Equilibrium and ^{31}P Chemical Shifts of the Adducts of Trialkylphosphines and Isothiocyanates, and Reactions of Triethylphosphine and Benzoyl Isothiocyanate

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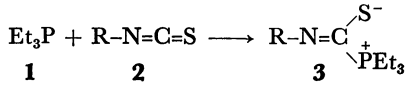
The adducts (**3**) of triethylphosphine (**1**) and several isothiocyanates (**2**) were prepared. Equilibrium constants of the adducts (**5**) from tributylphosphine (**4**) and phenyl (**2b**), benzoyl (**2e**), and *p*-toluenesulfonyl isothiocyanates (**2f**) were determined in some solvents. The ^{31}P chemical shifts of **5** were measured in DMF, and correlated with Hammett σ_p constants. Reactions of **3e** with **1** and **2e** gave phosphonium thiocyanates of **6** and **7**, and of **11**, respectively. Methylation of **3e** gave *S*-methyl *N*-benzoylmonothiocarbamate (**16**).

It has been known for 100 years that triethylphosphine forms the *1*:*1* adducts with carbon disulfide and isothiocyanates,[1] and the presence of *P–C* bond was exemplified by X-ray crystallographic study[2a] after much discussion. However, little is known on the reaction of the adducts and the formation of reactive alkylidenephosphoranes was recently reported by the reaction of tributylphosphine and carbon disulfide adduct with active acetylenes.[3]

This paper describes the general formation of the adducts of trialkylphosphines and several isothiocyanates, the equilibrium of the adducts in solution[4] and ^{31}P chemical shifts of the adducts,[4] and reactions of the adducts of triethylphosphine and benzoyl isothiocyanate.

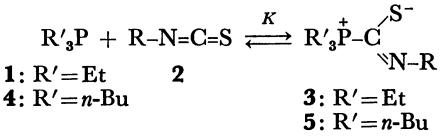
Formation of the Adducts (3). An equimolar mixture of triethylphosphine (**1**) and isothiocyanates (**2**) gave adducts (**3**) in hexane and/or ether. The results are summarized in Table 1.



a, R=Me; **b**, R=Ph; **c**, R=α-$C_{10}H_7$; **d**, R=MeCO; **e**, R=PhCO; **f**, R=*p*-$MeC_6H_4SO_2$; **g**, R=Ph_2P(S)

The yields of **3** were high when the substituent (R) is electron-withdrawing. The adducts (**3b, e,** and **f**) gave correct elemental analyses, but it was not possible to obtain them for other adducts. Especially, **3d** and **3g** decomposed during recrystallization. The adducts of tributylphosphine and methyl and phenyl isothiocyanates could not be precipitated from the reaction mixture under similar conditions. These facts are compatible with observed equilibrium constants (see below).

Equilibrium of the Adducts in Solution. The equilibrium constants (*K*) of the adducts (**3** and **5**) from isothiocyanates (**2**) and tributylphosphine (**4**) or **1** were determined for the first time in some solvents spectrophotometrically, although the presence of the equilibrium was suspected before.[2c]



1: R′=Et **4**: R′=*n*-Bu **2** **3**: R′=Et **5**: R′=*n*-Bu

In the present systems, the extinction coefficients due to starting materials, phosphine and isothiocyanates, were negligible at 340 nm. Therefore, the extinction

TABLE 1. THE ADDUCTS (**3**) OF TRIETHYLPHOSPHINE AND ISOTHIOCYANATES

3	R	Mp (°C)	Yield (%)	Elemental analyses (%)[a] C	H	N	S
3a	Me	79.5—80.0	67	50.05 (50.24)	8.98 (9.49)	7.50 (7.32)	18.71 (16.76)
3b	Ph	62.0—63.0 (lit,[1e] 63)	53				
3c	α-$C_{10}H_7$	112—114 (dec)	77	68.46 (67.30)	7.72 (7.31)	4.85 (4.62)	
3d	MeCO	62—66	89	49.08 (49.30)	8.21 (8.27)	7.24 (6.39)	14.17 (14.62)
3e	PhCO	106.5—109.0 (dec)	96	59.74 (59.77)	7.21 (7.16)	5.06 (4.98)	11.31 (11.40)
3f	*p*-$MeC_6H_4SO_2$[b]	148.5—149.5	94	50.95 (50.74)	6.75 (6.69)	4.20 (4.23)	19.19 (19.35)
3g	Ph_2P (S)	99—101	69	59.21 (58.00)	6.62 (6.40)	3.56 (3.56)	15.88 (16.30)

a) The values in the parentheses are the calculated values. b) Mol wt: 329 (VPO method in dioxane) (calcd: 331.9), indicating almost no dissociation in dioxane.

coefficients due to the formation of the adducts at 340 nm were measured at several ratios of phosphine to the corresponding isothiocyanate, and the K value was calculated according to Drago's method.[5] In most cases, isosbestic points were observed, indicating the presence of equilibrium.[4] A typical example is shown in Fig. 1. The results are summarized in Table 2.

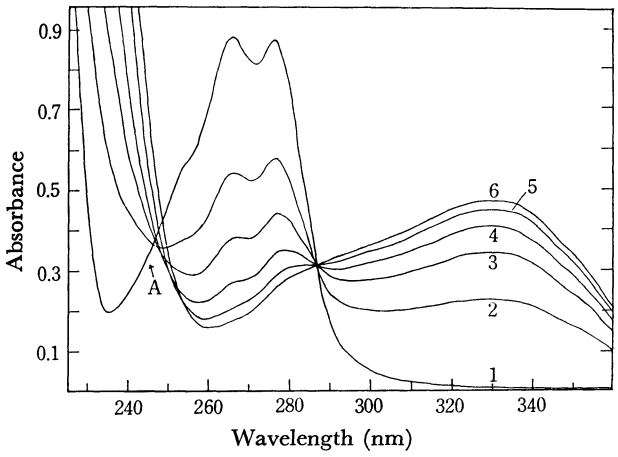


Fig. 1. UV Spectra of triethylphosphine (**1**) and phenyl isothiocyanate (**2b**) system in acetonitrile (24 °C). The ratio of **1** to **2b**: 2=4.22; 3=10.5; 4=21.1; 5=42.1; 6=84.3. 1 is the spectrum of **2b**. Concentration of **2b**, 7.42×10^{-5} M, was maintained constant throughout the measurement (*cf.* Table 4). A: One of isosbestic points should appear here, which is not observed due to absorption of excess **1**.

Table 2. Equilibrium Constants (K) at 24 °C

System	Solv.	K (1/mol)	ε (340 nm)	λ_{max} (nm)	Dielectric constant
4+**2b**	MeCN	840±43	6500	331	37.5
	Me_2CO	323±6	5600	337	20.7
	CH_2Cl_2	277±20	6400	334	8.9
	Et_2O	3.7—6.7		340	4.3
	n-C_6H_{14}	1.5—3.5		340	1.9
1+**2b**	MeCN	2910±120	6100	330	
4+**2e**	MeCN	$(3.4\pm1.0)\times10^4$		315	
4+**2f**	MeCN	$(2.4\pm0.5)\times10^4$		307	

The equilibrium constant becomes larger and hence the stability of the adducts increases according to the increase of polarity of solvents and the introduction of electron-withdrawing substituents. These effects are accompanied by blue shift of λ_{max} of absorption of the adducts. The result is consistent with $n\rightarrow\pi^*$ nature of the absorption but the molar extinction coefficient (*ca.* 6000) is very large for that. In the case of **5f**, the equilibrium lies completely to the adducts when two moles of **4** is added to one mole of **2f** in acetonitrile. The equilibrium constant of **2b** is smaller with **4** than that with **1**, probably because of the bulkiness of **4**, but this does not affect λ_{max} of the absorption. These results are consistent with the easiness of formation of the adducts during their preparation.

Since the attainment of the equilibrium between **4** and methyl isothiocyanate (**2a**) was very slow and isosbestic points could not be observed in the cases of allyl and diphenylphosphinothioyl isothiocyanates (**2g**), equilibrium constants for these systems could not be determined. Similar equilibrium of the betaine with *P–C* bond has been determined in the reaction of tributylphosphine (**4**) with benzylidenemalononitrile.[6a]

^{31}P Chemical Shifts of the Adducts (5). The ^{31}P-NMR chemical shifts (δ_P) of the adducts (**5**) were measured by mixing *N,N*-dimethylformamide (DMF) solutions of **4** and **2** to yield samples of about 0.83 M concentration for each reagent. The results are shown in Table 3.

Table 3. ^{31}P Chemical shifts of the adducts (**5**) in DMF at 34 °C

5	R	δ_P (ppm)	σ_p of R[a]
5a	Me	−18.3	−0.17
	CH_2=$CHCH_2$	−18.1	—
5b	Ph	−20.0	−0.01
5c	α-$C_{10}H_7$	−20.9	—
5g	Ph_2P (S)	−21.9 (J_{PP} 110 Hz)	0.28[8]
	Et_2NCS	−22.2	0.34[b]
5e	PhCO	−23.1	0.43[9]
5d	MeCO	−23.3	0.50
5f	p-$MeC_6H_4SO_2$	−26.8	0.72[c]

a) The σ_p values were taken from Ref. 7, unless otherwise stated. b) For MeNHCS group. c) For $MeSO_2$ group.

The δ_P values of the adducts (**5**) and the adduct of tributylphosphine with carbon disulfide (δ_P=−21.5 ppm in DMF) are similar to those of phosphonium salts (*cf.* $Bu_3\overset{+}{P}Et$ Br^-, δ_P=−35.5 ppm),[6b] supporting the betaine structure of **5** with *P–C* bond in solution.

Plots of the δ_P data against Hammett σ_p values of the R group gave a rather good straight line (ρ=−8.68, r=0.979), where two of σ_p values were quoted from those of the corresponding analogous substituents.

In these measurements, no residual **4** was detected except for **2a**, in which the rate of formation of the adduct should be slow. The equilibrium is shifted almost to the adducts (**5**) in the concentration used, as shown by a simple calculation using the K values shown in Table 2. However, when excess **4** was used for **2b**, two peaks were observed which correspond to **4** and **5b**, respectively, showing that the rate of equilibration is slow for observation by NMR.

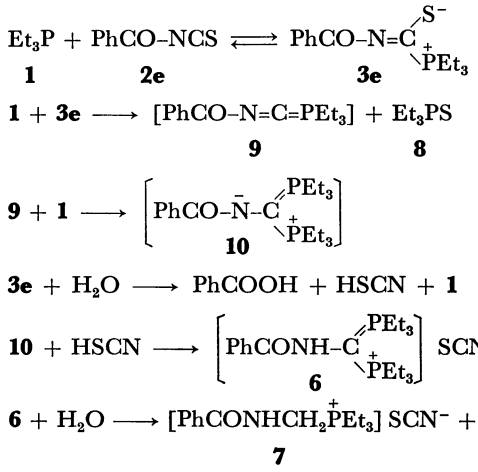
Some Reactions of the Adducts (3). In the measurement of the equilibrium constant of the adduct (**3e**), a deviation from isosbestic points in UV spectra was observed when a large excess of **4** was used.

Therefore, a mixture of benzoyl isothiocyanate (**2e**) and two molar amounts of **1** was refluxed in acetone for 2 h. α-Triethylphosphonio-α-benzoylaminomethylenetriethylphosphorane thiocyanate (**6**), benzoylaminomethyltriethylphosphonium thiocyanate (**7**), triethylphosphine sulfide (**8**), and benzoic acid were obtained in 73, 14, 72, and 53% yields, respectively.

Two phosphorus atoms in **6** were equivalent in ^{31}P-NMR spectrum. Reaction of an equimolar mixture of **1** and **3e** gave a similar result.

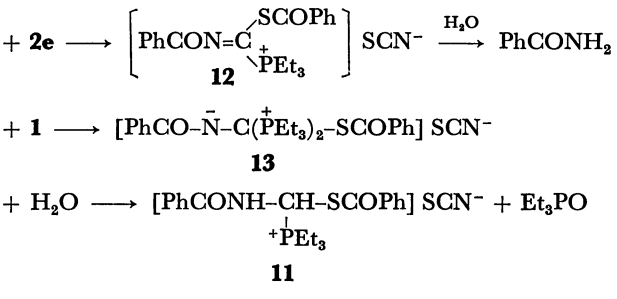
The compound **7** is considered to be a hydrolysis product of **6** by moisture in acetone. In fact, standing of a mixture of **2e** and two molar amounts of **1** in acetone at room temperature for 71 h gave no **6**, but **7**, **8**, and benzoic acid in 61, 65, and 34% yields, respectively.

Their formation can be rationalized by the following scheme.

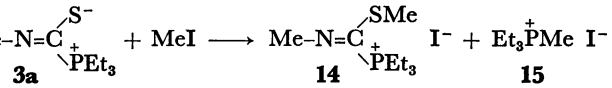


A facile desulfurization of **3e** by **1** to form a new heterocumulene (**9**) is assumed as a preceding step for formation of betaine (**10**), which is stabilized as the phosphonium salt (**6**).

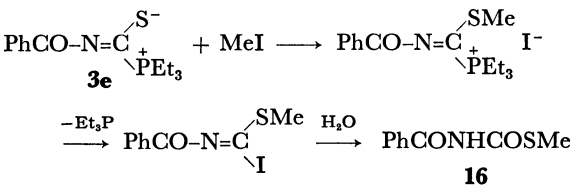
On the other hand, reaction of **1** with two molar amounts of **2e** in refluxing acetone afforded benzamide (23%) and α-benzoylamino-α-benzoylthiomethyltriethylphosphonium thiocyanate (**11**) (27%). This reaction is explained as follows.



Methylation of **3a** with methyl iodide in ether gave triethyl-α-methylimino-α-methylthiomethylphosphonium iodide (**14**, 44%) at room temperature along with a small amount of triethylmethylphosphonium iodide (**15**).

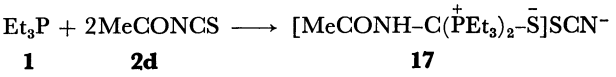


Similar methylation of **3b** gave only **15**. On the other hand, methylation of **3e** in refluxing acetone afforded 31% of *S*-methyl *N*-benzoylmonothiocarbamate (**16**) and 46% of benzamide. The formation mechanism is considered as follows.



The adduct (**3f**) was stable in refluxing acetonitrile against **1** or methyl iodide, but gave 22% of **15** and 64% of *p*-toluenesulfonamide in refluxing methyl iodide.

Reaction of **1** with two molar amount of **2d** afforded a substance considered to be **17** based on the spectral data but repeated elemental analyses could not give the correct values.



Experimental

All the boiling and melting points are uncorrected. The UV and IR spectra were taken with Hitachi EPS-3 and Hitachi EPI-G2 spectrophotometers, respectively. The ^{1}H-NMR spectra were measured with a Hitachi R-24 spectrometer using tetramethylsilane as an internal standard. The ^{31}P-NMR spectra were determined with a Hitachi R-20B-204-PB spectrometer using 85% phosphoric acid as an external standard. Concentration of each reagent was adjusted to be 0.83 M in DMF. The MS spectra were measured with a Hitachi RMU-6L spectrometer. All the reactions were carried out under nitrogen.

Materials. Triethylphosphine,[10] acetyl,[11] benzoyl,[12] *p*-toluenesulfonyl,[13] diphenylphosphinothioyl,[14] and *N,N*-diethylthiocarbamoyl isothiocyanates[15] were prepared by the reported methods. The others were commercially available and used after purification.

*Preparation of the Adducts (**3**).* A typical procedure is described for **3e**.

A mixture of 2.72 g (23.0 mmol) of triethylphosphine (**1**) and 3.80 g (23.3 mmol) of benzoyl isothiocyanate (**2e**) in 60 ml of hexane and 10 ml of ether was stirred at room temperature for 2 h. The resulting precipitates were recrystallized from benzene to give 6.18 g (96%) of **3e**, mp 106.5—109.0 °C (dec).

Preparation of **3a** was carried out in ether for 3 h, those of **3b**—**3d** in hexane for 2 h, and those of **3f** and **3g** in hexane–ether for 3 h. Adducts **3a** and **3b** were recrystallized from ether, and **3c**, **3f**, and **3g** from benzene. The results are summarized in Table 1.

Determination of Equilibrium Constants (K). According to Drago's method,[5] equilibrium constant (*K*) can be related to absorbance (d) of the mixture at a specified wavelength, where absorption of starting materials (A and B) can be neglected.

$$A + B \overset{K}{\rightleftharpoons} C$$

$$1/K = d/\varepsilon_c + \varepsilon_c/d \times ab - (a+b)$$

a, b: initial concentration of starting materials, A and B

ε_c: molecular extinction coefficient of the adduct (C) at a specified wavelength.

A typical example for the calculation of K and ε_c is shown in Table 4, and the UV spectra of this system is shown in Fig. 1.

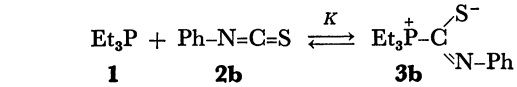


Table 4. Calculation of equilibrium constant of triethylphosphine (**1**) and phenyl isothiocyanate (**2b**) in acetonitrile (24 °C)

No. of the Solution	PhNCS ($\times 10^3$ M)	Et_3P ($\times 10^3$ M)	Absorbance (at 340 nm)
1	0.0742	0.000	0.000
2	0.0742	0.313	0.202
3	0.0742	0.782	0.309
4	0.0742	1.564	0.366
5	0.0742	3.128	0.407
6	0.0742	6.256	0.428

ε_c	$10^3/K$				
	2	3	4	5	6
6000	0.336	0.322	0.325	0.288	0.249
6100	0.347	0.340	0.356	0.344	0.357
6200	0.358	0.358	0.387	0.400	0.464
6300	0.369	0.376	0.418	0.456	0.571
6400	0.380	0.394	0.449	0.512	0.679
6500	0.391	0.412	0.479	0.568	0.786
6600	0.402	0.430	0.510	0.624	0.894
6700	0.413	0.448	0.541	0.680	1.001
6800	0.424	0.466	0.572	0.736	1.109

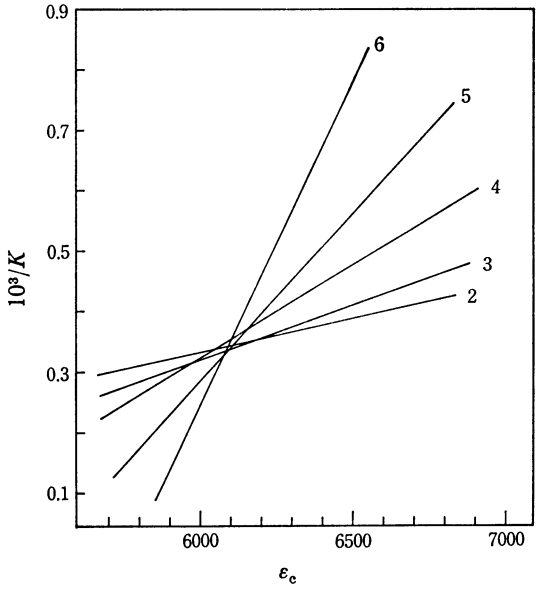


Fig. 2. Plot of ε_c against $10^3/K$ shown in Table 4.

Plot of $1/K$ *vs.* ε_c for each mixture gives a straight line, and $1/K$ and ε_c are determined at the cross point (Fig. 2).

Reactions of Triethylphosphine (1) with Benzoyl Isothiocyanate (2e). a) *2*: *1* reaction: 1) A mixture of 1.76 g (14.7 mmol) of **1** and 1.25 g (7.68 mmol) of **2e** in 30 ml of acetone was refluxed for 2 h. After evaporation of acetone, a small amount of benzene was added to the residue to precipitate 1.20 g (2.80 mmol, 73%) of **6**. Standing of the filtrate afforded 0.163 g (0.52 mmol, 14%) of **7**. The filtrate was chromatographed on silica gel. Elution with benzene–acetone (19: 1) gave 0.25 g (2.05 mmol, 53%) of benzoic acid and 0.415 g (2.76 mmol, 72%) of **8**, the separation of which was carried out using aqueous sodium carbonate. The spectral data of **8** were in agreement with those of an authentic sample.

6: mp 132.5—134.0 °C (from benzene–acetone); IR (KBr): 3240 (NH), 2050 ($^-$SCN), and 1660 cm^{-1} (CO). The ^{1}H-NMR spectrum in $CDCl_3$ showed a broad singlet at δ 8.65 due to NH (1H) proton and the signal disappeared by addition of D_2O; ^{31}P-NMR (DMF): δ_P −35 ppm.

Found: C, 59.13; H, 8.56; N, 6.65; S, 7.60%. Calcd for $C_{21}H_{36}N_2OP_2S$: C, 59.13; H, 8.51; N, 6.57; S. 7.52%.

7: mp 127.5—128.5 °C (from acetone); IR (KBr); 3210 (NH), 2050 ($^-$SCN), and 1650 cm^{-1} (CO). The ^{1}H-NMR spectrum in $CDCl_3$ showed signals at δ 4.51 (dd, J_{NHCH} 6.0, J_{PCH} 5.3 Hz, 2H, CH_2) and 9.35 (bs, 1H, NH). By addition of D_2O, the latter disappeared and the former changed to a doublet (J 5 Hz); ^{31}P-NMR (DMF): δ_P −28 ppm.

Found: C, 57.78; H, 7.75; N, 9.32; S, 10.18%. Calcd for $C_{15}H_{23}N_2OPS$: C, 58.04; H, 7.47; N, 9.02; S, 10.33%.

2) A mixture of 0.573 g (4.85 mmol) of **1** and 1.306 g (4.65 mmol) of **3e** in 50 ml of acetone was refluxed for 3 h. Similar treatment gave 0.543 g (1.27 mmol, 55%) of **6**, 0.133 g (0.43 mmol, 18%) of **7**, 0.283 g (1.9 mmol, 81%) of **8**, and 0.134 g (1.09 mmol, 47%) of benzoic acid.

3) Reaction of 0.959 g (8.11 mmol) of **1** and 0.721 g (4.42 mmol) of **2e** in 20 ml of acetone at room temperature for 71 h afforded 0.42 g (1.35 mmol, 61%) of **7**, 0.216 g (1.44 mmol, 65%) of **8**, and 91 mg (0.75 mmol, 34%) of benzoic acid.

b) *1*: *2* reaction. A mixture of 1.27 g (10.8 mmol) of **1** and 3.55 g (21.7 mmol) of **2e** in 50 ml of acetone was refluxed for 4.5 h. After evaporation, small amounts of benzene and acetone were added to precipitate 1.30 g (2.91 mmol, 54%) of **11**. The filtrate was chromatographed on silica gel. Elution with acetone gave 0.60 g (4.95 mmol, 23%) of benzamide. From other fractions, **8** and benzoic acid were identified by IR.

11: mp 151.0—152.0 °C (from benzene–acetone); IR (KBr): 3150 (NH), 2050 ($^-$SCN), 1652, and 1678 cm^{-1} (CO). The NMR spectrum in $CDCl_3$ showed signals at δ 6.97 (dd, J_{HNCH} 7.8, J_{PCH} 9.6 Hz, 1H, CH) and 10.3 (bd, 1H, NH). By addition of D_2O, the latter disappeared and the former changed to a doublet (J_{PCH} 9.6 Hz). Mol wt (VPO method in pyridine): 451.2 (calcd 477.8).

Found: C, 59.39; H, 6.18; N, 6.27; S, 14.75%. Calcd for $C_{22}H_{27}N_2O_2P_2S_2$: C, 59.17; H, 6.09; N, 6.27; S, 14.36%.

Methylation of 3. a) **3a**: A mixture of 0.761 g (3.98 mmol) of **3a** and 0.652 g of methyl iodide in 10 ml of ether was stirred overnight at room temperature to give 0.58 g (44%) of **14**, mp 101.5—103.0 °C (from 2-propanol).

Found: C, 32.51; H, 6.30; N, 4.06%. Calcd for $C_9H_{21}NPSI$: C, 32.44; H, 6.35; N, 4.20%.

Before the recrystallization of **14**, the presence of **15** was confirmed by NMR.

b) **3b**: A mixture of 1.08 g (4.27 mmol) of **3b** and 0.66 g of methyl iodide in 10 ml of ether was stirred overnight to precipitate **15** (1.01 g, 91%). The spectral data were in agreement with an authentic sample.

c) **3e**: A mixture of 0.622 g (2.21 mmol) of **3e** and 0.5 ml of methyl iodide in 30 ml of acetone was refluxed for 1 h. After evaporation, benzene was added to precipitate 37 mg of benzamide. The filtrate was chromatographed on silica gel. Elution with benzene–acetone (9: 1) gave 0.132 g (0.68 mmol, 31%) of **16**, mp 152 °C (from methanol) (lit,[16] 152—153 °C). IR (KBr): 3250 (NH), 1698 (SCO), and 1630 cm^{-1} (PhCO); MS: *m/e* 195 (M^+, 35%), 147 ($PhCONCO^+$, 95), 105 ($PhCO^+$, *ca.* 100), and 77 (Ph, 100).

Elution with benzene–acetone (3: 1) gave 74 mg of benzamide (46% in total).

d) **3f**: A solution of 0.978 g (2.96 mmol) of **3f** in 30 ml of methyl iodide was refluxed for 20 h. After evaporation, 0.171 g (22%) of **15** was obtained. The filtrate was chromatographed on silica gel. Elution with benzene–acetone (4: 1) gave 0.319 g (64%) of *p*-toluenesulfonamide.

Reaction of 1 and Acetyl Isothiocyanate (2d) in the Ratio of 1: 2.

A mixture of 0.68 g (5.75 mmol) of **1** and 1.15 g (11.4 mmol) of **2d** in 50 ml of acetone was stirred at room temperature for 6 days. The resulting precipitates were collected and recrystallized from methanol to give 0.279 g of **17**. The filtrate was chromatographed on silica gel. Elution with benzene–acetone (3: 1) gave 0.197 g (23%) of **8**. **17**: mp 158–159 °C (from MeOH); IR (KBr): 3150 (NH), 2050 (-SCN), and 1680 cm^{-1} (CO); NMR (D_2O): δ 2.2 (s, 3H, Me) and 0.9—3.0 (m, 30H, 6Et).

Found: C, 47.21—47.48; H, 8.18—8.48; N, 9.93—11.64; S, 14.51—19.09%. Mol wt: 372 (186×2: VPO method in pyridine). Calcd for $C_{16}H_{34}N_2OP_2S_2$: C, 48.46; H, 8.64; N, 7.06; S, 16.17%. Mol. wt.: 396.5.

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