TABLE III

MOLAL HEAT CONTENT AND ENTROPY INCREMENTS ABOVE
298.16 °K.

T, °K.	$H_T - H_{298.16}$	$S_T - S_{298.16}$	T, °K.	$H_T - H_{298.16}$	$-S_T$ $S_{298.31}$
350	860	2.65	700	7,210	15.22
400	1800	5.16	800	9,090	17.73
420	2180 (α)	6.09 (α)	900	11,000	19.98
420	2180 (β)	6.09 (β)	1000	12,970	22.05
500	3540	9.05	1100	15,020	24.00
600	5350	12.35			

Table III gives the smooth curve values of the heat content and entropy increments above 298.16° K., for use in thermodynamic calculations.

The heat content values are represented, to within the average deviations shown in parentheses, by the equations

$$\text{TiS}_2(\alpha): H_T - H_{298.16} = 8.08T + 13.67 \times 10^{-3}T^2 - 3624; \quad (1.0\%; 298\text{-}420°\text{K.})$$

$$\text{TiS}_2(\beta): H_T - H_{298.16} = 14.99T + 2.57 \times 10^{-3}T^2 - 4569; \quad (0.3\%; 420\text{-}1010°\text{K.})$$

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Use of the Hammett Equation in the Prediction of Product Ratios in the Schmidt Reaction of Unsymmetrical Diarylethylenes

BY WILLIAM E. McEWEN AND NARIMAN B. MEHTA

The Schmidt reaction has been applied to five additional m- and p-substituted 1,1-diphenylethylenes. The ratios of acetophenone to the m- or p-substituted acetophenone produced in the various reactions have been correlated by an adaptation of the Hammett equation.

In the pinacol–pinacolone rearrangement of a symmetrical pinacol[1] or the Schmidt reaction of an unsymmetrical diarylethylene,[2] a mixture of products is obtained, the ratio of the components depending on the relative rates of migration of the groups which, in the transition state, are in a position to migrate. This competitive migration, when applied to aryl groups, has been compared with the process of aromatic substitution.[3] More detailed treatments of a similar nature, with reference to other rearrangements, have recently appeared.[4]

Among numerous other applications, Hammett has shown that the relative reactivities of m- and p-positions in benzene derivatives with respect to nitration, are in accord with the Hammett equation.[5] This being the case, and extending the analogy between aromatic substitution and the process of migration of aryl groups in competitive rearrangements, the Hammett equation in the latter situation might be modified to

$$\log \text{intrinsic migratory aptitude} = \sigma\rho \quad (1)$$

An examination of the previous data on the Schmidt reaction of unsymmetrical diarylethylenes[2a] indicates that a linear relationship between the logarithms of the product ratios and the sigma

values of the aryl groups undergoing migration does exist. To verify this relationship, five additional reactions of m- or p-substituted diphenylethylenes with hydrazoic and sulfuric acids have been studied. The results are summarized in Table I. With reference to the mechanism of these reactions,[2a] it should be kept in mind that the aryl group which undergoes migration ends up as aniline or an aniline derivative and the remaining aryl group appears finally as acetophenone or a m- or p-substituted acetophenone. Hence a high product ratio of acetophenone to the m- or p-substituted acetophenone indicates preferential migration of the m- or p-substituted phenyl group.

TABLE I

YIELDS OF KETONES IN THE OLEFIN REACTIONS

Starting material
$C_6H_{5-n}X_n$
$\diagdown$ C=CH$_2$
C_6H_5 $\diagup$

X	Yield of ketones, %	
	Acetophenone	m- or p-X·Acetophenone
3,4-Di-CH$_3$	36.6	6.76
p-C$_2$H$_5$	44.6	9.75
m-CH$_3$	34.2	14.5
p-F	45.8	26.1
p-Br	16.0	29.6

An analysis by the method of least squares of the new data, together with the data previously reported,[2a] indicates that the following relationship between product ratios (migratory aptitudes) and the sigma values of the groups undergoing migration holds

$$\log \text{migratory aptitude} = -2.11\sigma + 0.293 \quad (2)$$

The experimental data fit this equation with an average accuracy of ±18%. Figure 1B summarizes the data. In Table II are listed the experimentally observed migratory aptitudes of the nine m- or p-substituted phenyl groups studied (phenyl = 1), and the modified values derived by use of equation (2). The intercept in equation

(1) (a) W. E. Bachmann and J. W. Ferguson, THIS JOURNAL, 56, 2081 (1934); (b) W. E. Bachmann and F. H. Moser, ibid., 54, 1124 (1932); (c) M. Tiffeneau and A. Orekhoff, Bull. soc. chim. France, 35, 1639 (1924); (d) H. H. Hatt, A. Pilgrim and E. F. M. Stephenson, J. Chem. Soc., 478 (1941); (e) R. Gaertner, J. Org. Chem., 15, 1006 (1950).

(2) (a) W. E. McEwen, M. Gilliland and B. I. Sparr, THIS JOURNAL, 72, 3212 (1950); (b) L. P. Kuhn and J. DiDomenico, ibid., 72, 5777 (1950).

(3) G. W. Wheland, "Advanced Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 517.

(4) (a) P. D. Bartlett and J. D. Cotman, Jr., THIS JOURNAL, 72, 3095 (1950); (b) P. I. Pollak and D. Y. Curtin, ibid., 72, 961 (1950); (c) W. von E. Doering and L. Speers, ibid., 72, 5515 (1950); (d) S. L. Friess and N. Farnham, ibid., 72, 5518 (1950); (e) D. J. Cram, ibid., 71, 3863 (1949).

(5) L. P. Hammett, "Physical Organic Chemistry," 1st ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 198.
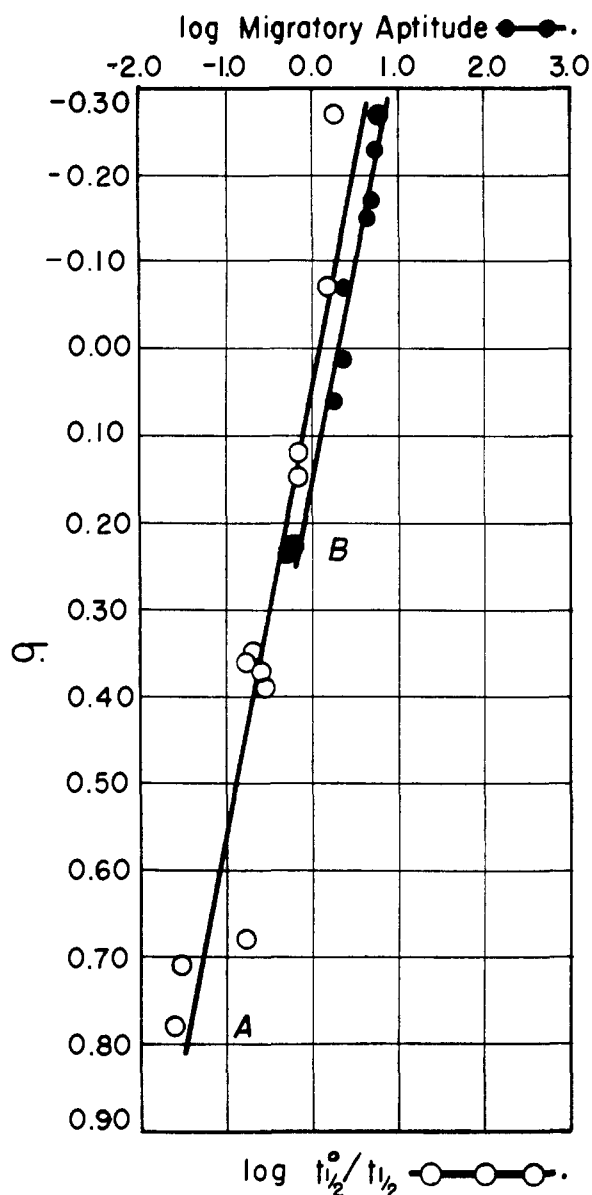
log Migratory Aptitude ●—●.

Fig. 1.—The Hammett equation applied to (A) the Schmidt reaction of *m*- and *p*-substituted benzoic acids and (B) the Schmidt reaction of *m*- and *p*-substituted unsymmetrical diarylethylenes.

(2) is probably due to some systematic error in the experimental data, possibly related to the by-products, which were not investigated in any of the

TABLE II

MIGRATORY APTITUDES IN THE SCHMIDT REACTION OF OLEFINS

Group	Found	Modified
p-Anisyl	6.12	7.20
3,4-Dimethylphenyl	5.41	5.95
p-Tolyl	5.00	4.47
p-Ethylphenyl	4.57	4.08
m-Tolyl	2.36	2.74
p-Biphenylyl	2.30	1.88
p-Fluorophenyl	1.75	1.45
Phenyl	1.00	—
p-Chlorophenyl	0.62	0.85
p-Bromophenyl	.54	.84

reactions except that of 1,1-diphenylethylene itself.[2a]

If the rate-determining step in the Schmidt reaction of *m*- and *p*-substituted benzoic acids were the migration of the aryl group with simultaneous loss of nitrogen from the adduct, I, then a comparison of the rates of nitrogen evolution would afford a measure of the relative migratory aptitudes of the various aryl groups. Briggs and Lyttleton have determined the $t_{1/2}$ of nitrogen evolution for a number of *m*- and *p*-substituted benzoic acids in the Schmidt reaction, at 40°, in trichloroethylene solution, with sulfuric acid as the catalyst.[6] A plot of log $t^0_{1/2}/t_{1/2}$, where $t^0_{1/2}$ refers to benzoic acid itself and $t_{1/2}$ represents a substituted benzoic acid, *versus* sigma (Fig. 1A) indicates a good agreement with the Hammett equation.

$$\begin{array}{c} OH \\ | \quad\; H \\ | \quad | \quad \oplus \\ Ar—C—N—N\!\!\equiv\!\!N \\ | \\ OH \quad I \end{array}$$
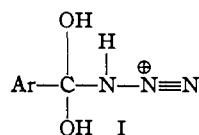
Analysis of these data by the method of least squares shows rho to have a value of −1.97, almost identical with the slope in the 1,1-diarylethylene case (equation 2). This fact suggests that the slow step in the acid reactions is indeed the migration step and further that the relative rate of migration is not markedly affected by the other groups bonded to the carbon atom from which the aryl group migrates.

It is of obvious interest to attempt an extension of the above approach to the pinacol–pinacolone rearrangement of symmetrical pinacols. Examination of Fig. 2 reveals that the migratory aptitudes[1] in this reaction do not fit equation (1). Even in this case, however, the data crudely fit a plot of
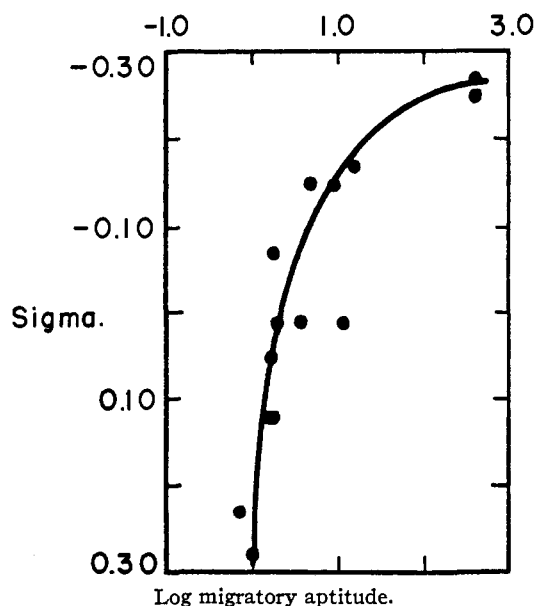

Log migratory aptitude.

Fig. 2.—Intrinsic migratory aptitudes of *m*- and *p*-substituted phenyl groups in the pinacol-pinacolone rearrangement of symmetrical pinacols correlated with Hammett's sigma values.

(6) L. H. Briggs and J. W. Lyttleton, *J. Chem. Soc.*, 421 (1943).

positive curvature.[7] Perhaps the use of this curve and available sigma values for *m*- and *p*-substituted phenyl groups not yet investigated in the rearrangement of symmetrical pinacols, would afford a fair prediction of the migratory aptitudes to be expected of these groups. In this connection, it is interesting that the migratory aptitude of the *p*-biphenylyl group (*σ* = 0.009), 11.5 according to Bachmann and Ferguson,[1a] does not fit the curve at all well. The more recently determined values for the *p*-biphenylyl group, 3.75 by the use of perchloric acid in effecting the rearrangement,[1d] or 1.87 by the use of acetyl chloride, benzene, acetic acid mixture,[1d] fit the curve much better.

In view of the fact that the migratory aptitudes for the pinacol–pinacolone rearrangement of symmetrical pinacols have been determined by a variety of workers, using different experimental conditions for effecting the rearrangements, and using indirect methods of analysis of the products, it is not surprising that the results afford only a rough correlation with the sigma values of the migrating groups. Also, no differentiation has been made between rearrangements of *meso*-pinacols as compared to racemic pinacols in most of the cases reported in the literature. Only Gaertner[1e] has reported the behavior of both stereoisomeric forms in the case of the two pinacols he subjected to the rearrangement. He found only a qualitative agreement on the migratory aptitudes of the aryl groups compared.

The main difference between the intrinsic migratory aptitudes found in the pinacol–pinacolone rearrangement of symmetrical pinacols and those found in the Schmidt reaction of olefins is the difference in the spread of the values. Perhaps the abnormally high heat of formation of molecular nitrogen, eliminated in the Schmidt reactions, as compared to water, eliminated in the pinacol rearrangements, influences this spread. Also, if the interpretation of Swain and Langsdorf[7] on the meaning of the various rho values found in the application of the Hammett equation to the correlation of the rates of displacement reactions of organic halides can be extended to the rearrangements under discussion, then the Schmidt reactions entail a more perfectly synchronous migration of the aryl group and elimination of nitrogen than the corresponding migration of the aryl group and loss of water in the pinacol rearrangements. The negative value of rho in both cases indicates that the atoms to which the aryl groups migrate, nitrogen in the Schmidt reactions and carbon in the pinacol rearrangements, are relatively more positive in the transition than in the ground states, with this effect more pronounced in the pinacol rearrangements.

Although it would be interesting to compare the spread in the values of migratory aptitudes in carbon to oxygen migrations with the spread of values in carbon to carbon and carbon to nitrogen migrations, no quantitative data in this connection appear to be available at the present time.

Of course, nothing which has been said concerning the relative rates of migration of aryl groups in the Schmidt reaction of olefins (and possibly carboxylic acids also) can be applied to the Schmidt reaction of ketones and aldehydes. In one sense, however, the data on the olefin reactions makes Smith's interpretation of the mechanism of the ketone reactions[8] seem all the more plausible. The olefin work provides a framework within which the apparent lack of influence of migratory aptitudes in determining product ratios in the ketone reactions can better be evaluated.[9]

Experimental[10]

Preparation of the Monosubstituted Diphenylethylenes.— The following olefins were prepared by methods described in the literature: 1-phenyl-1-(*p*-bromophenyl)-ethylene,[11] 1-phenyl-1-(*p*-ethylphenyl)-ethylene[12] and 1-phenyl-1-(*p*-fluorophenyl)-ethylene.[12]

1-Phenyl-1-(*m*-tolyl)-ethylene.—The Perrier modification[13] was used in the preparation of phenyl *m*-tolyl ketone from 81.0 g. (0.52 mole) of *m*-toluyl chloride, 70.0 g. of anhydrous aluminum chloride, 42.0 cc. of benzene and 400 cc. of carbon disulfide. The reaction proceeded at room temperature and was completed by refluxing for 30 minutes. The carbon disulfide was distilled, the last part *in vacuo*, the residue added to ice and hydrochloric acid solution, then extracted with benzene. The benzene solution was washed with sodium bicarbonate solution, and the benzene distilled until the distillate was no longer turbid. To the residual solution was added 200 cc. of a 4 *M* solution of methylmagnesium bromide in ether. The crude carbinol obtained from the reaction mixture was dehydrated by refluxing for one hour with 200 cc. of 20% sulfuric acid solution. Distillation of the organic layer afforded 61.0 g. (60%) of 1-phenyl-1-(*m*-tolyl)-ethylene, b.p. 122–123° (0.85 mm.).

Anal. Calcd. for C₁₅H₁₄: C, 92.74; H, 7.26. Found: C, 92.43, 92.71; H, 7.34, 7.31.

1-Phenyl-1-(3′,4′-dimethylphenyl)-ethylene.—Starting with 106.0 g. (1.0 mole) of *o*-xylene and 140.0 g. (1.0 mole) of benzoyl chloride, the preparation of 1-phenyl-1-(3′,4′-dimethylphenyl)-ethylene was carried out as described above for 1-phenyl-1-(*m*-tolyl)-ethylene, 141.9 g. (70%) being obtained, b.p. 203–206° (15 mm.).

Anal. Calcd. for C₁₆H₁₆: C, 92.25; H, 7.74. Found: C, 91.80; H, 7.92.

Reaction of the Olefins with Hydrazoic Acid.—The reactions were carried out according to the directions in the previous paper of this series.[2a] In every case but one (the reaction of 1-phenyl-1-(*p*-fluorophenyl)-ethylene) the ketone fractions were separated into their component parts by distillation *in vacuo* through an efficient column. The results are described in Table I. Each of the pure *m*- or *p*-substituted acetophenones so obtained was characterized by at least one known solid derivative.

In the reaction of 1-phenyl-1-(*p*-fluorophenyl)-ethylene, it was not possible to obtain a quantitative separation of acetophenone and *p*-fluoroacetophenone by fractional distillation. The entire ketone fraction was collected *in vacuo*, 27.9 g., b.p. 67–70° (5 mm.), being obtained from 61.6 g. (0.31 mole) of the olefin.

Anal. Found: C, 76.23, 76.19; H, 6.59, 6.54; F, 6.19.

On the basis of the carbon analysis it can be calculated that the mixture consisted of 36.3% of *p*-fluoroacetophenone

(7) Compare the discussion of C. G. Swain and W. P. Langsdorf, Jr. (THIS JOURNAL, **73**, 2813 (1951)) on the cause of positive curvature in the application of the Hammett equation to the correlation of rates of displacement reactions of certain organic halides.

(8) (a) P. A. S. Smith, *ibid.*, **70**, 320 (1948); (b) P. A. S. Smith and B. Ashby, *ibid.*, **72**, 2503 (1950); (c) P. A. S. Smith and J. P. Horwitz, *ibid.*, **72**, 3718 (1950).

(9) For an interpretation of the Schmidt reaction of aldehydes see a forthcoming paper by W. E. McEwen, W. E. Conrad and C. A. Vander-Werf.

(10) Analyses by Weiler and Strauss, Oxford, England, and by the Huffmann Laboratory, Denver, Colorado. All b.p.s' are uncorrected.

(11) R. Stoermer and M. Simon, *Ber.*, **37**, 4163 (1904).

(12) F. Bergmann and J. Szmuszkowicz, THIS JOURNAL, **70**, 2748 (1948).

(13) See L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath Co., Boston, Mass., 1941, p. 192.

and 63.7% of acetophenone. The fluorine analysis indicates 45% of p-fluoroacetophenone and 55% of acetophenone. We consider the carbon analysis to be more accurate than the fluorine analysis, and calculated yields based on the results of the carbon analysis are given in Table I.

In each reaction a copious amine fraction was also obtained, but no attempt was made to separate the components. Sulfonation derivatives were also formed in some of the reactions.

LAWRENCE, KANSAS　　　　　　　　RECEIVED AUGUST 6, 1951

The Reaction of s-Aliphatic Amines with Phosphorus Pentasulfide; Thiophosphoric Amides. II

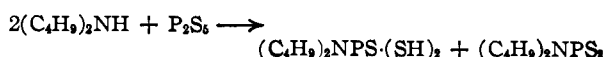## BY GENE WISE[1] AND HERMAN P. LANKELMA

s-Aliphatic amines, R_2NH, react with phosphorus pentasulfide to give thiophosphoric amides. Depending upon reaction conditions a monamide, $R_2N \cdot PS(SH)_2$, a mixed diamide, $R_2N{>}PS \cdot SH$, or a triamide $(RNH)_3PS$ is obtained. By further
$$\begin{array}{c} R_2N \\ RNH \end{array}{>}PS \cdot SH$$
reaction with the amine, the monamide is easily converted to the diamide and the latter to the triamide. Amides of the above types were prepared using di-n-propyl-, di-n-butyl-, di-n-amyl- and dibenzylamines. No diamides $(R_2N)_2PS(SH)$ or triamides $(R_2N)_3PS$ were obtained.

Previous work in this Laboratory[2] has shown that phosphorus pentasulfide forms diamides $(RNH_2)PS \cdot SH$, with primary aromatic amines and triamides $(RNH)_3PS$ with both primary aliphatic and aromatic amines. Attempts to prepare a monamide $(RHN)PS \cdot (SH)_2$, from aniline were unsuccessful. Attempts to prepare triamides, $(R_2N)_3PS$, from s-aliphatic amines and phosphorus pentasulfide gave oils which were not obtained in analytical purity. Michaelis[3] reported the preparation of the triamide, N,N',N"-hexaethylthiophosphoramide′[$C_2H_5)_2$-N]$_3$PS, from N-diethyl amidodichlorothiophosphate $(C_2H_5)_2N]_3P$, and sulfur. It was described as an oil which could not be distilled even in vacuo. It was identified by analysis for nitrogen which gave only fair agreement with the calculated value.

The present work is a further study of the reaction of s-aliphatic amines with phosphorus pentasulfide. The amines employed were di-n-propyl, di-n-butyl, di-n-amyl and dibenzyl. Parallel results were obtained with each. Di-n-butylamine will be used for discussion.

Buck, Bartleson and Lankelma[2] obtained diamides, $(RHN)_2PSSH$, by the action of aniline and o-chloroaniline with phosphorus pentasulfide in molar ratios of 4:1. The reaction was carried out at a temperature of about 30° in a diluent such as toluene. The reaction occurred rapidly, with a copious evolution of hydrogen sulfide. With dibutylamine, under the same conditions, we obtained a yellow insoluble product, but no hydrogen sulfide was released. Since the filtrate contained appreciable amounts of unreacted amine, the reaction was repeated, using two molar quantities of amine. The reaction proceeded as before, and the yield from a given amount of phosphorus pentasulfide was the same. The product was water insoluble and alkali soluble. Upon exposure to air, it hydrolyzed quite rapidly, releasing hydrogen sulfide but it could be kept in a desiccator over phosphorus pentoxide. Analysis agreed with the formula for the monamide.
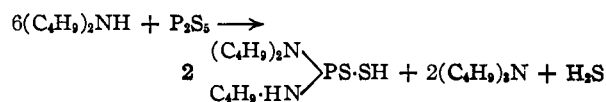
(1) Standard Oil Co. (Ohio) Fellow in Chemistry, Western Reserve University, 1949–1950.

(2) A. C. Buck, J. D. Bartleson and H. P. Lankelma, THIS JOURNAL, 70, 744 (1948).

(3) A. Michaelis, Ann., 326, 129 (1903).

The formation of the monamide could occur by the reaction

$2(C_4H_9)_2NH + P_2S_5 \longrightarrow$
$$(C_4H_9)_2NPS \cdot (SH)_2 + (C_4H_9)_2NPS_2$$

The identity of the second product of this reaction could not be established. The filtrate upon removal of the solvent yielded a viscous sticky resin which could not be purified.
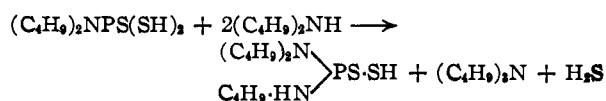
By heating six moles of amine with one mole of phosphorus pentasulfide at temperatures of 150–180° triamides, $(RHN)_3PS$, have been obtained from both aliphatic and aromatic primary amines. The cyclic s-amine, tetrahydroquinoline also gave a triamide, $(C_9H_{10}N)_3PS$.[2]

With s-aliphatic amines, such as dibutylamine, as previously stated, oils were obtained which were not identified, since attempts to purify them were unsuccessful. We found similarly that heating the amine with phosphorus pentasulfide using from one to eight moles of amine to one mole of phosphorus pentasulfide gave only brittle resins or sticky viscous oils. With higher molar ratios of amine, 12 to 15/1, however, a white crystalline solid separated at about 150°. This product was insoluble in water, but soluble in dilute sodium hydroxide solution. It was much more stable in air than the monamide and could be crystallized from methyl alcohol. The product was identified as a mixed diamide by analysis. The over-all reaction may be represented by the equation

$6(C_4H_9)_2NH + P_2S_5 \longrightarrow$
$$2 \begin{array}{c} (C_4H_9)_2N \\ C_4H_9 \cdot HN \end{array}{>}PS \cdot SH + 2(C_4H_9)_3N + H_2S$$

The tributylamine was not identified here but was shown to be present in the next stage of the reaction, the formation of the triamide.

The same mixed diamide was obtained in good yield by heating the monamide with an excess of amine for about an hour at 160°.

$(C_4H_9)_2NPS(SH)_2 + 2(C_4H_9)_2NH \longrightarrow$
$$\begin{array}{c} (C_4H_9)_2N \\ C_4H_9 \cdot HN \end{array}{>}PS \cdot SH + (C_4H_9)_3N + H_2S$$

When the reaction mixture just described was