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(18) Ionization potentials (I_p) of *o*-, *m*-, and *p*-methylanisoles are 8.1, 8.1, and 8.0 eV, respectively.[19] I_p of aromatic compounds correlates linearly with the oxidation potential.[20] Appearance potentials of *m*- and *p*-methylanisoles cation radicals are 8.56 and 8.48 eV, respectively.[21]
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(23) It should be noted that although the relative positive charge adjacent to the methoxy group in methylanisole cation radicals is generally great, methoxyl displacement by nitrile was rather inefficient, because the intermediate **4** would be of higher energy than the intermediate **2**.
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Reaction of Isocyanides with Thio Acids[1]

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Reaction of isocyanides, **1**, with thiocarboxylic acids, **2**, have been found to give novel *N*- thioformyl-*N*- acylamides, **3**, and in certain instances, thioformamide **4**. The formation of **3** thus represents a departure from the usual reaction of mercaptans or carboxylic acids with **1**. The former usually give simple alkylthio α adducts, while formamide and acid anhydride formation results from reaction of the latter with **1**. When phosphorus thio acids are herein substituted for **2**, simple α adducts **5** are first formed which, *via* measurable first-order kinetics, are transformed to novel, stable *N*- thioformyl-*N*- phosphoramides, **6**. The reaction rates are shown to depend on the nature of both the phosphorus thio acid and the isocyanide, with no **6** evident from reaction of phosphinodithioic acid with **1**. Finally, reaction of dithiocarbamic acids (*via* their salts) with **1**, is shown to give the α adduct **7** in a reaction that is largely reversible at high temperatures.

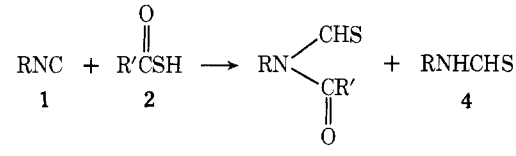
The reaction of mercaptans with organic isocyanides has been shown to give α adducts or isothiocyanates, depending upon the reactants, catalyst, and reaction systems.[2] On the other hand, α adducts arising from carboxylic acids are unstable, with formamide and acid anhydrides as the products isolated.[3]

It was therefore of interest to study the reaction of isocyanides with thio acids. These latter materials have chemi-

cal properties akin to those of both mercaptans and carboxylic acids and consequently could form either the respective analogous α adducts or thioformamides; alternatively, possessing unique features of their own, thio acids might be expected to react *via* a singular reaction mode with isocyanides.

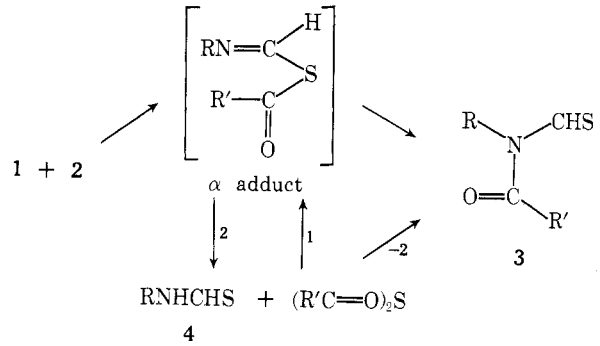
Combination of isocyanide 1 and thiocarboxylic acids, **2**, in inert solvents such as ether or benzene, produced an exotherm with quick disappearance of 1 (as observed by monitoring the diminishing isocyanide ir absorption maximum at 4.7 μ). Depending upon the thio acid and isocyanide employed, *N*-alkyl-*N*-acylthioformamide, **3**, is formed, along with varying amounts of *N*-alkylthioformamide 4 (Scheme I).

Scheme I



By-product 4 most likely arises *via* cleavage of the initial but unstable α adduct, with formation of anhydrosulfide. This pathway is similar to that suggested for the reaction of carboxylic acids with isocyanides. Moreover, it is entirely possible that this route facilitates the formation of 3 *via* acylation of 4 by the anhydrosulfide. In fact, it has been demonstrated (see Experimental Section) that these latter two reagents, in the presence of added base, give appreciable amounts of 3. Of course, this acylation may well occur initially at the thiono sulfur (with isocyanide behaving as a base), giving rise to the identical α adduct intermediate derived from simple α addition of thio acid 2 to isocyanide 1. Less likely would be direct acylation of nitrogen in 4 to form 3. These various pathways are set forth in Scheme II.

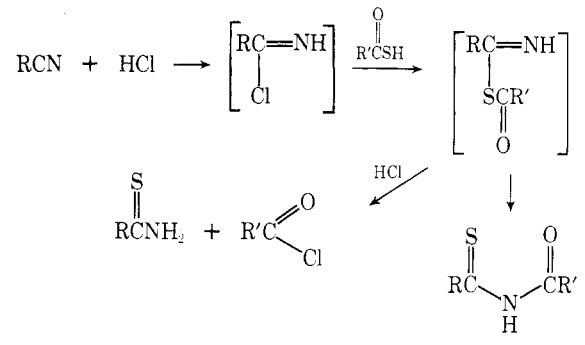
Scheme II



Formation of 3 *via* the α adduct shows a similarity to the acid-catalyzed conversion of nitriles to thioamides. In this classical synthesis,[4] hydrogen chloride both promotes the addition of thio acid to nitrile and serves to cleave the adduct to thioamide and acid chloride. However, if the adduct contains an acyl group with a fair degree of migratory aptitude (such as chloroacetyl), *N*-acylthioamides can be exclusively formed[5] (Scheme III).

Due partly to this undesirable migration when preparing primary thioamides from nitriles, the readily available phosphorodithioic acids $[(RO)_2PS_2H]$ can be successfully substituted in place of thiocarboxylic acids.[6] The thiophosphoryl group apparently is slow to migrate to nitrogen and hence is completely cleaved to $(RO)_2PSCl$ and primary thioamide.

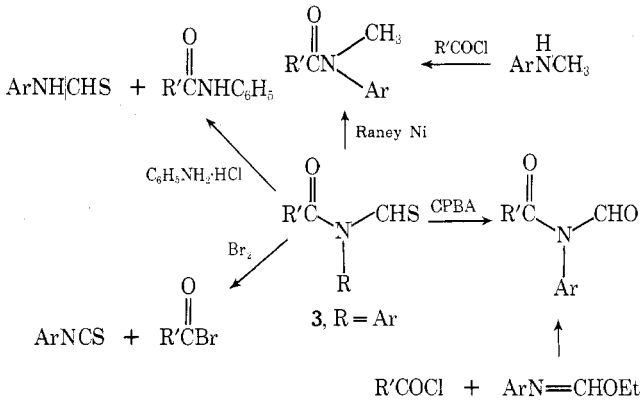
Scheme III



The contrasting properties of different thio acids are also apparent in their reaction with isocyanides. While thioacetic and thiopropionic acids gave about 10–20% thioformamide 4 with aryl isocyanides and *ca.* 50% thioformamide with α-methylbenzyl isocyanide, both thiobenzoic and chlorothioacetic acids gave wholly 3 with aryl isocyanides.

Structure proof for the *N*-acylthioformanilides rests on both chemical transformations and spectral evidence. Raney nickel reduction of 3 reduced the thioformyl group to *N*-methyl, while oxidation with *m*-chloroperbenzoic acid (CPBA) gave the *N*-formyl analog. These degradation products had been prepared previously by other methods[7] as shown in Scheme IV. Finally, bromination of 3 gave carbon–nitrogen cleavage with formation of isothiocyanate and acyl bromide, while this same bond was cleaved by aniline to anilide and thioformanilide.

Scheme IV



The yellow *N*-formyl-*N*-acylamides, **3**, are characterized spectrally by a carbonyl absorption at 5.8–5.9 μ. This of course is at higher frequency than found for the normal amide carbonyl absorption, undoubtedly due to the shortened carbonyl bond (more sp^2 character) which results from greater nitrogen lone-pair interaction with the thiono group. The thioformyl proton is also quite explicit as recorded *via* nmr. The sharp singlet appears at *ca.* δ 10.5, downfield by about 60–100 Hz from the thioformyl proton in the by-product thioformamides, **4**.

The facile reaction of thiocarboxylic acids and isocyanides to form **3** prompted an investigation of this reaction with thiophosphoric acids. These easily derived materials are generally more stable than thiocarboxylic acids. Furthermore, excellent synthetic methods also exist for some of the analogous phosphono- and phosphinodithioic acids.[8]

Mixing any of the phosphorus thio acids with isocyanide produced an immediate reaction, with nearly, but not complete, disappearance of the isocyanide band at 4.7 μ. Simultaneously, there was noted the appearance of a medium to

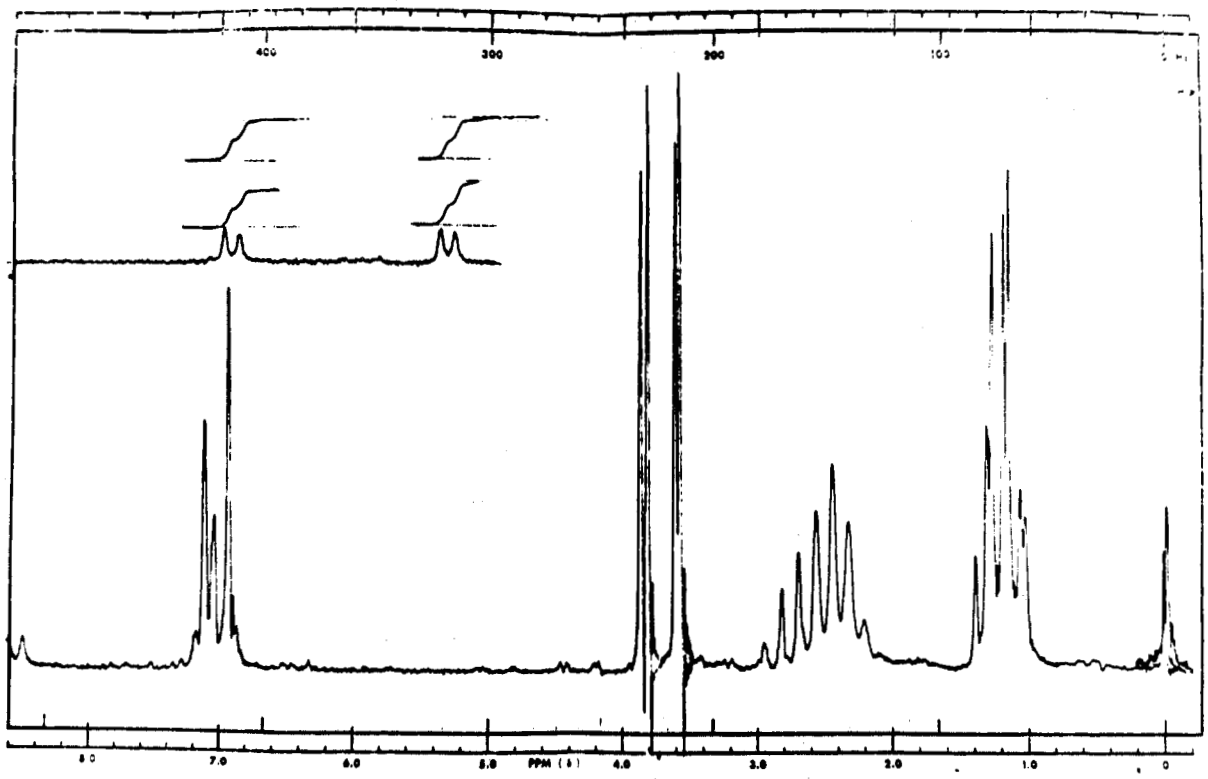


Figure 1. Nmr (CCl_4) at *ca.* 1 half-life of **5**, derived from 2,6-diethylphenyl isocyanide and $(CH_3O)_2PS_2H$, in its conversion to **6c**.

intense C=N band at 6.1–6.2 μ. Nmr spectra of the reaction mixtures usually revealed a doublet at *ca.* δ 8.7 (J = 6 Hz), resulting from coupling with phosphorus. These properties would indicate the initial product to be the α adduct. Both the nmr and ir absorptions agree well with those observed for a similar moiety (–S—CH=N) in α adducts of mercaptans to isocyanide.[2] There are however, some sharply delineating distinctions of these α adducts, **5**, that differentiate them from earlier mercaptan α adducts.

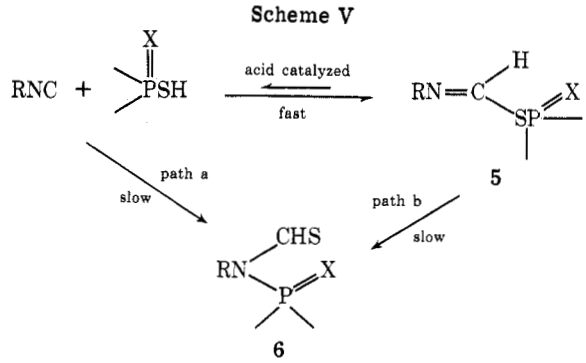
First, no pairs of syn and anti adducts are clearly distinguishable in **5**. In favorable circumstances, only one sharp low-field doublet is observed with no other absorption in that region. In other instances, small, minor peaks, some broadened, are seen in this region, but this is interpreted as arising from side reaction (thioformamide formation) rather than evidence of syn–anti isomerism.

Second, the α adducts from phosphorus thio acids appear to exist in equilibrium with small amounts of isocyanide and thio acid. Indeed, even with excess thio acid present, a small but distinguishable isocyanide ir absorption is still evident. Moreover, the presence of small amounts of excess thio acid invariably causes the low-field doublet to collapse to a singlet. This is interpreted as an acid-catalyzed dissociation of the α adduct (at least breakage of one bond between phosphorus and the α proton).

Finally the most distinguishing characteristic of the α adducts from phosphorus thio acids and isocyanide, **5**, are their measurable rearrangement to *N*-thioformylphosphoramides, **6**. The new materials are characterized by a downfield nmr absorption greater than δ 10, which invariably appears as a doublet (J = 7 Hz) regardless of the acid concentration. The C=N absorption at 6.2 μ is no longer present in **6**. Figure 1 shows an nmr spectrum of **5c** partially converted to **6c**.

The facile but slightly reversible α addition of phosphorus thio acids to isocyanide, followed by a slow irreversible rearrangement to the *N*-thioformylphosphoramide, is shown in Scheme V.

Scheme V



It is apparent from examination of Scheme V that at least two possible alternative mechanisms exist for formation of the final product. Path Va represents a direct attack on the isocyanide nitrogen, while path Vb involves an intramolecular migration of the phosphorus group with cleavage of the P–S bond. If the latter is correct, the migration must necessarily be slower than that observed in reaction of thiocarboxylic acids with isocyanides, to allow **5** to be observed at all. This lesser migratory aptitude is in accord with the reaction of phosphorus thio acids with nitriles, discussed earlier.

Rate data were compiled by measuring, as a function of time, the area under the nmr peaks (1) for the α proton from the initially formed α adduct and (2) for the *N*-thioformyl proton. The measurements show that the formation of **6** is first order with respect to [**5**] and independent (within limits) of thio acid concentration. Unfortunately the observed kinetics do not serve to distinguish between path a and path b, as rates *via* either mechanism would be independent of thio acid concentration. The measured rates do however distinguish between rearrangement proclivities of the original adducts from the various phosphorus thio acids, and these are plotted in Figure 2.

It is apparent that phosphorodithioic acids rearrange

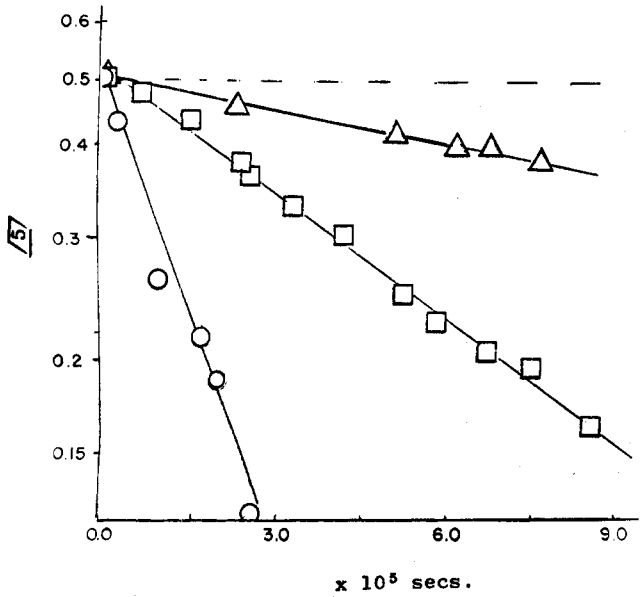


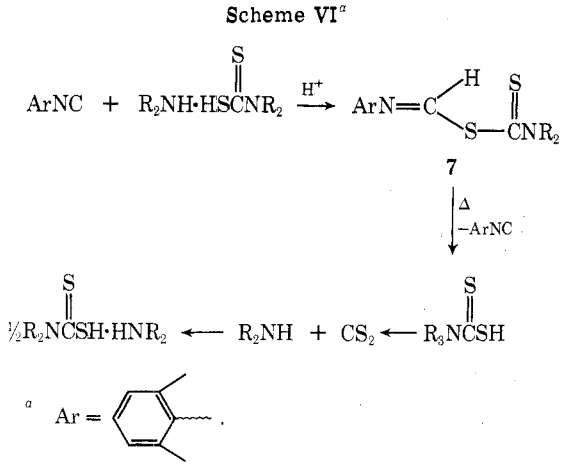
Figure 2. Rearrangement rates of α adducts **5** to thioformylphosphorus amides **6**. Material **5** was derived from 2,6-diethylphenyl isocyanide and phosphorus acids as follows: (○) $(CH_3O)_2PS_2H$; (□) $(C_2H_5O)_2PS_2H$; (△), $C_2H_5OP(CH_3)S_2H$; (– – –) $(C_6H_5)_2PS_2H$.

faster than the analogous phosphonic acids, while α adducts from phosphinodithioic acids do not measurably convert to **6**, even at elevated temperatures. Rationales for the observed order would at present be necessarily speculative without further concrete evidence regarding the mechanism.

Although dithiocarbamic acids are particularly unstable,[9] an isocyanide adduct can be isolated from such acids. One method which met with some success was to neutralize the dithiocarbamate salt formed from carbon disulfide and morpholine in the presence of isocyanide. Reaction could be effected by placing the salt in tetrahydrofuran with 2,6-xylyl isocyanide, cooling to 0–5° and slowly adding 85% phosphoric acid.

The reaction mixture, as monitored by ir methods, displayed a much diminished isocyanide absorption. This absorption did not entirely disappear, even when small additional amounts of phosphoric acid or morpholine dithiocarbamate were added. The reaction mixture was then poured into ice water and the insoluble solid separated and recrystallized. The product so derived displayed spectral properties entirely consistent with that of the α adduct **7** (Scheme VI), including a single resonance at δ 9.6 (–S—CH=N, 1 proton), while the ir spectrum shows prominent C=N absorption at 6.1 μ.

Scheme VI[a]



[a] Ar = .

The α adduct, **7**, could be recrystallized from methylcyclohexane, without change, but with no improvement in melting point. This observation indicated a decomposition mode upon heating. In view of the formation of acylthioformamide **3** and *N*-thioformylphosphoramide **6**, a similar transformation was looked for upon heating **7**. Instead, upon treatment in an inert solvent, a precipitate was formed which was shown to be the morpholine salt of the dithiocarbamate, while 2,6-xylyl isocyanide was recovered in the filtrate (Scheme VI).

Extensions of the thiocarbamic acid addition to isocyanide were disappointing, and the scope and utility of the reaction appear limited. Acidification of the morpholine salt of morpholine thiolcarbamate failed to give an α adduct. Instead, a strong ir absorption for carbonyl sulfide was observed, with no diminution of the isocyanide band. Upon treatment with water only isocyanide was recovered. Obviously, the thiolcarbamic acid from neutralization of the salt decomposes faster than its addition to isocyanide. The same results were obtained even at −40 to −50°.

Even employing dithiocarbamate salts of amines other than morpholine, poor yields and low-quality adducts were obtained. Presumably morpholine with carbon disulfide forms one of the more stable dithiocarbamic acids, while others decompose faster than their addition to isocyanides.

Experimental Section

***N*-Thioformyl-2′,6′-diethylpropionanilide (3a).** 2,6-Diethylphenyl isocyanide[10] (**1a**) (5.1 g, 0.032 mol) was placed in ether and 2.9 g (0.032 mol) of thiopropionic acid was added. After standing overnight, ir analysis indicated (4.7 μ) some unreacted isocyanide present. The material was heated for 2 hr, with no change in isocyanide concentration. To the reaction mixture was then added 20% excess thiopropionic acid and the material was refluxed 1 additional hr. All isocyanide had reacted, and the ether solution was washed with sodium bicarbonate solution, followed by a water wash, drying over magnesium sulfate, and filtering. The ether was removed under vacuum and the residual oil taken up in pentane. A small amount of white solid (1.2 g) insoluble in pentane was isolated as 2,6-diethylthioformanilide, **4a**, mp 98–101°.[11] The clear pentane solution on cooling gave 5 g (63% yield) of yellow crystals, mp 34–36°: pertinent nmr ($CDCl_3$) δ 10.8 (s, 1, NCHS); ir ($CHCl_3$) 5.8 μ (C=O).

Anal. Calcd for $C_{14}H_{19}NOS$: C, 67.43; H, 7.68; N, 5.62. Found: C, 67.59; H, 7.72; N, 5.81.

***N*-Thioformyl-2′,6′-diethylacetanilide (3b). A.** A 10% molar excess of thioacetic acid was refluxed with 4.2 g of **1a** in ether for 2 hr. The cooled ether solution was washed with sodium bicarbonate solution followed by a water wash. The dried (magnesium sulfate) ether solution was evaporated, and the residue taken up in pentane. From this, **4a** was isolated in small amounts, while **3b** was isolated upon cooling as crystals, mp 40–42°, in 83% yield: nmr ($CDCl_3$) δ 1.92 (s, 3, CH_3CO), 10.8 (s, 1, NCHS); ir ($HCCl_3$) 5.8 μ (C=O).

Anal. Calcd for $C_{13}H_{17}NOS$: C, 66.34; H, 7.28; N, 5.95. Found: C, 67.00; H, 7.62; N, 5.72.

B. In *ca.* 50 ml of dry ether, 1.2 g (0.01 mol) of acetyl sulfide,[12] 1.9 g (0.01 mol) of 2,6-diethylthioformanilide, and 0.8 g (0.01 mol) of pyridine were mixed and refluxed for 18 hr. The ether solution on cooling was washed successively with sodium carbonate solution and water and then dried over $MgSO_4$. After removal of the drying agent and distillation of the solvent, the residue was recrystallized from pentane to give 0.7 g of starting 2,6-diethylthioformanilide and 0.95 g of **3b** assaying by nmr at 86% (42% yield).

2′,6′-Diethyl-*N*-thioformylbenzanilide (3c). In 100 ml of ether, 4.5 g (0.029 mol) of **1a** was mixed with 3.8 g (0.029 mol) of thiobenzoic acid **2c**. A slight exotherm was noted. After the mixture stood at ambient temperature for 16 hr, a small amount of isocyanide was detected, which still remained after adding an additional 1 g of **2c** and refluxing for 3 hr. The ether solution was washed with sodium bicarbonate, followed by a water wash. After drying over magnesium sulfate and solvent evaporation, the resi-

due could be recrystallized from cold hexane to give 5.2 g (62% yield) of yellow crystals, mp 64–65°: nmr ($CDCl_3$) δ 10.6 (s, 1, NCHS); ir ($CHCl_3$) 5.82 μ (C=O).

Anal. Calcd for $C_{18}H_{19}NOS$: C, 72.69; H, 6.44; N, 4.71. Found: C, 72.64; H, 6.48; N, 4.87.

2′,6′-Diethyl-*N*-thioformyl-2-chloroacetanilide (3d). To 100 ml of ether were added **1a** (6.4 g, 0.04 mol) and 0.045 mol of freshly distilled chlorothioacetic acid. An exotherm was noted, and the solution was allowed to stand 16 hr. Inspection of the reaction mixture by ir after this time revealed complete reaction of **1a**. The ether solution was washed once with dilute sodium bicarbonate, followed by water. After drying over magnesium sulfate, the filtered ether solution was evaporated, and the resulting residue recrystallized from cold heptane to give 9.1 g (84% yield) of yellow crystals, mp 93–94°: nmr ($CDCl_3$) δ 3.98 (s, 2, $ClCH_2CO$), 10.9 (s, 1, NCHS); ir ($CHCl_3$) 5.8 μ (C=O).

Anal. Calcd for $C_{13}H_{16}ClNOS$: Cl, 13.14; N, 5.19; S, 11.89. Found: Cl, 13.25; N, 5.23; S, 12.18.

2,2′,6′-Trichloro-*N*-thioformylacetanilide (3e). In ether solvent, 3.4 g (0.02 mol) of 2,6-dichlorophenyl isocyanide,[10] **1b**, was mixed with 2.5 g of α-chlorothioacetic acid. An exotherm was noted; then the resulting solution was heated at reflux for 3 hr. During this time yellow solid was deposited. After standing at room temperature overnight, the solution was filtered to give 4.9 g (83%) of **3e**, mp 164–165°: nmr ($CDCl_3$) δ 3.98 (s, 2, $ClCH_2CO$), 7.4–7.6 (m, 3, Ar H), 10.7 (s, 1, NCHS); ir ($CHCl_3$) 5.8 μ (C=O).

Anal. Calcd for $C_9H_6Cl_3NOS$: Cl, 37.64; N, 4.96; S, 11.35. Found: Cl, 38.20; N, 5.23; S, 11.27.

2′,6′-Dichloro-*N*-thioformylacetanilide (3f). Following the procedure given for **3e**, 3 g of thioacetic acid combined with 5.1 g (0.03 mol) of **1b** gave, after recrystallization from methylcyclohexane, 5.1 g of **3f**, mp 91–92°: nmr ($CDCl_3$) δ 2.02 (s, 3, CH_3CO), 7.3–7.6 (m, 3, Ar H), 10.5 (s, 1, NCHS); ir ($CDCl_3$) 5.8 μ (C=O).

Anal. Calcd for $C_9H_7Cl_2NOS$: C, 43.56; H, 2.84; N, 5.67. Found: C, 43.14; H, 2.95; N, 6.17.

6′-*tert*-Butyl-2-chloro-*N*-thioformyl-*o*-acetotoluidide (3g). In 100 ml of ether solvent were dissolved 5.2 g (0.03 mol) of 6-*tert*-butyl-*o*-tolyl isocyanide (mp 63–65°) and 3.9 g of α-chlorothioacetic acid. The mixture was heated at reflux for 1 hr, cooled, and washed once with sodium bicarbonate solution, followed by a water wash. After drying over magnesium sulfate, the ether solution was filtered and then evaporated to give, after trituration with pentane–ether, 5.9 g of **3g**, mp 115°: nmr ($CDCl_3$) δ 1.4 (s, 9, $(CH_3)_3C$), 2.2 (s, 3, Ar CH_3), 4.02 (AB quartet, 2, J = 15 Hz, $ClCH_2CO$, 7.2–7.8 (m, 3, Ar H), 10.9 (s, 1, NCHS); ir ($CHCl_3$) 5.8 μ (C=O).

Anal. Calcd for $C_{14}H_{18}ClNOS$: Cl, 12.49; N, 4.94; S, 11.30. Found: Cl, 12.91; N, 5.05; S, 11.51.

2′-*tert*-Butyl-6′-ethyl-*N*-thioformylacetanilide (3h). In ether, 2-*tert*-butyl-6-ethylphenyl isocyanide [bp 81–87° (0.7 mm), $n^{25}D$ 1.5165)] (5.4 g) was mixed with 3.0 g of thioacetic acid, and the mixture was refluxed until the isocyanide band (ir 4.7 μ) had vanished. The material was washed with sodium bicarbonate, followed by water. After ether drying ($MgSO_4$) and solvent removal the residual oil was allowed to deposit crystals of 2-*tert*-butyl-6-ethylthioformanilide, **4b**, mp 98–100° (identified by spectra and mixture melting point with authentic material obtained from the formanilide and P_2S_5). The residual oil was identified as **3h** (containing traces of **4b**), but it was suitable for the transformation described below: pertinent nmr ($CDCl_3$) δ 10.4 (s, 1, NCHS); ir ($CDCl_3$) 5.8 μ (C=O).

Anal. Calcd for $C_{15}H_{21}NOS$: N, 5.32. Found: N, 5.30.

Mixture of *N*-(α-Methylbenzyl)-*N*-thioformylacetamide (3i) and *N*-(α-Methylbenzyl)thioformamide (4c). In ether, α-methylbenzyl isocyanide (0.04 mol, 5.2 g) was mixed with 5 g (0.045 mol) of thioacetic acid; the material was refluxed 3 hr and then permitted to stand overnight at room temperature. After treatment with sodium bicarbonate solution, followed by a water wash, the ether solution was dried over magnesium sulfate, filtered, and vacuum treated to remove solvent. The residual oil consisted of a *ca.* 50:50 mixture of **3i** and **4c**, as determined by ir and nmr spectra. **3i** could be obtained pure by taking the residue up in hot pentane, decanting the solution from residual oil, and permitting **3i** to crystallize from pentane with scratching, mp 68–71°: nmr ($CDCl_3$) δ 1.75 (d, 3, J = 7 Hz, $CHCH_3$), 2.2 (s, 3, CH_3CO), 6.85 (q, 1, J = 7 Hz, $CHCH_3$), 10.5 (s, 1 CHS); ir (CCl_4) 5.8 μ (C=O).

Anal. Calcd for $C_{11}H_{13}NOS$: C, 63.74; H, 6.32; N, 6.76; S, 15.47. Found: C, 64.04; H, 6.48; N, 6.79; S, 15.75.

Transformations of 3. A. Oxidation of 3 with *m*-Chloroperbenzoic Acid. Several of the thioformyl materials, **3**, were converted to their oxygen analogs (Scheme IV). The conversion of **3g** is illustrative. In 25 ml of dichloromethane was charged 1.4 g (0.005 mol) of 6-*tert*-butyl-2-chloro-*N*-thioformyl-*o*-acetotoluidide and 3.1 g of 85% *m*-chloroperbenzoic acid. There was a noticeable exotherm, after which the mixture was stirred at ambient temperature for 2 hr. The slurry of *m*-chlorobenzoic acid was filtered off and the filtrate washed with a solution of combined sodium carbonate and sodium sulfite, followed by a separate water wash. The organic layer was then dried over magnesium sulfate, filtered, and vacuum treated to remove solvent, not permitting the contents of the flask to warm above room temperature. The solid residue was washed with pentane and recrystallized from methylcyclohexane, mp (sealed capillary) 128–129°: nmr ($CDCl_3$ plus deuteriodimethyl sulfoxide) δ 1.1 (s, 9, $(CH_3)_3C$), 2.02 (s, 3, Ar CH_3), 4.1 (br s, 2, $ClCH_2CO$), 7.05–7.6 (m, 3, Ar H), 9.4 (br s, 1, CHO); ir (chloroform) 5.75 and 5.86 μ (HC=O and CC=O, respectively). The melting point is identical with that previously reported for 6′-*tert*-butyl-2-chloro-*N*-formyl-*o*-acetotoluidide[13] and the spectral results were entirely consistent with those previously discussed for the respective α-bromo derivative.[7]

B. Raney Nickel Treatment. To 5 g of freshly prepared Raney nickel in 100 ml of ethanol was added 1 g of **3h**. The mixture was refluxed 3 hr, cooled, and filtered. The filtrate was vacuum treated and the resulting residue recrystallized from heptane to give a product entirely identical (melting point, mixture melting point, ir, nmr) with authentic *N*-methyl-2′-*tert*-butyl-6′-ethylacetanilide, mp 58–59°, prepared from *N*-methyl-2′-*tert*-butyl-6′-ethylaniline[7] and acetyl chloride.

Anal. Calcd for $C_{15}H_{23}NO$: N, 6.00. Found: N, 6.05.

C. Reaction with Aniline Hydrochloride. In 50 ml of toluene, 3.0 g (0.01 mol) of **3c** was mixed with 1.4 g of aniline hydrochloride and the whole was refluxed for *ca.* 20 hr. Hydrogen chloride rather than hydrogen sulfide evolution was observed during this time. Upon cooling, 1.3 g of crystals, mp 159–160°, was deposited. These were identified as benzanilide. Solvent evaporation gave crystals of 2′,6′-diethylthioformanilide, **4a**.

D. Reaction with Bromine. In 75 ml of CCl_4 was dissolved 3.0 g (0.011 mol) of **3d** and to this solution, with stirring, was added 1.8 g (0.011 mol) of bromine, contained in *ca.* 20 ml of the same solvent. The reaction was monitored by nmr. It showed ready disappearance of the thioformyl proton, and a shift of the chloromethylene group. After solvent had been removed, the residue was distilled, with chloroacetyl bromide collected at bp 53° (50 mm) and 2,6-diethylphenyl isothiocyanate at bp 139° (10 mm). The 2,6-diethylphenyl isothiocyanate thus prepared possessed ir and nmr spectra identical with those of authentic material prepared from 2,6-diethylaniline and thiophosgene. The chloroacetyl bromide, which possessed consistent ir (C=O at 5.52 μ) and nmr spectra ($ClCH_2$, δ 4.50, s), could be further converted to α-chloroacetanilide upon reaction with aniline.

***N*-(2,6-Diethylphenyl)thiolformimidic Acid–*O,O*-Diethylphosphorodithioic Acid Mixed Anhydrosulfide (5a).** 2,6-Diethylphenyl isocyanide (8.0 g, 0.05 mol) was dissolved in ether and 10 g (0.054 mol) of *O,O*-diethylphosphorodithioic acid was added dropwise. The isocyanide ir band at 4.7 μ had nearly completely disappeared after 0.5 hr at room temperature. The solution was washed with sodium carbonate solution and then dried over magnesium sulfate. After solvent evaporation under high vacuum, the residual oil (which would not crystallize) was filtered through clay to give 13 g of a light amber oil: nmr ($CDCl_3$) δ 1.2 and 1.4 (two t, 12, J = 7 Hz, CH_2CH_3), 2.5 (4, J = 7 Hz, Ar CH_2CH_3), 4.2 (m, 4, $POCH_2CH_3$), 7.0 (3, Ar H), 8.8 (d, 1, J = 6 Hz, =CH); ir (film) trace at 4.7 (Ar NC), 6.2 μ (C=N).

Anal. Calcd for $C_{15}H_{24}NO_2PS_2$: N, 4.05; P, 8.97; S, 18.56. Found: N, 4.01; P, 8.69; S, 18.43.

***O,O*-Diethyl *N*-(2,6-Diethylphenyl)-*N*-thioformylphosphoramidothioate (6a).** Material **5a** (12.5 g) was allowed to stand for 2 weeks at room temperature, after which time it had completely solidified. Spectral analyses were recorded on this solid and found identical with those recorded after the material had been recrystallized from cold hexane to give 9.1 g of yellow crystals, mp 42–43°: nmr ($CDCl_3$) δ 1.2 and 1.25 (2 t, 12, J = 7 Hz, CH_2CH_3), 2.60 (q, 4, J = 7 Hz, Ar CH_2CH_3), 4.2 (m, 4, $POCH_2CH_3$), 7.1 (3, Ar H), 10.4 (d, 1, J = 7 Hz, NCHS); ir ($CDCl_3$), no absorption at 6.0–6.2 μ (no C=N).

Anal. Calcd for $C_{15}H_{24}NO_2PS_2$: N, 4.05; P, 8.97; S, 18.56. Found: N, 4.05; P, 8.88; S, 18.38.

***O,O*-Diethyl *N*-(2,6-Xylyl)-*N*-thioformylphosphoramidothioate (6b).** 2,6-Xylyl isocyanide (3.3 g, 0.025 mol) was dissolved in 50 ml of CCl_4 and 4.65 g (0.025 mol) of *O,O*-diethylphos-

phorodithioic acid was added dropwise. After addition, inspection by ir and nmr spectra revealed the α adduct, **5b:** nmr (CCl_4) δ 1.38 (t, 6, J = 7 Hz, OCH_2CH_3), 2.05 (s, 6, Ar CH_3), 4.2 (m, 4, $POCH_2CH_3$), 6.8 (3, Ar H), 8.63 (s or d (J = 6 Hz) depending on acid concentration, =CH); ir (CCl_4) 6.1 μ (C=N). After sufficient time had elapsed, the α adduct rearranged. The CCl_4 solution was removed under vacuum and the residue crystallized by scratching, with recrystallization from hexane to give 4.0 g of yellow solid, mp 53–56°: nmr ($CDCl_3$) δ 1.3 (t, 6, J = 7 Hz, OCH_2CH_3), 2.21 (s, 6, Ar CH_3), 4.15 (m, 4, $POCH_2CH_3$), 7.1 (3, Ar H), 10.4 (d, 1, J = 6 Hz, PNCHS); ir ($CHCl_3$), no absorption at 6.0–6.2 μ (no C=N).

Anal. Calcd for $C_{13}H_{20}NO_2PS_2$: C, 49.19; H, 6.35; N, 4.41. Found: C, 49.61; H, 6.11; N, 4.32.

***O,O*-Dimethyl *N*-(2,6-Diethylphenyl)-*N*-thioformylphosphoramidothioate (6c).** 2,6-Diethylphenyl isocyanide (4.0 g, 0.025 mol) was mixed in 50 ml of CCl_4 with 3.95 g of *O,O*-dimethylphosphorodithioic acid. The initial nmr and ir spectra were consistent for the α adduct (d (J = 17 Hz) at δ 3.70 for $(OCH_3)_2$ and d (J = 6 Hz) at δ 8.52 for =CH; ir 6.2 μ (C=N)), although the nmr spectra also showed the presence of **6c.** After standing, the carbon tetrachloride solution was washed with 5% sodium carbonate solution, followed by water; it was then allowed to dry over $MgSO_4$. After solvent removal under vacuum, the residual oil **6c,** which did not crystallize, possessed an nmr spectrum consistent with that of the assigned structure: d (J = 18 Hz) at δ 3.75 for $P(OCH_3)_2$ and d (J = 6 Hz) at δ 10.27 for CHS.

Anal. Calcd for $C_{13}H_{20}NO_2PS_2$: N, 4.41; P, 9.76; S, 20.20. Found: N, 4.22; P, 9.54; S, 19.64.

***O*-Ethyl *N*-(2,6-Diethylphenyl)-*N*-thioformylmethylphosphonamidothioate (6d).** *O*-Ethylmethylphosphonodithioic acid[14] (3.9 g, 0.025 mol) was dissolved in carbon tetrachloride and the isocyanide was added dropwise. The reaction was immediate, and the nmr and ir spectra of the organic solution were consistent with the formation of the α adduct: d (J = 15 Hz) at δ 8.63, =CHS; ir 6.2 μ (C=N). The rate of conversion to **6d** was sufficiently slow that, to obtain the latter material, the organic solution was subsequently heated at reflux for 2 hr. The solvent was then removed under vacuum, ether added to the residue, and the solution washed with aqueous sodium bicarbonate, followed by water. After drying over magnesium sulfate, the solvent was removed to give 4.8 g of oil, which failed to crystallize: nmr ($CDCl_3$) δ 1.2 (t, 9 protons, CH_2CH_3), 1.84 (d, J = 15 Hz, 3 protons, CH_3P), 2.53 (m, 6 protons, Ar CH_2CH_3), 4.21 (m, 4 protons, $POCH_2CH_3$), 7.2 (m, 3, Ar H), 10.40 (d, J = 6 Hz, 1, CHS).

Anal. Calcd for $C_{14}H_{22}NOPS_2$: N, 4.44; P, 9.82; S, 20.33. Found: N, 4.43; P, 9.56; S, 19.92.

***N*-(2,6-Diethylphenyl)thiolformimidic Acid–Diphenylphosphinodithioic Acid Mixed Anhydrosulfide (5e).** Diphenylphosphinodithioic acid[8] (3.0 g, 0.0125 mol) was mixed in 25 ml of CCl_4 with 2.0 g (0.0125 mol) of 2,6-diethylphenyl isocyanide and the material permitted to stand. The α adduct appeared to form immediately as discerned by ir and nmr spectra. On prolonged standing, even with heating, the material failed to rearrange. The solvent was removed under vacuum, and the oily residue taken up in ether and washed with aqueous sodium bicarbonate, followed by water. After drying over magnesium sulfate and ether evaporation, the product obtained was an oil that would not crystallize: nmr (CCl_4) δ 1.02 (t, J = 7 Hz, 6, Ar CH_2CH_3), 2.5 (q, J = 7 Hz, 4, Ar CH_2CH_3), 6.8–8.0 (m, 13, Ar H) 8.77 (d, J = 7 Hz, 1, =CH); ir (CCl_4) 6.25 μ (C=N).

Anal. Calcd for $C_{23}H_{24}NPS_2$: N, 3.42; P, 7.56; S, 15.66. Found: N, 3.41; P, 7.36; S, 15.50.

Rate Measurements for Rearrangement of α Adducts 5, to 6. As described above, the requisite phosphorus thiol acid and aryl isocyanide were placed in CCl_4, usually in equimolar quantities, at an initial concentration of 0.5 *M*. An aliquot was withdrawn and placed in a sealed nmr tube. The tubes were stored at 25 ± 0.5°. Periodically their nmr spectra were examined and the concentrations of the initially formed α adduct **5** and *N*-thioformyl rearrangement product **6** were calculated from the ratio of the olefinic proton (doublet) at 510–525 Hz (*ca.* δ 8.10) to that of the thioformyl proton (doublet) (*ca.* δ 10.4). The rearrangement was followed kinetically until at least 60% of **5** had been converted. As described above, the final rearrangement products, **6,** were isolated upon completion of the reaction. The kinetic results were plotted as log [**5**] *vs.* time and first-order rate constants were obtained from the slope of the straight lines thus obtained. An average linear correlation coefficient of 0.9966 was obtained for all plots.

4-Morpholinecarbodithioic Acid–*N*-(2,6-Xylyl)thiolformimidic Acid Mixed Anhydrosulfide (7a). 2,6-Xylyl isocyanide (3.23 g, 0.025 mol) was dissolved in a THF slurry of an equimolar amount of morpholine salt of morpholine dithiocarbamate. The mixture was allowed to stir at room temperature over a period of *ca.* 54 hr. There was no apparent change in density of the slurry, so the mixture was heated to reflux. After 1.5 hr there was no apparent change, so 4 drops of methanesulfonic acid was added and the mixture refluxed an additional 2.5 hr. Again, there was no apparent decrease in morpholine salt slurry, so the mixture was cooled to 0–5° and 2.9 g (0.025 mol) of 85% phosphoric acid was added dropwise in THF solution. The ir spectrum after this addition was complete showed a small isocyanide band (4.7 μ) still present. An additional 1 g of morpholine salt was added, without diminishing isocyanide concentration. Therefore, several additional drops of phosphoric acid was added, without further reducing the isocyanide absorption. The reaction mixture was then poured into 500 ml of ice water and the insoluble material was filtered and air-dried to give a 3.8-g yield, mp 93–95°. Recrystallization from methylcyclohexane gave mp 94–97°. There was no change in nmr when the material was aged at room temperature for several days. Upon heating **7a** in refluxing methylcyclohexane, the morpholine salt of dithiocarbamate was again formed, with appreciable quantities of isocyanide present (ir 4.7 μ) in the mother liquors: **7a,** nmr ($CDCl_3$) δ 2.1 (s, 6, Ar CH_3), 3.6–4.5 (m, 8, morpholine protons), 7.0 (3 protons, Ar H), 9.6 (s, 1, N=CH); ir ($CHCl_3$) 6.2 μ (C=N).

Anal. Calcd for $C_{14}H_{18}N_2OS_2$: C, 57.11; H, 6.16; N, 9.51. Found: C, 57.03; H, 6.15; N, 9.17.

Registry No.—**1a,** 2980-92-9; **1b,** 6697-95-6; **1** (R = 6-*tert*-butyl-*o*-tolyl), 52559-62-3; **1** (R = 2-*tert*-butyl-6-ethylphenyl), 53042-88-9; **1** (R = α-methylbenzyl), 17329-20-3; **1** (R = 2,6-xylyl), 2769-71-3; **2c,** 98-91-9; **2** (R′ = CH_3CH_2), 1892-31-5; **2** (R′ = CH_3), 507-09-5; **2** (R′ = $ClCH_2$), 867-49-2; **3a,** 53042-89-0; **3b,** 53042-90-3; **3c,** 53042-91-4; **3d,** 53042-92-5; **3e,** 53042-93-6; **3f,** 53042-94-7; **3g,** 53042-95-8; **3h,** 53042-96-9; **3i,** 53042-97-0; **4a,** 53042-98-1; **4b,** 53042-99-2; **4c,** 20278-33-5; **5a,** 53043-00-8; **5b,** 53043-01-9; **5c,** 53043-02-0; **5d,** 53043-03-1; **5e,** 53043-04-2; **6a,** 53043-05-3; **6b,** 53043-06-4; **6c,** 53043-07-5; **6d,** 53043-08-6; **7a,** 53043-09-7; acetyl sulfide, 3232-39-1; 2,6-diethylthioformanilide, 53042-98-1; *m*-chloroperbenzoic acid, 937-14-4; 6′-*tert*-butyl-2-chloro-*N*-formyl-*o*-acetotoluidide, 4655-12-3; *N*-methyl-2′-*tert*-butyl-6′-ethylacetanilide, 53043-10-0; 2′-*tert*-butyl-6′-ethylaniline, 13117-97-0; acetyl chloride, 75-36-5; aniline hydrochloride, 142-04-1; bromine, 7726-95-6; chloroacetyl bromide, 15108-06-1; 2,6-diethylphenylisothiocyanate, 25343-69-5; *O,O*-diethylphosphorodithioic acid, 298-06-6; *O,O*-dimethylphosphorodithioic acid, 756-80-9; *O*-ethylmethylphosphonodithioic acid, 999-83-7; diphenylphosphinothioic acid, 1015-38-9; morpholinedithiocarbamic acid morpholine salt, 5327-10-6.

References and Notes

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