Organometallic Reactions. Addition Reactions of Benzenethiol to Unsaturated Systems Catalysed by Trimethyl(phenylthio)-silane or -stannane

By **Alfredo Ricci**,* Istituto di Chimica Organica dell'Università, Via G. Capponi 9, 50121 Firenze, Italy

Roberto Danieli* and **Graziella Pirazzini,** Consiglio Nazionale delle Ricerche, Via Tolara di Sotto 89, Ozzano-Emilia, Bologna, Italy

Trimethylphenylthiosilane has been shown to catalyse the addition of benzenethiol to isocyanates. isothiocyanates. activated double and triple bond. and ketens. This silicon catalyst appears much more effective than the tin and lead counterparts. for most of the systems investigated.

The slow formation at room temperature of the 1 : 1 adduct between the catalyst and the unsaturated system, and the low reactivity of the adduct itself towards benzenethiol exclude the intermediate formation of an insertion product in the catalytic process. A probable mechanism for these reactions is presented.

THE reactions of Group 4B organometallic derivatives with multiply bonded reagents have been thoroughly investigated [1] with particular attention to the nature of the 1:1 adducts formed. Recently Davies [2] reported that trialkyl-lead alkoxides are very effective in catalysing the addition of methanol to unsaturated molecules. However in spite of the extensive studies in this field, corresponding information concerning the insertion reactions and the catalytic efficiency of organosilicon derivatives is lacking. In continuation of our work [3] on the chemistry of the Group 4B organometallic sulphides containing a sulphur–metal bond, we report an investigation of the catalytic effect of the sulphides $PhSMMe_3$ (M = Si, Sn, or Pb) in the addition of benzenethiol to various unsaturated systems [reaction (i)]. Our aim

$$Ph-SH + A=B \longrightarrow H-A-B-SPh \qquad (i)$$

was to evaluate the suitability of some new catalysts for the synthesis of organic sulphur compounds not easily accessible by normal methods.

RESULTS AND DISCUSSION

The multiply bonded reagents studied are listed in the Table, together with the products and the catalysts used.

no complications arose due to the formation of by-products.

Whereas isocyanates and benzenethiol react relatively slowly under standard conditions,[4] small amounts of trimethyl(phenylthio)silane generally cause a dramatic enhancement of the addition rate: in the presence of 5 mol % of this catalyst in fact the addition of phenyl isocyanate to the aromatic thiol occurs instantaneously and exothermically and the conversions of ethyl and isopropyl isocyanates require reaction times much shorter than those for the uncatalysed addition.

In the addition of benzenethiol to isothiocyanates a similar catalytic effect occurs. When phenyl isothiocyanate and the thiol were mixed with 10 mol % of the thiosilane in the absence of solvent, the exothermic reaction was half complete in 1 min, and phenyl N-phenyldithiocarbamate was recovered in 98% yield; in the absence of catalyst the same reaction required not less than 50 min. With methyl, ethyl, and n-butyl isothiocyanates, which are weaker acceptors,[5] besides the increase in rate, the main advantage of using the catalyst is that N-alkyldithiocarbamates are formed in 85—98% yields. If in the catalyst M is changed from Si to Sn or

Catalysed addition of benzenethiol to unsaturated systems

Acceptor A=B	Catalyst	Product	Yield (%)
PhNCO	⎫	PhNH·CO·SPh	96
RNCO [a]	⎪ PhS·SiMe$_3$	RNH·CO·SPh	80—96
PhNCH	⎬	PhNH·CS·SPh	98
RNCS [b]	⎭	RNH·CS·SPh	85—98
Ph$_2$C=C=O	PhS·SnMe$_3$	Ph$_2$CH·CO·SPh	92
MeCH=CH·CHO	⎫	MeCH(SPh)·CH$_2$·CHO	90
PhCH=CH$_2$	⎪	PhCH$_2$·CH$_2$·SPh	96
CH$_2$=CH·CN	⎬ PhS·SiMe$_3$	PhS·CH$_2$·CH$_2$·CN	90
MeO$_2$C·C≡C·CO$_2$Me	⎪	MeO$_2$C·C(SPh)=CH·CO$_2$Me [c]	90
Cl$_3$C·CN	⎭	Cl$_3$C·C(SPh:NH)	60

[a] R = Et or Pr^i. [b] R = Me, Et, or Bu^n. [c] cis—trans-Mixture (see text).

In all cases the products were characterized by i.r., mass, and ¹H n.m.r. spectra as well as by elemental analysis. Moreover g.l.c. of reaction mixtures and the nearly quantitative yields in catalysed reactions indicated that

Pb, its efficiency is greatly reduced: thus for example, under the usual experimental conditions, the yield of phenyl N-phenyldithiocarbamate from benzenethiol and

[1] T. A. George, K. Jones, and M. F. Lappert, *J. Chem. Soc. (C)*, 1965, 2157; A. G. Davies and P. G. Harrison, *J.C.S. Perkin I*, 1976, 1313; A. G. Davies and W. R. Symes, *J. Chem. Soc. (C)*, 1967, 1009; A. G. Davies and J. D. Kennedy, *ibid.*, 1968, 2630; A. J. Bloodworth and A. G. Davies, *ibid.*, 1965, 5239.

[2] A. G. Davies and R. J. Puddephatt, *J. Chem. Soc. (C)*, 1968, 1479.

[3] (a) G. Pirazzini, R. Danieli, A. Ricci, and C. A. Boicelli, *J.C.S. Perkin II*, 1974, 853; (b) G. Distefano, A. Ricci, F. P. Colonna, and D. Pietropaolo, *J. Organometallic Chem.*, 1974, **78**, 93, and references therein.

[4] J. Hetflejs, L. Svoboda, M. Jakoubková, and V. Chvalovský, *Coll. Czech. Chem. Comm.*, 1973, **38**, 717; E. Gyer and J. F. Glenn, *J. Amer. Chem. Soc.*, 1957, **79**, 366.

[5] C. Larsen and P. Jakobsen, *Acta Chem. Scand.*, 1973, **27**, 2001.

phenyl isothiocyanate in the presence of phenylthio-trimethylstannane is 50% in 3 h. This is surprising since halogeno-tin and -lead compounds have been reported [6] as being the most effective catalysts in the addition of weakly acidic alcohols to isocyanates.

In the absence of benzenethiol the sulphur–metal bond of the catalyst can add to the acceptor molecule, but this reaction is generally very slow: for example an equimolar mixture of phenyl isocyanate and the silicon catalyst afforded a 1 : 1 adduct (1) (see Experimental section) only after 4—5 days; the product was not very reactive

$$PhNCO + PhS-SiMe \longrightarrow PhN(SiMe_3)COSPh \quad (1)$$

towards benzenethiol; again the formation of the 1 : 1 adduct between the silyl catalyst and phenyl isothiocyanate is very slow, the acceptor being converted in yields not greater than 20% after 10 days as shown by changes in i.r. spectra.

The addition of benzenethiol to ketens has also been investigated, in view of the similarity in structure of these compounds to isocyanates,[7] but the main features of the catalysed reactions appear fundamentally different for these two classes of compound. As with isocyanates, thiols react slowly with ketens in the absence of catalyst. However in contrast with the previous picture, whereas silyl and plumbyl catalysts have no observable effect on the reactivity, the stannyl derivative is an efficient catalyst; also chloro(trimethyl)stannane exhibits an appreciable catalytic effect. In the presence of small amounts of trimethyl(phenylthio)stannane in fact, even in carbon tetrachloride as solvent, the reaction is instantaneous and exothermic and affords quantitative yields of phenyl diphenylthioacetate. In further contrast with the previous systems, the formation of the 1 : 1 adduct between the acceptor and trimethyl(phenylthio)stannane, as indicated by the disappearance of the keten stretching i.r. band at 2 100 cm^{-1}, is rapid in the absence of solvent. The 1 : 1 adduct, probably of structure (2), can be isolated as a solid but is rapidly transformed in air into an oil, presumably by hydrolysis of the C–SnMe$_3$ bond; furthermore the adduct (2) is more reactive towards benzenethiol than the starting keten.

$$Ph_2C=C=O + PhS-SnMe_3 \longrightarrow Ph_2C(SnMe_3)CO\cdot SPh \quad (2)$$

The addition of benzenethiol to activated C=C bonds is also assisted to some extent by the catalyst: thus if a mixture of crotonaldehyde and benzenethiol in carbon tetrachloride is treated with 10 mole % of trimethyl-(phenylthio)silane, β-phenylthiobutyraldehyde[8] is formed within 3 h in quantitative yield. Without a catalyst, the same reaction is 20% complete in 24 h. Also the addition of benzenethiol to styrene in the presence of the silyl catalyst occurs at a noticeably greater rate: quantitative yields of β-phenylthioethylbenzene are obtained after only 20 h whereas, in the absence of catalyst, 40 h are required for 40% reaction. The

largest catalytic effect in this series is found, however, in addition to the C=C bond of acrylonitrile: benzenethiol does not add very easily to this acceptor at room temperature and needs several hours even in the presence of radical catalysts such as benzoyl peroxide or on irradiation.[9] In contrast to this relatively low reactivity, in the presence of trimethyl(phenylthio)silane, an exothermic reaction takes place and β-phenylthiopropionitrile is formed instantaneously in nearly quantitative yield (Table). Even for these compounds the catalytic effect of trimethyl(phenylthio)-stannane and -plumbane is less pronounced. With regard to adduct formation between activated C=C bonds and the catalyst, this step has been investigated with crotonaldehyde: the olefinic signals in the ^{1}H n.m.r. spectrum of an equimolecular mixture of the catalyst and the acceptor have disappeared after ca. 24 h, and the methyl resonance is shifted upfield (by 0.7 p.p.m.). The final spectrum appears consistent with the presence of ca. 90% of the 1 : 1 adduct (3), which can be isolated (see Experimental section) pure directly from the reaction mixture. Addition of the adduct (3) to an equimolar amount of

$$MeCH=CH\cdot CHO + PhS-SiMe_3 \longrightarrow \underset{\underset{SPh}{|} \; \underset{SiMe_3}{|}}{MeCH-CH\cdot CHO} \quad (3)$$
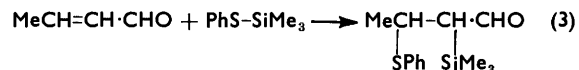
benzenethiol at room temperature does not lead to any reaction during several days (^{1}H n.m.r. spectra).

Acceptors having activated C≡C bonds also undergo addition reactions with benzenethiol at a greater rate in the presence of these catalysts. For this class of compound, the addition of benzenethiol to dimethyl but-2-ynedioate has been studied in some detail. The main features are as follows: (i) whereas in the absence of catalyst the reaction is 50% complete in 12 h, 10 mole % of trimethyl(phenylthio)silane induces an instantaneous and exothermic reaction, which affords quantitative yields of vinyl sulphide; (ii) the stannyl and plumbyl derivatives do not cause any appreciable acceleration of the reaction; (iii) neither the catalysed nor the uncatalysed reaction is stereospecific: the ^{1}H n.m.r. spectrum indicates the presence of cis- and trans-isomeric products, in ratios estimated according to the rule [10] that an olefinic proton is deshielded by 0.5—0.9 p.p.m. by a CO$_2$R group in the cis-position. The proportions of cis- and trans-compounds in the uncatalysed reaction mixture (35 and 65% respectively) appear unchanged even when the catalyst is then added, provided that the reaction mixture is cooled at −30 °C during mixing. However if during the addition the reaction temperature is allowed to rise, the proportions of the geometrical isomers are slightly modified to ca. 1 : 1. The trans-isomer has been recovered directly from the reaction between toluene-p-thiol and the acceptor in the presence of trimethyl-(p-tolylthio)silane. Trimethyl(phenylthio)-

[6] A. Farkas and G. A. Mills, Adv. Catalysis, 1962, 13, 393; S. G. Entelis and O. V. Nesterov, Russ. Chem. Rev., 1966, 35, 917.
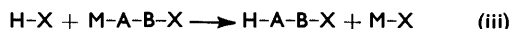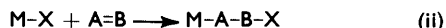
[7] D. P. N. Satchell and R. S. Satchell. Chem. Soc. Rev., 1975, 231.

[8] K. Sirotanovic, M. Bajlon-Rocen, and D. Galovic, Glasnik Hem. Dustra, Beograd, 1960, 25—26, 509 (Chem. Abs., 1963, 59, 8635d).

[9] C. D. Hurd and L. L. Gershbein, J. Amer. Chem. Soc., 1947, 69, 2328.

[10] L. M. Jackman and R. H. Wiley, J. Chem. Soc., 1960, 2886.

silane and its tin and lead counterparts do not react with dimethyl but-2-ynedioate at room temperature to give the expected adduct, even during several days.

A relevant catalytic activity is exhibited by trimethyl-(phenylthio)silane in the addition of benzenethiol to trichloroacetonitrile. In the presence of the catalyst this reaction affords S-phenyl trichlorothioacetimidate in 60% yield after 4 days, whereas the uncatalysed reaction shows no significant progress even after 4 weeks.

Any mechanistic approach to these reactions would require more detailed and quantitative studies. However, evidence has been obtained which affords preliminary indications of the mechanism of the catalysis. The most relevant features common to the catalysed reactions studied here, are as follows. (a) The S–Si derivative appears more effective than the tin and lead analogues, and Me_3SnCl or BF_3,Et_2O do not exhibit appreciable catalytic activity, for all the reactions investigated with the exception of those of ketens; it seems therefore unlikely that the catalyst simply acts as a Lewis acid. (b) Insertion of the catalyst into the unsaturated bond of the acceptor is unlikely to be involved since (i) as shown by i.r. and ^1H n.m.r. spectra such adducts are generally formed slowly; (ii) even in 50 mole % solution of trimethyl-(p-tolylthio)silane as catalyst the n.m.r. spectrum of the product of addition of benzenethiol to the acceptor, does not show the incorporation of large amounts (not exceeding 10%) of the p-methyl derivative; (iii) protolysis of the 1 : 1 adducts with thiols is generally very slow; (iv) in Group 4B there are no clear-cut examples of insertions involving an M–S bond.

On these grounds the thiosilylation and protolysis steps cannot be combined in a catalytic process such as that [reactions (ii) and (iii)] proposed [2] by Davies for explaining the addition reactions catalysed by organolead compounds; in the present study both reactions (ii) and

$$M\text{-}X + A\text{=}B \longrightarrow M\text{-}A\text{-}B\text{-}X \qquad (ii)$$

$$H\text{-}X + M\text{-}A\text{-}B\text{-}X \longrightarrow H\text{-}A\text{-}B\text{-}X + M\text{-}X \qquad (iii)$$

(iii) are much slower than the overall catalysed process.

The possibility that a complex may be formed between the catalyst and the acceptor, previously suggested for the reactions of isocyanates with alcohols,[11] is also unlikely since the tin and lead catalysts would be expected to exhibit a larger catalytic efficiency than trimethyl-(phenylthio)silane, in contrast with observation.

One possible mechanism which reasonably fits the bulk of the experimental data is shown in reaction (iv). Such a scheme, substantially equivalent to the mechanism reported [3a] for acid-catalysed cleavage of the S–Si bond, is based on complex formation between the catalyst and the thiol, followed by reaction of the complex itself or of the incipient benzenethiolate ion, with the acceptor molecule, probably in a rate-determining step.* This

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* Substitution in the phenyl group of the catalyst would affect the proton transfer equilibrium between the two sulphur atoms in the intermediate and would change the importance of $(p\text{–}d)_\pi$ contribution in the S–M bonds, as well as the PhS⁻ leaving group ability; this might explain, for example, the low incorporation of $p\text{-MeC}_6H_4S$ in the adduct.

scheme offers an attractive explanation for the low catalytic efficiency of the tin and lead counterparts. In conformity with reaction (iv) and in line with Robins' requirements,[12] trimethyl(phenylthio)silane possesses

$$H\text{-}A\text{-}B\text{-}SPh + PhS\text{-}MR_3 \qquad (iv)$$
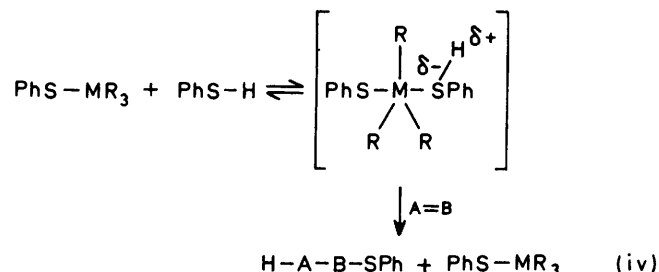
without doubt some capacity for complex formation, but unlike tin and lead derivatives or boron trifluoride–ether, it does not yield, with thiols or with reaction products, stable complexes, which would make it difficult to transfer the combined sulphur to the acceptor. Neither does it exhibit a tendency to increase externally its co-ordination number by intermolecular formation of intermediate complexes [13] involving five-co-ordinate metal [as in (4)].
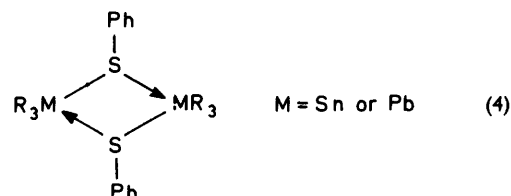
The scheme shown as reaction (iv) however does not apply to ketens, which in fact seem to experience a Lewis-acid type catalysis. The 1 : 1 adduct is formed rapidly and undergoes protolysis at a relevant rate. In this particular case the Davies mechanism [2] seems more likely, even if a radical path contribution [14] to the increase of reactivity cannot be completely dismissed.

A more detailed kinetic study on the mechanistic aspects of this catalysis is in progress.

EXPERIMENTAL

I.r. spectra of neat liquids or solutions were recorded with a Perkin-Elmer SP 1100 instrument. ^1H N.m.r. spectra were determined at probe temperature for solutions in carbon tetrachloride with a JEOL C60HL spectrometer. Mass spectra were run with a Varian MAT-111 instrument.

Trimethyl(phenylthio)-silane, -stannane, and -plumbane were prepared as described elsewhere.[3a] Isocyanates, isothiocyanates, and olefinic and acetylenic derivatives were commercial samples, purified by distillation before use. Diphenylketen was synthesised as previously described.[15]

[11] S. Ozaki, Chem. Rev., 1972, 72, 457.

[12] J. Robins, J. Appl. Polymer Sci., 1965, 9, 821.

[13] R. C. Poller, J. Organometallic Chem., 1965, 3, 321; J. D. Kennedy, W. McFarlane, G. S. Pyne, P. L. Clarke, and J. L. Wardell, J.C.S. Perkin II, 1975, 1234.

[14] P. J. Lillford and D. P. N. Satchell, J. Chem. Soc. (B), 1970, 1303.

[15] E. C. Taylor, A. McKillop, and G. H. Hawks, Org. Synth., 1972, 52, 36.

Addition of Benzenethiol to Isocyanates.—Trimethyl-(phenylthio)silane (0.09 g, 0.5 mmol) was added at room temperature to a solution of phenyl isocyanate (1.19 g, 10 mmol) and benzenethiol (1.1 g, 10 mmol) in carbon tetrachloride (5 ml). There was an immediate exothermic reaction and a solid was precipitated which, filtered off and washed with n-pentane, gave phenyl N-phenylthiocarbamate (2.2 g, 96%), which after recrystallisation from light petroleum had m.p. 123° (lit.,[16] 125°).

With less reactive isocyanates the reaction was carried out in the absence of solvent by the foregoing procedure: thus ethyl isocyanate and benzenethiol in the presence of 5 mole % of trimethyl(phenylthio)silane had reacted after 2—3 min, and the solid product, washed with n-pentane, gave *phenyl* N-*ethylthiocarbamate* (96%), m.p. 81°; τ 9.0 and 6.8 (Et), 2.6 (ArH), and 3.7 (NH) (Found: C, 60.2; H, 6.15; N, 7.65. $C_9H_{11}NOS$ requires C, 59.6; H, 6.1; N, 7.7%); $\nu_{max.}$ 3 420 (NH) and 1 690 cm^{-1} (C=O). No heat was evolved when trimethyl(phenylthio)silane (0.09 g, 0.5 mmol) was added to a mixture of isopropyl isocyanate (0.85 g, 10 mmol) and benzenethiol (1.1 g, 10 mmol), but the solution became dark almost immediately. After 10 h, a solid product was formed which, washed with n-pentane and crystallised from benzene, afforded the *isopropylthio-carbamate* (1.52 g, 78%), m.p. 100—102°; $\nu_{max.}$ 3 340 (NH) and 1 700 cm^{-1} (C=O); τ 9.0 and 6.2 (Pr^{i}), 4.7 (NH), and 2.8 (ArH) (Found: C, 61.3; H, 6.6; N, 7.2. $C_{10}H_{13}NOS$ requires C, 61.5; H, 6.7; N, 7.2%).

Addition of Benzenethiol to Isothiocyanates.—After the addition of the silicon catalyst (0.18 g, 1 mmol) to a mixture of phenyl isothiocyanate (1.35 g, 10 mmol) and benzenethiol (1.1 g, 10 mmol) an exothermic reaction occurred and a crystalline solid was precipitated. This, washed with n-pentane and dried, gave phenyl N-phenyldithiocarbamate (2.4 g, 98%), m.p. 131° (lit.,[5] 133—134°).

The same procedure was employed with methyl, ethyl, and n-butyl isothiocyanates. After 10, 40, and 60 min, respectively, the addition products were recovered, after the usual work-up, in 85—98% yields. The physical and analytical properties of the phenyl N-methyl-, -ethyl-, and -n-butyl-dithiocarbamates obtained are consistent with those reported.[5]

Addition of Benzenethiol to Diphenylketen.—The progress of the reaction between diphenylketen (0.97 g, 5 mmol) and benzenethiol (0.55 g, 5 mmol) in carbon tetrachloride (5 ml) was followed by integration of the n.m.r. signal due to SH (τ 7.8). The addition was half complete in 1 h. In the presence of trimethyl(phenylthio)stannane (0.14 g, 0.5 mmol) the reaction was exothermic and instantaneous. Evaporation and crystallisation from light petroleum gave *phenyl diphenylthioacetate* (1.4 g, 92%), m.p. 84—85°; $\nu_{max.}$ 1 710 cm^{-1} (C=O); τ 5.1 (s, CH) and 2.8 (ArH) (Found: C, 78.8; H, 5.3; S, 10.2. $C_{20}H_{16}SO$ requires C, 78.9; H, 5.3; S, 10.5%).

Addition of Benzenethiol to Double Bonds.—(*a*) Trimethyl-(phenylthio)silane (0.18 g, 1 mmol) was added to a solution of crotonaldehyde (0.7 g, 10 mmol) and benzenethiol (0.55 g, 10 mmol) in carbon tetrachloride (5 ml). After 3 h the reaction was completed as shown by the disappearance of the ethylenic proton n.m.r. signals (τ 3.9 and 3.2). Evaporation, and distillation of the residual oil under high vacuum gave β-phenylthiopropionaldehyde,[8] b.p. 104° at 0.4 mmHg (1.1 g, 88%).

(*b*) The catalysed addition of benzenethiol to styrene, performed by the foregoing procedure, afforded β-*phenyl-*

thioethylbenzene (96%), b.p. 143—145° at 1 mmHg; τ 7.15 (CH$_2$·CH$_2$) and 2.9 (ArH) (Found: C, 78.4; H, 6.5; S, 14.9. $C_{14}H_{14}S$ requires C, 78.5; H, 6.5; S, 15.0%).

(*c*) To a mixture of acrylonitrile (0.53 g, 10 mmol) and benzenethiol (1.1 g, 10 mmol), trimethyl(phenylthio)silane (0.09 g, 0.5 mmol) was added. An exothermic reaction took place and after *ca.* 5 min the n.m.r. spectrum showed complete disappearance of the olefinic proton signal (τ 4.3). Distillation under high vacuum afforded β-phenylthiopropiononitrile (1.3 g, 80%), b.p. 105—106° at 0.1 mmHg (lit.,[9] 154° at 8 mmHg).

Addition of Benzenethiol to Triple Bonds.—With dimethylbut-2-ynedioate the usual procedure was employed. The reaction was followed by observing the increase of the olefinic proton n.m.r. signals at τ 4.75 and 3.9. The mixture of isomeric *dimethyl-2-phenylthiobut-2-enedioates* was isolated as a pale yellow oil (90%), b.p. 140—142° at 0.5 mmHg; $\nu_{max.}$ 1 680 (C=C) and 1 735 cm^{-1} (C=O); τ 6.85 and 6.4 (Me *trans*), 6.5 (Me *cis*), 4.75 (=CH– *cis*), 3.9 (=CH– *trans*), and 2.8 (ArH) (Found: C, 58.2; H, 4.65; S, 12.8. $C_{12}H_{12}SO_4$ requires C, 57.1; H, 4.8; S, 12.7%). No satisfactory separation of isomers was achieved even by fractional distillation through a spinning-band column.

In the addition reaction of toluene-*p*-thiol (0.6 g, 5 mmol) to dimethyl but-2-ynedioate (0.71 g, 5 mmol) in the presence of trimethyl-(*p*-tolylthio)silane (0.09 g, 0.5 mmol), after 10 min the *trans*-vinyl sulphide[17] (0.5 g, 38%) was isolated as a crystalline product after washing with n-pentane. Evaporation of the n-pentane washings followed by high vacuum distillation gave a mixture (0.6 g, 46%) of *cis*- (65%) and *trans*- (35%) isomers, b.p. 150—155° at 0.3 mmHg.

In the reaction between benzenethiol and trichloroacetonitrile in the presence of 5 mole % of catalyst, S-*phenyl trichlorothioacetimidate* was isolated after high-vacuum distillation of the reaction mixture (b.p. 114—115° at 0.5 mmHg) as a solid, m.p. 38—40°; $\nu_{max.}$ 1 620 (C=N) and 3 270 cm^{-1} (NH); τ 2.9 (ArH) and 0.6 (NH) (Found: C, 38.2; H, 2.25; Cl, 41.9. $C_8H_6Cl_3NS$ requires C, 37.7; H, 2.4; Cl, 41.8%).

Adduct Formation and Reactions.—*Addition of Trimethyl-*(*phenylthio*)*silane to phenyl isocyanate.* From a mixture of phenyl isocyanate (0.6 g, 5 mmol) and trimethyl(phenylthio)-silane (0.9 g, 5 mmol) after 4 days a crystalline product had been formed, which, crystallised from n-hexane, gave the 1 : 1 *adduct* (1) (1.4 g, 93%), m.p. 112—113° (Found: C, 65.0; H, 5.6; N, 4.8. $C_{16}H_{19}NOS$ requires C, 63.7; H, 6.3; N, 4.6%). This adduct (1.3 g, 4.3 mmol) in carbon tetrachloride (5 ml) was treated with benzenethiol (0.47 g, 4.3 mmol). After 3 days the crystalline product was filtered off and washed with n-pentane to give phenyl N-phenylthiocarbamate (65%),[16] m.p. 123°.

Addition of trimethyl(*phenylthio*)*stannane to diphenylketen.* Trimethyl(phenylthio)stannane (1.35 g, 5 mmol) and diphenylketen (0.97 g, 5 mmol) reacted exothermically on mixing. After 30 min a crystalline solid had been formed which, however, was not characterised, being deliquescent and moisture-sensitive; its structure (2) is supported by the i.r. spectrum: $\nu_{max.}$ 1 670 cm^{-1} (C=O). Addition of benzenethiol (0.55 g, 5 mmol) to the adduct (2) (1.85 g, 5 mmol) induced an exothermic reaction and the solution became immediately colourless. After 30 min, the solvent was evaporated off and n-pentane (10 ml) was added to the

[16] H. L. Snape, *Ber.*, 1885, **18**, 2428.
[17] W. E. Truce and R. B. Kruse, *J. Amer. Chem. Soc.*, 1959, **81**, 5372.

residue. On cooling at -10 °C, a white solid was precipitated; this was collected and washed with n-pentane to give phenyl diphenylthioacetate (1.3 g, 86%), m.p. 84—85°.

Addition of trimethyl(phenylthio)silane to crotonaldehyde. The n.m.r. spectrum of a mixture of trimethyl(phenylthio)-silane (0.9 g, 5 mmol) and crotonaldehyde (0.35 g, 5 mmol) after 24 h showed the disappearance of the olefinic reson-ances. Distillation under high vacuum afforded the *adduct* (3) (0.95 g, 76%), b.p. 86° at 0.1 mmHg; $v_{max.}$ 1 660 cm^{-1} (C=O); τ 8.75 (d, Me), 6.55 (m, =CH-Si), 5.3 (2 d, =CH-S-), 4.25 (d, CHO), and 3.05 (ArH) (Found: C, 61.8; H, 7.7. $C_{13}H_{20}OSSi$ requires C, 61.9; H, 8.0%).