sponding to limits of error of about ± 0.3 for C_1 and ± 10 for C_2 at the 5% probability level. However, examination of the results for runs number 1–3, 8, and 9 in Table I shows that a small but significant constant error is introduced by the change in mercaptan to monomer ratio as the reaction proceeds. Correction for this would raise the line slightly especially at the lower end. The resulting change in slope is small, but the relative change in intercept is substantial.[9]

Discussion

It is of interest to note that Sivertz[10] in reporting a study of the kinetics of addition of butanethiol to styrene estimated a value for the average k_p of 230 at thiol concentrations at which the propagation was assumed to be chiefly due to the one-unit radical. Combination of this with his value of 1.24×10^3 for K_d indicates a value of about 5.4 for C_1, which is comparable to the value reported above for the styrene–ethanethiol system.

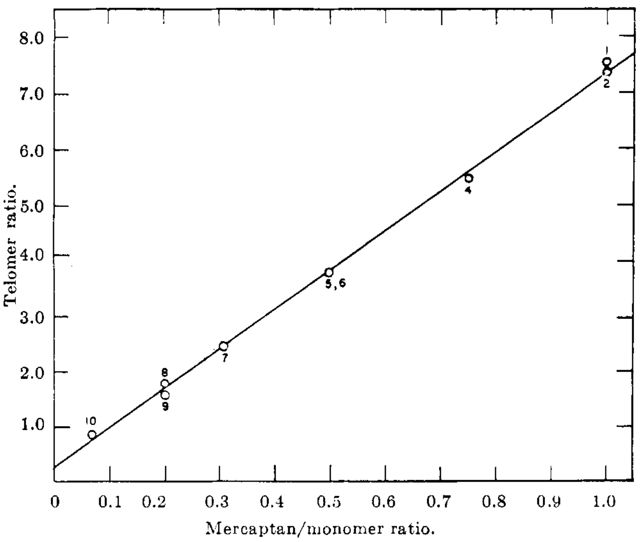

Fig. 2.—Relationship between one-unit to two-unit telomer mole ratio and ethanethiol to styrene mole ratio.

The increase by a factor of 2.4 in the styrene ethanethiol transfer constant going from C_1 to C_∞ is substantially less than has been reported for the haloalkanes.[3] Since the electronegativity of sulfur on the Pauling scale is essentially the same as carbon, it seems unlikely that any polar effect would account for even this difference. Models indicate, however, that there should be appreciably less interference with the formation of the transition state for addition of monomer units to the one-unit radical as compared to radicals possessing two or more styrene units. Results indicate that the value for C_2 is certainly substantially higher than C_1 and may possibly be even higher than C_∞.

Information about the chain transfer constants C_3 to C_5 would be especially interesting for comparison with the bromotrichloromethane–styrene system[3c]; however, a different approach will probably be required because of the difficulty in isolating higher telomers.

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(9) Extrapolation of results from runs 1–3, 8 and 9 to zero per cent styrene consumed and substitution of the resulting ratios in equation 4 would lead to values of 7.03 for C_1 and 14 for C_2.

(10) C. Sivertz, *J. Phys. Chem.*, **63**, 34 (1959).

Photodimers of 4'-Substituted 2-Styrylpyridines[1]

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Photodimers of 2-styrylpyridine and 5-ethyl-2-styrylpyridine substituted with CH_3O, CH_3, NO_2, and $(CH_3)_2N$ in the 4'-positions have been prepared. Irradiation of the free bases or the methiodide salts in solution gave difficultly separable mixtures of dimers, *cis* isomers, and *trans* isomers. Irradiation of the methiodide salts in the solid state yielded the dimeric salts in the cases of 2-styrylpyridine, 5-ethyl-2-styrylpyridine, and to a lesser degree with 4'-methyl-2-styrylpyridine. All other methiodide salts failed to dimerize when irradiated as solids. Solid-state dimerization of the methosulfate derivatives except the two 4'-dimethylamino-substituted derivatives was achieved. The dimeric methosulfates were then converted by anion exchange to the corresponding methiodide salts. Photodimerizations of the substituted styrylpyridine hydrochlorides in aqueous solution were successful in all cases except those of the 4'-nitro-substituted derivatives. Irradiation of suspensions of the hydrochloride salts in heptane gave similar results.

In preceding papers[2,3] the preparation of two photodimers of *trans*-2-styrylpyridine (Ia) was described and their relationship to the *trans–cis* photoisomerization of *trans*-2-styrylpyridine (Ia) was demonstrated. Solid-state irradiation of the methiodide (Ic) and the hydrochloride (Ie) salts to *trans*-2-styrylpyridine (Ia) produced dimers with the same configurations, as indicated by physical data. Solution irradiation of Ia produced only a mixture of *cis* and *trans* isomers. On the other hand, solution irradiation of the methiodide (Ic) or the hydrochloride (Ie) gave mixtures of *cis* and *trans* isomers as well as dimers. Dimer Id, obtained by irradiation of 2-styrylpyridine hydrochloride (Ie), in solution or in the solid state, followed by isolation and quaternization of the dimeric free base (Ib), was identical with dimer Id, obtained by solid-state irradiation of *trans*-2-styrylpyridine methiodide (Ic). In order to extend the dimerization study to substituted derivatives of *trans*-2-styrylpyridine and *trans*-5-ethyl-2-styrylpyridine, a group of derivatives with CH_3O, CH_3, NO_2, and $(CH_3)_2N$ in the 4'-positions were prepared.[4]

In the present work, it was found that 5-ethyl-2-styrylpyridine methiodide (VIc) photodimerized quan-

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(1) Contribution no. 2331 from the Kodak Research Laboratories.

(2) J. L. R. Williams, *J. Org. Chem.*, **25**, 1839 (1960).

(3) J. L. R. Williams, S. K. Webster, and J. A. VanAllan, *ibid.*, **26**, 4893 (1961).

(4) J L. R. Williams, *et al.*, *J. Org. Chem.*, in press.

TABLE I

DIMERS OF SUBSTITUTED 2-STYRYLPYRIDINES

Code	Empirical formula	Analysis			M.p., °C.	Mol. wt., found (Calcd.)	λ_{max}, mμ	$\epsilon \times 10^{-3}$
		Found (calcd.)						
		C	H	N				
Ib	$C_{26}H_{22}N_2$				190–191		264	13.5
IIb	$C_{28}H_{26}O_2N_2$	79.1	5.9	6.7	164–165	409	264	10.5
		(79.6)	(6.2)	(6.2)		(422.5)		
IIIb	$C_{28}H_{26}N_2$	85.7	6.8	7.4	184–185	401	264	9.8
		(86.1)	(6.7)	(7.2)		(390.5)		
IVb	$C_{26}H_{20}N_4O_4$	68.7	4.5	12.1	161–162	*a*	271	34.0
		(69.0)	(4.4)	(12.4)				
Vb	$C_{30}H_{32}N_4$	80.0	7.6	12.0	248–250	505	260	47.0
		(80.3)	(7.2)	(12.5)		(448.6)		
VIb	$C_{30}H_{30}N_2$	85.9	7.3	6.5	143	430	270	10.0
		(86.2)	(7.2)	(6.6)		(418)		
VIIb	$C_{32}H_{34}N_2O_2$	80.2	6.9	6.4	120	536	270	10.8
		(80.3)	(7.2)	(6.7)		(479)		
VIIIb	$C_{32}H_{34}N_2$	86.1	7.6	6.3	115	431	269	15.4
		(85.7)	(7.6)	(6.1)		(446)		
IXb	$C_{30}H_{28}N_4O_4$	70.5	5.7	10.9	180	*b*	273	28.6
		(70.9)	(5.5)	(11.0)				
Xb	$C_{34}H_{40}N_4$	81.3	7.9	10.8	158–159	504	261	36.4
		(81.0)	(7.9)	(11.1)		(504.8)		

[a] Prepared by direct nitration of Ib. [b] Prepared by direct nitration of VIb.

TABLE II

DIMERS OF SUBSTITUTED 2-STYRYLPYRIDINE METHIODIDES

Substituents		Code	Empirical formula	Analysis				M.p., °C.	λ_{max}, mμ	$\epsilon \times 10^{-3}$
				Found (calcd.)						
5-Position	4′-Position			C	H	N	I			
H	H	Id	$C_{28}H_{28}N_2I_2$					310	271	19.3
H	CH_3O	IId	$C_{30}H_{32}N_2I_2O_2$	51.1	4.8	4.6	36.0	251–252	270	17.0
				(51.0)	(4.6)	(4.6)	(35.9)			
H	CH_3	IIId	$C_{30}H_{32}N_2$	53.0	4.8	4.3	37.5	245	270	13.1
				(53.5)	(4.8)	(4.2)	(37.6)			
H	NO_2	IVd	$C_{28}H_{26}N_4I_2O_4$	46.0	3.5	8.0	*a*	265	271	40.1
				(45.7)	(3.5)	(7.6)				
H	$(CH_3)_2N$	Vd	*c*							
C_2H_5	H	VId	$C_{32}H_{36}N_2I_2$	54.7	5.2	4.0	36.3			
C_2H_5	CH_3O	VIId	$C_{34}H_{40}N_2I_2O_2$	53.7	5.1	3.6	33.1	243–244	277	17.6
				(53.4)	(5.3)	(3.7)	(33.2)			
C_2H_5	CH_3	VIIId	$C_{34}H_{40}N_2I_2$	55.6	5.7	3.8	34.2	256–257	275	19.8
				(56.0)	(5.6)	(3.8)	(34.6)			
C_2H_5	NO_2	IXd	$C_{32}H_{34}N_4I_2O_4$	48.5	4.3	7.1	*b*	245–246	277	36.1
				(48.3)	(4.0)	(7.3)				
C_2H_5	$(CH_3)_2N$	Xd	*c*							

[a] Prepared by nitration and quaternization of Ib. [b] Prepared by nitration and quaternization of VIb. [c] Quaternization of Vb and Xb led to doubly quaternized salts, not Vd and Xd.

titatively when irradiated in the solid state. Attempts to photodimerize 4′-methyl-2-styrylpyridine methiodide (IIIc) in the solid state by the benzene suspension method were only partly successful since the dimerizations were shown by ultraviolet studies to be only 90% complete. Similar treatment of 4′-methoxy-2-styrylpyridine methiodide (IIc), 4′-nitro-2-styrylpyridine methiodide (IVc), and 4′-dimethylamino-2-styrylpyridine methiodide (Vc) failed to produce dimers. The analogous 4′-substituted compounds in the 5-ethyl series, VIIc, VIIIc, and Xc, behaved similarly.

When aqueous solutions of the *trans* isomers of Ic to Xc were irradiated, mixtures of dimers, residual *trans* isomers and *cis* isomers resulted. The ratios of the products varied with substitution, and in all cases tedious fractional crystallization of the irradiation mixtures was required to yield the dimers. A more general and facile method for dimer preparation was realized when 5×10^{-2} *M* aqueous solutions of the various 2-styrylpyridine hydrochlorides (Ie–Xe) were irradiated as previously reported[3] for Ie. In preliminary experiments, 500-watt, water-cooled, medium-pressure, immersion-type Hanovia lamps were employed. However, it was found more convenient to expose the stirred aqueous dimerization solutions in open dishes to the light from General Electric GRS lamps. The dimerizations in aqueous solution of 4′-nitro-2-styrylpyridine hydrochloride (IVe) and 4′-nitro-5-ethyl-2-styrylpyridine hydrochloride (IXe) were unsuccessful. Under similar conditions, 4′-dimethylamino-2-styrylpyridine dihydrochloride (Ve) and 4′-dimethylamino-5-ethyl-2-styrylpyridine dihydrochloride (Xe) were converted in low yield to the corresponding dimers Vf and Xf. In all other cases (Ie, IIe, IIIe, VIe, VIIe, VIIIe), the desired dimers were obtained and converted to the free bases, the physical constants of which are listed in Table I. The corresponding methiodides listed in Table II were prepared by quaternization of the dimeric bases.

Since the dimerizations of the nitro derivatives (IVc and IVe, and IXc and IXe) were unsuccessful, direct nitration of Ia and IXa was carried out in order to obtain the 4′-substituted nitro dimers, IVb and IXb, which were then converted through the methosulfates to the dimer methiodides, IVd and IXd.

The differences in the degree of photodimerization of the various substituted methiodides, Ib–Xb, in the solid state are considered to be related to the crystal parameters which dictate the distance between the double bonds of different adjacent molecules in the crystal lattices. Topochemical control by lattice parameters during photodimerization of a group of substituted cinnamic acids has been described by Schmidt.[5] It thus seemed reasonable that substitution and the nature of the anion might control the crystal parameters and therefore the ease of dimerization. Accordingly, a group of 1-alkyl-2-styrylpyridinium salts was prepared in each of which the iodide anion was replaced by the methosulfate in the hope that modification of the lattice parameters might facilitate dimerization. By this method, the solid-state benzene suspension irradiation of 4′-methyl-2-styrylpyridine methosulfate (IIIe), 4′-methoxy-2-styrylpyridine methosulfate (IIe), 4′-nitro-2-styrylpyridine methosulfate (IVe), 4′-ethyl-4′-methoxy-2-styrylpyridine methosulfate (VIIe), and 5-ethyl-4′-nitro-2-styrylpyridine methosulfate (IXe) provided the corresponding methosulfate dimers (IIIf, IIf, IVf, VIIf, and IXf) in quantitative yields. The analogous, doubly quaternized dimethosulfate salts of 4′-dimethylamino-2-styrylpyridine (Ve) and 5′-ethyl-4-dimethylamino-2-styrylpyridine (Xe) failed to yield the corresponding photodimers (Vf and Xf). The methosulfate photodimers, IIIf, IIf, IVf, VIIf, and IXf, were converted by anion exchange in water solution to the corresponding methiodides, all of which were identical in physical properties with those prepared by the other methods mentioned. Compounds IVd and IXd prepared by this route were identical with samples prepared by nitration of the dimers of Ia and VIa.

The 4′-dimethylamino-substituted dimer (Vb) was prepared by solid-state irradiation of the suspension which resulted when a benzene solution of Va was saturated with dry hydrogen chloride. The dimeric free base was then produced by neutralization of the dimer hydrochloride (Vg) with aqueous sodium carbonate. This method failed to give the corresponding dimer from 5-ethyl-4′-dimethylamino-2-styrylpyridine dihydrochloride since a noncrystallizable oil resulted when the irradiated hydrochloride was treated with aqueous sodium carbonate. The method was successful when Ic, IIc, IIIc, VIc, VIIc, and VIIIc were irradiated in the solid state as suspensions in heptane. Compounds IVc and IXc did not dimerize under these conditions. The yields and irradiation times for the preparation of the dimeric bases by irradiation of suspensions of the various hydrochlorides are listed in Table III.

TABLE III

DIMER YIELDS *vs.* IRRADIATION TIMES FOR SUBSTITUTED 2-STYRYLPYRIDINE HYDROCHLORIDES

	In aqueous solution[a]		In solid state[a]	
Dimer	Yield, %	Time, min.[c]	Yield, %	Time, hr.[c]
Ib			67	7
IIb	81	44	23	6
IIIb	38	48	65	11
IVb	0	44	0	16
Vb	10	55	67	7
VIb	48	44	47	8
VIIb	38	46	47	11
VIIIb	24	72	40	7
IXb	0	44	0	16
Xb	26	237	[b]	7

[a] The yield reported is based on isolated dimer. Yields of *cis* isomers produced simultaneously were not determined. [b] Product failed to crystallize. [c] The times listed indicate the period to reach approximate photostationary condition for the equilibrium, *trans* isomer:*cis* isomer:dimer.

Experimental

The methosulfate salts were prepared by quaternization of the corresponding styrylpyridines with dimethyl sulfate. The salts were recrystallized from acetone or acetone–methanol mixtures and submitted for analyses as indicated in Table IV.

The preparations of the *trans*-2-styrylpyridines used in this work were described previously.[4]

All ultraviolet spectra were determined in methanol solution (5×10^{-5} *M*), using a 1-cm. quartz cell in a Cary Model 14 instrument.

TABLE IV

2-STYRYLPYRIDINE METHOSULFATES

				Analysis				
				Found (calcd.)				
5-Position	4′-Position	Code	Empirical formula	C	H	N	S	M.p., °C.
H	CH_3O	IIg	$C_{16}H_{19}NO_5S$	56.5 (57.0)	5.7 (5.7)	3.9 (4.2)	9.2 (9.5)	158
H	CH_3	IIIg	$C_{16}H_{19}NO_4S$	59.5 (59.8)	5.8 (5.9)	4.2 (4.4)	10.1 (10.0)	209–211
H	NO_2	IVg	$C_{15}H_{16}N_2O_6S$	51.2 (51.2)	4.5 (4.6)	7.7 (8.0)	9.1 (9.1)	172
C_2H_5	CH_3O	VIIg	$C_{18}H_{23}NO_5S$	59.3 (59.2)	6.5 (6.3)	3.9 (3.8)	8.7 (8.8)	134
C_2H_5	NO_2	IXg	$C_{17}H_{20}N_2O_6S$	53.7 (53.7)	5.3 (5.3)	7.0 (7.4)	8.8 (8.4)	175
H	H	Ig	$C_{21}H_{21}NO_3S$	68.5 (68.8)	5.9 (5.8)	3.6 (3.8)	8.4 (8.5)	189–190
C_2H_5	H	VIg	$C_{17}H_{21}NO_4S$	61.0 (60.9)	6.4 (6.3)	4.0 (4.2)	9.3 (9.6)	109–111
C_2H_5	CH_3	VIIIg	$C_{18}H_{23}NO_4S \cdot H_2O$	59.1 (58.9)	6.7 (6.9)	3.8 (3.8)	9.4 (8.7)	*a*

[a] An oily solid was obtained and was irradiated as such in suspension.

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(5) G. M. J. Schmidt, at the XVIIIth International Congress of Pure and Applied Chemistry, Montreal, August, 1961.

Irradiations. A. Solid State.—Solid-state photodimerizations of the styrylpyridine methiodides and methosulfates were conducted as benzene suspensions according to the previous description.[3]

Solid-state photodimerizations of the styrylpyridine hydrochlorides were conducted in a manner similar to that described earlier,[3] except that the suspension medium used was heptane since certain of the 5-ethyl-2-styrylpyridinium salts show slight solubility in benzene and irradiations of the salts in solution generally promoted photoisomerization.

B. Solution. In previous work a Hanovia medium-pressure lamp was used. A more convenient method is as follows: In a typical irradiation, a solution of 10 g. (0.55 mole) of *trans*-2-styrylpyridine in a mixture of 10 ml. of concentrated hydrochloric acid and 1 l. of water was placed in a 2-l. evaporating dish. The solution was stirred by means of a Teflon-covered stirrer bar magnetically driven through the bottom of the dish. A GRS sunlamp was placed 12 in. above the surface of the solution. Periodically, aliquots were withdrawn and diluted with water to give 2.5×10^{-5} *M* solutions for ultraviolet examination. Prior to irradiation, the solution had the following characteristics: λ_{max} 328 mμ, ϵ 25,300. After 21 hr. of irradiation, the characteristics of the solution were: λ_{max} 264 mμ, ϵ 8,800, and λ_{max} 321 mμ, ϵ 4,640. The irradiation product was isolated in the manner described.[3]

Nitration of the Dimer of 2-Styrylpyridine (Ib): IVb.—A solution of 7.2 g. of the dimer of Ia (Ib) in 50 ml. of concentrated sulfuric acid was cooled to 10° in an ice bath and to this stirred solution was slowly added 2.6 ml. of concentrated nitric acid. The mixture was allowed to warm up to room temperature, poured into 250 ml. of ice–water, and made basic with ammonium hydroxide. The precipitated solid was collected, washed with water, and recrystallized from ethanol to yield 6.5 g. of product (IVb), m.p. 161–162°.

Anal. Calcd. for $C_{26}H_{20}N_4O_4$: C, 69.0; H, 4.4; N, 12.4. Found: C, 68.7; H, 4.5; N, 12.1.

Nitration of the Dimer of 5-Ethyl-2-styrylpyridine (Vb): IXb.—By the procedure described for IVb there was obtained from 8.4 g. of the dimer (Vb), 6 g. of the dinitro derivative (IXb), melting at 180°.

Anal. Calcd. for $C_{30}H_{28}N_4O_4$: C, 70.9; H, 5.5; N, 11.0. Found: C, 70.5; H, 5.7; N, 10.9.

Quaternization of IVb: Di(1-methyl-2-pyridinium)di(4-nitrophenyl)cyclobutane Iodide (IVd).—A mixture of 1 g. of IVb, obtained by nitration of the dimer of Ia (Ib), and 5 ml. of dimethyl sulfate was heated on a steam bath for 30 min. The solid that separated from the solution was collected, washed with ether, dissolved in 15 ml. of warm water, and 1 g. of potassium iodide was added to the solution. The solid that separated was collected and dried to yield 1.1 g. of the quaternary salt (IVd), m.p. 265°.

Anal. Calcd. for $C_{28}H_{26}N_4O_4I_2$: C, 45.7; H, 3.5; N, 7.6. Found: C, 46.0; H, 3.5; N, 8.0.

Quaternization of IXb: Di(1-methyl-5-ethyl-2-pyridinium)-di(4-nitrophenyl)cyclobutane (IXd).—The preparation of IXd was carried out by the procedure used for the quaternization of IVb. The dimer IXd melted at 245–246°.

Anal. Calcd. for $C_{32}H_{34}N_4O_4I_2$: C, 48.5; H, 4.3; N, 7.1. Found: C, 48.3; H, 4.0; N, 7.3.

The Chemistry of Pyridine. I. Nucleophilic Substitution of 1-Alkoxypyridinium Salts by Mercaptide Ions

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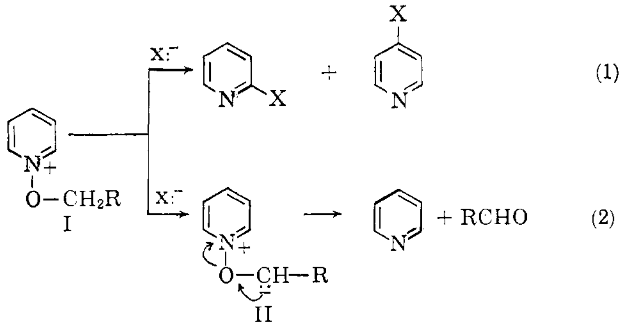
The reaction of 1-alkoxypyridinium salts with propyl- and octylmercaptide ions is described. In each instance, the product consisted of pyridine and a mixture of 3- and 4-alkylmercaptopyridines, predominantly the 3-isomer. These reactions are discussed in the light of existing knowledge of nucleophilic attack on pyridine N-oxides. Unequivocal syntheses of the corresponding 2-, 3-, and 4-alkylmercaptopyridines as reference compounds is reported.

Current interest is centered on the use of pyridine N-oxide and 1-alkoxypyridinium salts as intermediates for the synthesis of substituted pyridines.[2] Nucleophilic substitution in the 1-alkoxypyridinium cation, I, has received considerable attention recently. It was shown that cyanide ion (X = CN) reacted with these salts to form 2- and 4-pyridinecarbonitriles[3] (equation 1) and no substitution was observed at the 3-position of the pyridine ring. The reaction of Grignard reagents with 1-alkoxypyridinium salts was reported recently to yield only 2-substituted pyridines and apparently substitution did not occur at the 3- or 4-position of the ring.[4] These authors offer a mechanism which satisfactorily accounts for the formation of the 2- and 4-substituted pyridines (equation 1).

In our studies, we treated 1-alkoxypyridinium salts with mercaptide and thiophenoxide ions with the aim of introducing the alkyl- and arylmercapto group into the pyridine ring. Initially, this reaction was explored with



the anions of propyl- and octylmercaptide ions and these were found to effect substitution in the pyridine ring to yield the corresponding alkylmercaptopyridines. The reaction of 1-ethoxypyridinium ethyl sulfate with sodium *n*-propylmercaptide was studied in some detail and is presented first. When this reaction was conducted in a mixture of 1-propanethiol and ethanol (10:1) two major fractions were obtained. The first one was identified as pyridine (70%). This product can arise from nucleophilic attack at the α-carbon of the 1-alkoxy side chain *via* the intermediate, II, which decomposes to pyridine and an aldehyde (equation 2).[5]

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[1] Taken from the Ph.D. thesis of Libero A. Gardella, University of Illinois at the Medical Center, Chicago 12, Ill., June, 1962.

[2] For recent reviews on this topic, see (a) D. V. Ioffe and L. S. Eiros, *Russ. Chem. Rev. (Eng. Transl.)*, **30**, 569 (1961); (b) K. Thomas and D. Jerchel, in W. Foerst's "Neuere Methoden der Präparativen Organischen Chemie," Band III, Verlag Chemie, GmbH, Weinheim/Bergstr., 1961, p. 61; (c) A. R. Katritzky and J. M. Lagowski, "Heterocyclic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 61, 102; (d) E. N. Shaw, "Pyridine and Its Derivatives, Part Two," E. Klingsberg, ed., Interscience Publishers, Inc., New York, N. Y., 1961, Chap. IV, pp. 97–153.

[3] (a) W. E. Feeley and E. M. Beavers, *J. Am. Chem. Soc.*, **31**, 4004 (1959); (b) H. Tani, *Chem. Pharm. Bull., Japan*, **7**, 930 (1959); *J. Pharm. Soc., Japan*, **81**, 141 (1961), and papers quoted therein.

[4] O. Cervinka, *Collection Czech. Chem. Commun.*, **27**, 567 (1962).