TREATMENT OF pK_a 's^a

X varied	Y = H	$\rho = +2.3$
X varied	Y = CN	$\rho = +2.3$
X varied	Y = CH ₃	$\rho = +2.2$
X = H	Y varied	$\rho = +2.6$
X = NO ₂	Y varied	$\rho = +3.1$
X = Br or Cl	Y varied	$\rho = +2.9$

^a σ constants are those for substituted benzoic acids except for Y = 4-CN and 4-COCH₃, where σ was employed.

Synthesis of Pyridinium Ylides.—The method of Krohnke was followed.² An aqueous solution of 10% sodium carbonate was added to an aqueous solution of the pyridinium salt. The ylide was then filtered off and dried. In cases where the ylide was soluble in water, the solution was extracted with chloroform. Table II is a summary of the results. In some cases, the methine proton was not seen in the nmr because of exchange with CDCl₃.

Measurement of pK_a Values.—The pK_a values were determined by the method given in ref 14. The ρ 's were determined by a least-squares treatment of the data.

N-(4-Nitrophenacyl)pyridazinium Bromide.—To 29.3 g (0.125 mol) of 4-nitrophenacyl bromide in benzene was added 10.0 g (0.125 mol) of pyrazine. After stirring overnight, 30.1 g of a precipitate was filtered off, mp 226-227°.

Anal. Calcd for C₁₂H₁₀BrN₃O₂: C, 44.46; H, 3.11; N, 12.96. Found: C, 44.62; H, 3.30; N, 12.75.

N-(4-Nitrophenacyl)pyrimidinium Bromide.—To 6.1 g (0.025 mol) of 4-nitrophenacyl bromide in 300 ml of benzene was added 2.0 g (0.025 mol) of pyrimidine. After heating overnight on a steam bath, 1.5 g of a precipitate which formed was filtered off, mp 187-188°.

Anal. Calcd for C₁₂H₁₀BrN₃O₂: C, 44.46; H, 3.11; N, 12.96. Found: C, 44.59; H, 3.18; N, 12.79.

N-(4-Nitrophenacyl)pyrazinium Bromide.—To 30 g of 4-nitrophenacyl bromide in benzene was added 10.0 g (0.125 mol) of pyrazine. After stirring overnight, 4.5 g of a precipitate was filtered off, mp 208-209°.

Anal. Calcd for C₁₂H₁₀BrN₃O₂: C, 44.46; H, 3.11; N, 12.96. Found: C, 44.62; H, 3.11; N, 12.99.

Registry No.—Table I—*a*, 16883-69-5; *b*, 17282-37-0; *c*, 7250-28-4; *d*, 25357-39-5; *e*, 16844-13-6; *f*, 25407-29-8; *g*, 25357-41-9; *h*, 25407-30-1; *i*, 25357-42-0; *j*, 25357-43-1; *k*, 25357-44-2; *l*, 25357-45-3; *m*, 25407-31-2; *n*, 25407-32-3; *o*, 25357-46-4; *p*, 6299-99-6; Table II—*a*, 17282-43-8; *b*, 17282-45-0; *c*, 25357-50-0; *d*, 25357-51-1; *e*, 25407-33-4; *f*, 25357-52-2; *g*, 25357-53-3; *h*, 25357-54-4; *i*, 25357-55-5; *j*, 25357-56-6; *k*, 25357-57-7; *l*, 25357-58-8; *m*, 25357-59-9; *n*, 25357-60-2; *o*, 25357-61-3; *p*, 25357-62-4; N-(4-nitrophenacyl)pyridazinium bromide, 25357-63-5; N-(4-nitrophenacyl)pyrimidinium bromide, 25357-64-6; N-(4-nitrophenacyl)pyrazinium bromide, 25357-65-7.

Methyl Aryl Ether Cleavage in Benzazole Syntheses in Polyphosphoric Acid

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Received January 22, 1970

The polyphosphoric acid method¹ has been extensively employed as a general synthesis of benzazole compounds. As part of some recent studies, a number of substituted 2-phenylbenzazoles have been prepared in PPA, and we now wish to report an interesting ether cleavage reaction accompanying benzazole formation using this method.

The condensation reactions of *o*-methoxybenzoic acid

(1) (a) D. W. Hein, R. J. Alheim, and J. J. Leavitt, *J. Amer. Chem. Soc.*, **79**, 427 (1957). (b) D. W. Hein, R. J. Alheim, and J. J. Leavitt, American Cyanamid Company, U. S. Patent 2,985,611; *Chem. Abstr.*, **57**, 11203c (1962).