Benzonitrile Formation in the Pyrolysis of Aromatic Nitrogen Compounds

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Benzonitrile is one of the major nitrogen-containing products obtained from the 700° pyrolysis of various nitroarenes (including nitrobenzene, nitrophthalic acids, and isomeric nitrotoluenes), nitrosobenzene, and *N*-methyleneaniline. Since the thermolysis of *N*-methyleneaniline, a possible interaction product of phenylnitrene and carbene, gave larger benzonitrile conversions than either nitroarene or phenyl azide pyrolyses, it is suggested that such an interaction contributes to benzonitrile formation.

In an investigation of the pyrolyzate composition of substituted phthalic acids, it was found that the major component of the neutral fraction obtained from the pyrolysis of 3- and 4-nitrophthalic acids at 700° was benzonitrile.[1] This and the observations that *N*-sulfinylaniline[2] at 1000° and phenyl azide[3] at 700° both produce benzonitrile suggest that benzonitrile formation might be a general reaction of *N*-aryl compounds during pyrolysis and that this formation might involve nitrene intermediates. Because previous studies of the pyrolysis of nitroarenes under a variety of conditions[4] and of nitrosobenzene[5] did not report the formation of benzonitrile, we have reinvestigated these pyrolyses at 700°.

TABLE I

YIELDS[a] OF SELECTED COMPONENTS PRODUCED IN THE PYROLYSIS OF AROMATIC NITROGEN COMPOUNDS AT 700°

	Nitrobenzene	Nitrosobenzene	*N*-Methyleneaniline	Phenyl azide
Benzonitrile	1.2[b]	0.5	7.7	0.5
Nitrobenzene	0.6			
Naphthalene	0.4	0.2	*c*	0.2
Biphenyl	3.9	1.9	*c*	2.2
Dibenzofuran	3.3	1.4		
Phenol	5.2	3.0		
Aniline	0.04	0.01	11.7[d]	0.2
Diphenylamine	0.1	5.4	*c*	1.4
N-Methylaniline			0.9	
Hydrogen cyanide[e]	6.4	1.0	24.6	8.3

[a] Yields are reported as moles of compound per mole of substance pyrolyzed × 100 and were determined by glpc using internal standards. [b] Yields of benzonitrile from nitrobenzene at 600, 800, and 900° were 1.2, 1.8, and 1.1, respectively. [c] Not determined. [d] Some contribution to aniline yield arises from the hydrolysis of starting material during acid extraction (see Experimental Section). [e] Yields reported as grams of hydrogen cyanide per mole of substance pyrolyzed.

Tables I–III summarize the results of the pyrolyses of nitrobenzene, nitrosobenzene, and isomeric nitrotoluenes at 700°. Results obtained in the pyrolysis under identical conditions of phenyl azide and *N*-methyleneaniline, a possible intermediate in benzonitrile formation, are included for comparison. Benzonitrile was also produced from nitrobenzene (neat) over the temperature range 600–900°, from isomeric nitrotoluenes over the range 500–700°, and from nitrobenzene–benzene solutions at 700°. In experiments where mixtures of nitrobenzene and benzene (ratios ranging from 1:1 to 1:4) were pyrolyzed, the benzonitrile yield (based on total mixture pyrolyzed) was proportional to the nitrobenzene concentration in the mixture.

Possible modes of formation of the major nitrobenzene pyrolyzate constituents, excepting benzonitrile, have been discussed previously.[4,6]

The production of benzonitrile is likely the result of several simultaneous processes including the addition of hydrogen cyanide to benzyne, the coupling of phenyl and cyanide radicals and the decomposition and/or isomerization of phenylnitrene.[3,7] Although the formation of naphthalene in the *N*-aryl compound pyrolyses (see tables) suggests the intermediacy of benzyne, benzyne formation as compared to phenyl radical formation appears to represent a relatively minor path in the decomposition of nitrobenzene[4a] and nitrosobenzene.[4c]

Various oxygen acceptors such as alkyl phosphites,[8,9] metals, and activated charcoal[10] have been reported to convert aromatic nitro and nitroso compounds into nitrenes, and "intractable tars" apparently functioned in this way in the conversion of 2-nitro-*p*-terphenyl into 2-phenylcarbazole.[11] The facts that the pyrolyses of nitrobenzene and nitrosobenzene produce sizable quantities of tar and that carbon monoxide, carbon dioxide, aniline, pyridine, diphenylamine, and benzonitrile are present in the pyrolyzates are indicative of a phenylnitrene intermediate in these reactions. A comparison of benzonitrile yields from phenyl azide (a known phenylnitrene precursor[12]) and nitrobenzene (Table I) shows that benzonitrile formation in the nitrobenzene (and nitrosobenzene) pyrolyses involves additional or more efficient routes than those involved in the decomposition of phenylnitrene. A possible explanation for the higher benzonitrile yields in the nitrobenzene pyrolyses is that, in these experiments, phenylnitrene interacts further with "active" carbon fragments (carbenes) to produce *N*-methyleneaniline, which, after dehydrogenation, isomerizes to benzonitrile. If "tar"

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[1] From 3-nitrophthalic acid (22.8 g) there was obtained 0.4 g of neutrals of which 34% was benzonitrile (glpc area %). Similarly 4-nitrophthalic acid (13.2 g) gave 0.15 g of neutrals of which 20% was benzonitrile.

[2] C. Wentrup, *Tetrahedron*, **27**, 1027 (1971).

[3] E. Hedaya, M. E. Kent, D. W. McNeil, F. P. Lossing, and T. McAllister, *Tetrahedron Lett.*, 3415 (1968).

[4] (a) E. K. Fields and S. Meyerson, *Accounts Chem. Res.*, **2**, 272 (1969); (b) E. K. Fields and S. Meyerson, *Tetrahedron Lett.*, 719 (1971); (c) A. I. Feinstein and E. K. Fields, *J. Org. Chem.*, **37**, 118 (1972); (d) R. A. Marty and P. deMayo, *Chem. Commun.*, 127 (1971).

[5] A. I. Feinstein and E. K. Fields, *J. Org. Chem.*, **36**, 3878 (1971).

[6] E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **89**, 3224 (1967).

[7] W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 4379 (1967).

[8] J. I. Cadogan, *Accounts Chem. Res.*, **5**, 303 (1972).

[9] R. J. Sundberg, *J. Amer. Chem. Soc.*, **88**, 3781 (1966).

[10] H. C. Waterman and D. L. Vivian, *J. Org. Chem.*, **14**, 289 (1949).

[11] G. W. Gray and D. Lewis, *J. Chem. Soc.*, 3501 (1964).

[12] R. A. Abramovitch and E. P. Kyba in "The Chemistry of the Azido Group," S. Patai, Ed., Interscience, New York, N. Y., 1971, Chapter 5.

TABLE II

RELATIVE CONCENTRATIONS[a] OF PYROLYZATE CONSTITUENTS OBTAINED FROM AROMATIC NITROGEN COMPOUNDS AND FROM AN EQUIMOLAR MIXTURE OF *N*-METHYLENEANILINE AND PHTHALIC ANHYDRIDE AT 700°

Component	Nitrobenzene	Nitrosobenzene	Phenyl azide	*N*-Methyleneaniline	*N*-Methyleneaniline–phthalic anhydride[f]
A. Neutral Fraction					
Benzene	7.9	6.3	1.8	2.2	4.1
Toluene				1.1	1.0
Styrene	0.3			0.2	0.6
Benzonitrile	10.4	4.4	20.8	68.3	33.8
Nitrobenzene	2.3				
Naphthalene	4.0	1.0	5.9	0.3	3.5
Cinnamonitrile	0.6[b]	0.3[b]			
Indole			2.2[c]		
Biphenyl	29.8	17.3	17.8	4.8	11.9
1-Naphthonitrile	0.3	0.4	4.5		
2-Naphthonitrile	0.4		2.8		
Dibenzofuran	23.7	13.4			
Carbazole	4.5	8.7	12.4	1.0[d]	0.2[g]
Diphenylamine[e]	1.9	45.2	9.8	0.8	0.2
Wt neutral fraction, g	2.3	6.1	1.5	2.4	3.1
B. Base Fraction					
Pyridine	4.9		0.8	0.2	
Aniline	9.3	18.5	34.3	74.8	17.6
Quinoline	12.8	7.8	9.3	0.5	1.7
Isoquinoline	3.6	1.4	1.1		
Acridine	6.0	8.4	0.4		41.3
Phenanthridine	5.1		3.9	6.7	31.1
Quinaldine			0.7		
Diphenylamine		43.1	2.8		
N-Methylaniline				9.9	3.8
Wt base fraction, g	0.3	0.3	0.4	3.2	1.9
C. Acid Fraction					
Phenol	83.6	89.7			
o-Cyanophenol	0.6				
o-Hydroxybiphenyl	10.5	7.9			
Wt acid fraction, g	1.3	1.1			
Wt compound pyrolyzed, g	9.0	14.4	3.8	6.5	12.1

[a] Relative concentrations are area % as determined by glpc analysis. [b] Glpc analysis does not separate indole and cinnamonitrile. Peak mainly cinnamonitrile on basis of spectra data. [c] Peak mainly indole on the basis of spectra data. [d] *N*-Methylcarbazole also observed in 1.1% concentration. [e] Found in both the neutral and base fraction due to incomplete separation. [f] Fluorene present in 0.9% concentration. [g] *N*-Methylcarbazole.

TABLE III

RELATIVE CONCENTRATION[a] OF BENZONITRILE IN NEUTRAL FRACTIONS OBTAINED ON PYROLYSIS OF ISOMERIC NITROTOLUENES AT 700°

Component	Ortho	Meta	Para
Benzonitrile	14.7	8.3	8.7
o-Tolunitrile	2.6		
m-Tolunitrile		1.9	
p-Tolunitrile			0.2
Naphthalene	5.4	0.1	0.9
Wt neutral fraction, g	2.3	2.4	4.0
Wt acid fraction, g	0.9	1.2	*b*
Wt base fraction, g	1.1	0.4	*b*
Wt substance pyrolyzed, g	10.3	11.5	69.6

[a] Relative concentrations are area % as determined by glpc. [b] Not determined.

formation is taken as a measure of "active" carbon production, then the nitrobenzene pyrolysis produces *ca.* twice the "active" carbon as does the phenyl azide pyrolysis and thus the greater benzonitrile yields. To test the efficiency of benzonitrile production from the probable nitrene–carbene interaction product, *N*-methyleneaniline was pyrolyzed at 500, 600, and 700°. The benzonitrile yields, 0.5, 5.1, and 7.7%, respectively, indicate that *N*-methyleneaniline could be a precursor to benzonitrile in nitrobenzene and nitrosobenzene pyrolyses.

The major nitrogen-containing products from the *N*-aryl compound pyrolyses (in addition to benzonitrile) include diphenylamine, carbazole, and phenanthridine (from *N*-methyleneaniline). The formation paths of diphenylamine and carbazole from phenylnitrene[8] and from nitrosobenzene and phenyl radicals[5] have been proposed previously. Although the conversion of diphenylamine into carbazole has been observed,[13] the extent of reaction is probably small.[14,15] Phenanthridine (low yield) and acridine are produced in the pyrolysis of *N*-benzalaniline[16] and *N*-benzylaniline,[15] respectively, which in turn could arise from the addition

$$\mathrm{Ar\cdot} + \mathrm{ArN{=}CH_2} \longrightarrow \mathrm{Ar\dot{N}{-}CH_2Ar} + \mathrm{Ar_2N{-}CH_2\cdot}$$

of phenyl radicals to *N*-methyleneaniline. *N*-Methylcarbazole could also originate from such an addition followed by ring closure. Product production (phenan-

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(13) A. R. Bruzel and I. Schmeltz, *Tobacco Sci.*, **15**, 44 (1971).

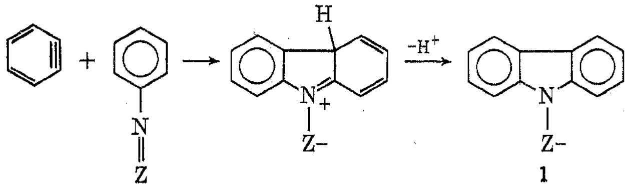
(14) C. Graebe, *Justus Liebigs Ann. Chem.*, **167**, 125 (1873).

(15) H. Meyer and A. Hofmann, *Monatsh.*, **37**, 698 (1916).

(16) G. Pyl, *Chem. Ber.*, **60**, 287 (1927).

thridine, carbazole, *N*-methylcarbazole) in *N*-methyleneaniline pyrolysis is consistent with the proposed path. The pyrolysis of *N*-methylcarbazole under conditions used in the nitroarene experiments results in a 51% yield (isolated) of phenanthridine.

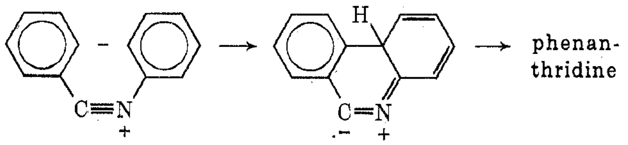
The report[17] that benzyne reacts with nitrosobenzene in tetrahydrofuran to form carbazoles suggests that a similar route to carbazoles from *N*-aryl compounds and benzyne might be available in the vapor phase. In the pyrolyses of nitrosobenzene and phenyl azide, 1



Z = CH$_2$, CH·, N=N, O

loses oxygen and nitrogen, respectively, to form carbazole. In the pyrolysis of *N*-methyleneaniline, 1 couples with H to form *N*-methylcarbazole, loses methylene to form carbazole, or undergoes ring enlargement to form phenanthridine.

Isocyanides have been found to add to benzyne[18] and the adduct 2 arising from the interaction of phenyl



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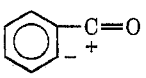
isocyanide and benzyne could produce phenanthridine on ring closure.

An equimolar mixture of *N*-methyleneaniline and phthalic anhydride (a benzyne precursor) was pyrolyzed to test the postulated benzyne–methyleneaniline interaction and subsequent phenanthridine production. While the pyrolysis produced enhanced phenanthridine yields (Table II), a substantial yield of acridine was also observed. Since acridine was not found in the pyrolysis of *N*-methyleneaniline, this experiment means either that benzyne interaction is not important in the *N*-methyleneaniline pyrolyses or that acridine formation (in the methyleneaniline–phthalic anhydride experiment) results from an interaction of *N*-methyleneaniline with a partial breakdown product of phthalic anhydride.



Experimental Section

Ultraviolet spectra were measured in cyclohexane using a Perkin-Elmer Model 202 spectrophotometer, infrared spectra were measured in chloroform or carbon tetrachloride using a Beckman IR-8 spectrophotometer equipped with a mirror beam condenser, and nmr spectra were measured in deuteriochloroform or carbon tetrachloride (TMS internal standard) using a Varian T-60 spectrometer. Mass spectra were determined on a Hitachi RMU-6E double focusing mass spectrometer using 70-eV ionizing energy with the inlet system at 200°. Glpc analyses and preparative separations of the pyrolyzate constituents were carried out on an F & M Model 810 gas chromatograph using a thermal conductivity detector.

Materials.—Nitrobenzene and nitrosobenzene were commercially available samples and were used as received. Nitrobenzene was redistilled prior to use and purity checked by glpc analysis. Phenyl azide was synthesized by the method of Lindsay and Allen,[19] bp 33–35° (1.2 mm), and *N*-methyleneaniline was synthesized by an adaptation of the procedure of Bigelow and Eatough.[20] The properties of the *N*-methyleneaniline were mp 142–144° (lit.[21] mp 140°); uv max (cyclohexane) 211, 253 nm; ir (CCl$_4$) 2840, 1600, 1495, 700 cm^{-1}; nmr (CDCl$_3$) δ 7.3 (m, 5), 4.85 ppm (s, 2); mass spectrum[22] m/e (rel intensity) 105 (MI, 98), 104 (94), 78 (16), 77 (100), 76 (8), 75 (7), 74 (11), 65 (8), 64 (5), 63 (12), 62 (6), 52.5 (10), 52 (25), 51.5 (1), 51 (51), 50 (28), 39 (19), 38 (12), 37 (9), 28 (6), 27 (10).

Pyrolyses.—The pyrolyses were carried out in the apparatus previously described[23] using 14 ml of Berl saddles or Vycor beads, a nitrogen flow of 100 ml/min, and a rotating screw device (driven by a Troemner monodrum unit) for the introduction of the solid samples (or syringe for liquids) into the pyrolysis tube. Samples were introduced at the same rate and contact times were *ca.* 24 sec. The liquid products were collected in two traps, each of which was cooled in a Dry Ice–chloroform–carbon tetrachloride mixture, dissolved in ether, and separated into neutral, acid, and base fractions by extraction with 5% HCl and 5% NaOH (each saturated with NaCl). Separate pyrolysis experiments in which cold traps were eliminated were used in the determination of gaseous products. Hydrogen cyanide was identified by comparison of its infrared spectrum with that obtained from an authentic sample and the quantity produced determined by the Liebig method[24] after trapping in NaOH solution.

Separation and Identification of Components.—Components of the neutral, base, and acid fractions were separated by glpc using a 25 ft × 0.375 in. 20% Apiezon L (Anakrom 50/60 U) column heated at 90° for 8 min and then programmed at 2°/min to 280°.

Identification of components is based on comparisons of glpc retention times and ultraviolet spectra with those obtained from authentic samples. The identities of the following components were additionally confirmed by comparisons of the indicated spectral data with that obtained from authentic materials: ir and nmr, benzonitrile, naphthalene, phenol, diphenylamine; ir, aniline, indole, cinnamonitrile; nmr, *N*-methylaniline, acridine, phenanthridine, biphenyl, dibenzofuran; mass, *o*-cyanophenol, *o*-hydroxybiphenyl. Estimation of relative abundance of constituents are based on area per cent values obtained from glpc using a 12 ft × 0.125 in. Hewlett-Packard Hi-pak Apiezon L column for the neutral and base fractions and a 12 ft × 0.125 in. 2% polyphenyl ether (six ring) column for the acid fraction. The results are reported in Tables II and III. The average deviation of the results of three pyrolyses of nitrobenzene was ±10% of the figure quoted. Yields of selected components were determined in the acid, base, and neutral fractions using the internal standard method. 2-Methylnaphthalene was used as internal standard in the neutral and base fraction analyses and naphthalene in the acid fraction analysis. The results are reported in Table I.

Pyrolysis of *N*-Methylcarbazole.[25]—The pyrolysis of *N*-methylcarbazole (0.70 g), using the conditions above, produced 0.61 g of pyrolyzate. Analysis (glpc) using a 6 ft × 0.125 in. Carbowax 20M column showed the following substances: phenanthridine (63%), carbazole (21%), and *N*-methylcarbazole (14%). The pyrolyzate was separated into a base and neutral fraction by extraction with 5% HCl (saturated with NaCl). Work-up of the base fraction gave 0.36 g of solid which showed only one peak on glpc and had a glpc retention time and uv and ir spectra identical with those of phenanthridine. Carbazole in

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[17] G. W. Steinhoff and M. C. Henry, *J. Org. Chem.*, **29**, 2808 (1964).

[18] R. Knorr, *Chem. Ber.*, **98**, 4038 (1965).

[19] R. O. Lindsay and C. F. H. Allen, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 710.

[20] L. A. Bigelow and H. Eatough, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1932, p 80.

[21] M. M. Sprung, *Chem. Rev.*, **26**, 311 (1940).

[22] Reference 21 reports that *N*-methyleneaniline exists as a cyclic trimer in the solid phase and as a monomer in the vapor phase.

[23] J. M. Patterson, A. Tsamasfyros, and W. T. Smith, Jr., *J. Heterocycl. Chem.*, **5**, 727 (1968).

[24] J. von Liebig, *Justus Liebigs Ann. Chem.*, **77**, 102 (1851).

[25] The authors are indebted to Dr. C. F. Mayer for carrying out this pyrolysis.

the neutral fraction was tentatively identified by its glpc retention time.

Hydrolysis of *N*-Methyleneaniline.—A solution of 4.9 g of *N*-methyleneaniline in 200 ml of ether was extracted with three 300 ml-portions of 5% HCl. The acid extracts were combined and made alkaline by the addition of NaOH pellets. The basic solution was extracted with ether and the ether extract dried over Na_2SO_4. Removal of the ether produced 3.8 g (78%) of oil, identified as aniline by nmr spectroscopy.

Registry No.—Benzonitrile, 100-47-0; nitrobenzene, 98-95-3; nitrosobenzene, 586-96-9; *N*-methyleneaniline, 100-62-9; phenyl azide, 622-37-7; *N*-methylcarbazole, 1484-12-4; *o*-nitrotoluene, 88-72-2; *m*-nitrotoluene, 99-08-1; *p*-nitrotoluene, 99-99-0.

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Synthesis of [1]Benzothieno[3,2-*d*]pyrimidine Derivatives

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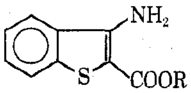
[1]Benzothieno[3,2-*d*]pyrimidine and several of its derivatives have been synthesized. Also described is the first reported example of the [1]benzothieno[3,2-*d*]-*v*-triazine ring system.

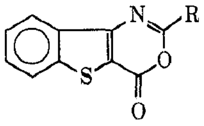
The literature contains only scattered reports concerning the synthesis of [1]benzothieno[3,2-*d*]pyrimidines. McCelland and Stammers[1] described the preparation of 2-methyl-4*H*-[1]benzothieno[3,2-*d*][1,3]oxazin-4-one (**2a**) from 3-acetamidobenzo[*b*]thiophene-2-carboxylic acid by treatment with acetic anhydride. The oxazinone was then converted to the corresponding pyrimidinone (**3a**) by reaction with ammonia. Travin and Magidson[2] later synthesized 4-chloro-2-methyl[1]-benzothieno[3,2-*d*]pyrimidine by treatment of **3a** with phosphorus oxychloride. Mamaev and Lyubimova[3] reported the synthesis of 3,4-dihydro-4-phenyl[1]benzothieno[3,2-*d*]pyrimidin-2(1*H*)-one 5,5-dioxide by the reaction of benzo[*b*]thiophen-3(2*H*)-one 1,1-dioxide with 1,1′-benzylidenediurea.

In a recent paper[4] we described a facile synthesis of methyl 3-aminobenzo[*b*]thiophene-2-carboxylate esters from *o*-nitrobenzonitriles. The synthesis involved nucleophilic displacement of an activated nitro function by methyl thioglycolate anion followed by base-catalyzed ring closure. Using these esters and their corresponding amides as starting materials, we set out to synthesize a variety of [1]benzothieno[3,2-*d*]-pyrimidine derivatives.

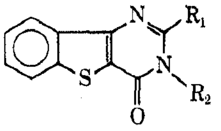
Saponification of the methyl ester **1a**[4] with potassium hydroxide in aqueous alcohol yielded 3-aminobenzo[*b*]-thiophene-2-carboxylic acid (**1b**),[5] characterized as its potassium salt (87% yield). Treatment of **1b** (potassium salt) with acetic anhydride in pyridine produced the previously described oxazinone **2a** (90%). Similar treatment with benzoyl chloride formed the oxazinone **2b** (46%). Reaction of **2a** with ammonia, methylamine, and aniline, respectively, produced **3a** (70%), **3b** (85%), and **3c** (28%). Condensation of **2b** with ammonia yielded **3d** (72%) and with methylamine gave **3e** (98%). Similar treatment with aniline, however, yielded the uncyclized product **4**. All attempts to cyclize **4** to the pyrimidinone were unsuccessful.



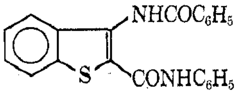
1a, R = CH_3
b, R = H



2a, R = CH_3
b, R = C_6H_5



3a, $R_1 = CH_3$; $R_2 = H$
b, $R_1 = CH_3$; $R_2 = CH_3$
c, $R_1 = CH_3$; $R_2 = C_6H_5$
d, $R_1 = C_6H_5$; $R_2 = H$
e, $R_1 = C_6H_5$; $R_2 = CH_3$
f, $R_1 = H$; $R_2 = H$
g, $R_1 = H$; $R_2 = CH_3$



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When the methyl ester **1a** was allowed to react with formamide at reflux temperature, the product formed was the pyrimidinone **3f** (59%).[6] Alkylation of **3f** with methyl iodide in base gave **3g** (75%). The position of methylation was ascertained by comparison of the nmr, ir, and uv spectra of **3g** and **3b**. They were nearly identical, thus ruling out methylation at the 1 position of **3f**. The chloropyrimidine **5a** (82%)[6a,b] was formed by treatment of **3f** with phosphorus oxychloride. Nucleophilic displacement of the active chlorine of **5a** gave the substituted pyrimidines **5b** (81%), **5c** (82%), and **5d** (92%).[6b] Catalytic hydrogenation of **5a** in the presence of sodium acetate yielded [1]benzothieno-[3,2-*d*]pyrimidine (**5e**, 94%).[6a]

For the preparation of other [1]benzothieno[3,2-*d*]-pyrimidines, it was necessary to synthesize carboxamide analogs of the methyl ester **1a**. Conditions could not be found for the direct conversion of **1a** to the amide **6a** by

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[1] E. W. McClelland and D. W. Stammers, *J. Chem. Soc.*, 78 (1948).

[2] A. I. Travin and O. Y. Magidson, *Khim. Geterctsikl. Soedin.* (Engl. trans.), **3**, 54 (1967).

[3] V. P. Mamaev and E. N. Lyubimova, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 96 (1969); *Chem. Abstr.*, **71**, 70566 (1969).

[4] J. R. Beck, *J. Org. Chem.*, **37**, 3224 (1972).

[5] P. Friedlander and A. Laske, *Justus Liebigs Ann. Chem.*, **351**, 412 (1907).

[6] During the writing of this manuscript, two similar preparations of **3f** were reported: (a) M. Robba, P. Touzot, and R. M. Riquelme, *Tetrahedron Lett.*, 4549 (1972); (b) G. G. De Angelis and H. E. Hess, U. S. Patent 3,706,747 (1972).