Chemistry of *N*-Thiosulfinylanilines. V.[1] Reactions of *N*-Thiosulfinylanilines with Nucleophilic Reagents

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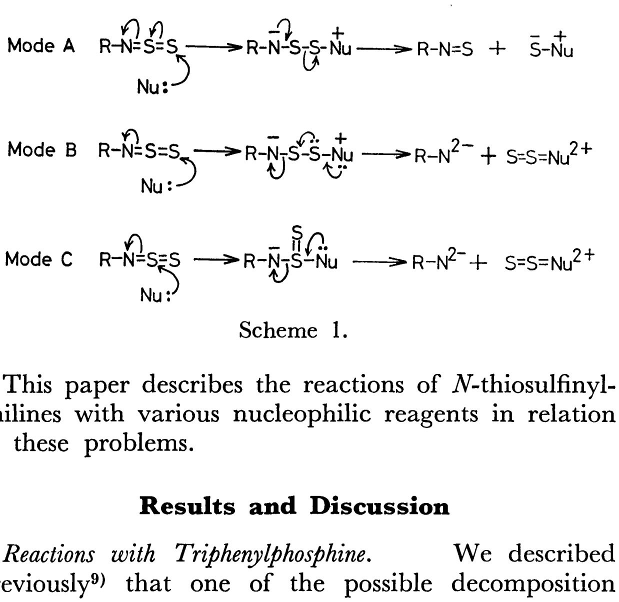
2,4-Di-*t*-butyl-6-methyl-*N*-(thiosulfinyl)aniline (**1**) gave 2,4-di-*t*-butyl-6-methylaniline in the reactions with such reagents as alkylamines, thiourea, butyllithium, alkylmagnesium halides, 1-(1-pyrrolidinyl)cyclopentene, and hydrogen sulfide. Triphenylphosphine reacted with **1** to give (2,4-di-*t*-butyl-6-methylphenylimino)triphenylphosphorane and bis(2,4-di-*t*-butyl-6-methylphenyl)sulfur diimide. Reaction of triphenylphosphine with 2,4,6-tri-*t*-butyl-7,8-dithia-9-azabicyclo[4.3.0]nona-2,4,9-triene afforded 2,4,6-tri-*t*-butylaniline, bis(2,4,6-tri-*t*-butylphenyl)-sulfur diimide, and 2,4,6-tri-*t*-butyl-*N*-sulfinylaniline (**7**). The sulfur diimide was considered to be formed *via* intermediary 2,4,6-tri-*t*-butylthionitrosobenzene, which was trapped by oxygen to give the *N*-sulfinyl derivative **7**.

It is an interesting subject which atom of a thiocumulene of the type X=S=Y is attacked by a nucleophile. Some thiocumulenes are attacked on the central sulfur atom (*e.g.* sulfur dioxide,[2] sulfinylamines,[3] sulfur diimides,[4] and sulfines[5]), while some others are attacked on the terminal atom, X or Y (*e.g.* thiocarbonyl imines[6] and sulfines[7]). The latter type of reaction is known to occur when the difference in electronegativity between the two ligand atoms, X and Y, is small.[8] We became interested in the attacking point of a nucleophile in the case of an *N*-thiosulfinyl group. There seem three conceivable modes as depicted in Scheme 1, and the formation of Nu=S and Nu=S=S is of interest from the standpoint of utilization of thiosulfinylamino compounds as thiotransfer reagents.



Scheme 1.

This paper describes the reactions of *N*-thiosulfinylanilines with various nucleophilic reagents in relation to these problems.

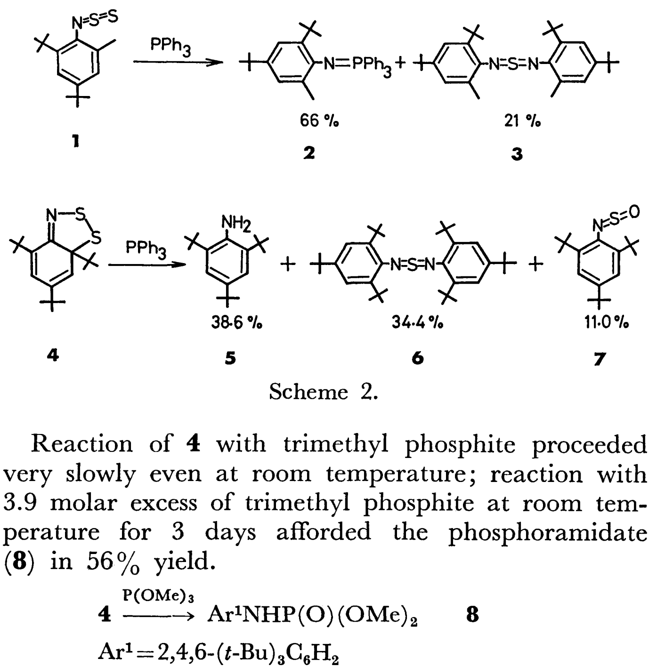
Results and Discussion

Reactions with Triphenylphosphine. We described previously[9] that one of the possible decomposition pathways of a thiosulfinylamino compounds was extrusion of one sulfur atom leading to sulfur diimide *via* thionitroso intermediate and that this explained the instability of the thiosulfinylamino group.

$$\text{Ar-N=S=S} \xrightarrow{-\text{S}} \text{Ar-N=S} \xrightarrow{-\text{S}} 1/2\text{Ar-N=S=N-Ar}$$

It is conceivable, therefore, that elimination of one sulfur atom from thiosulfinylamino group by phosphines would also afford sulfur diimide. In order to examine such a possibility, desulfurization of *N*-thiosulfinylanilines with triphenylphosphine was investigated.

Reactions of 2,4-di-*t*-butyl-6-methyl-*N*-thiosulfinylaniline (**1**) or 2,4,6-tri-*t*-butyl-7,8-dithia-9-azabicyclo-[4.3.0]nona-2,4,9-triene (**4**) with an equimolar amount of triphenylphosphine proceeded even at −78 °C to give products shown in Scheme 2. Since about 50% of **1** or **4** was recovered in these reactions, the yields of the products were calculated based on the consumed **1** or **4**.



Scheme 2.

Reaction of **4** with trimethyl phosphite proceeded very slowly even at room temperature; reaction with 3.9 molar excess of trimethyl phosphite at room temperature for 3 days afforded the phosphoramidate (**8**) in 56% yield.

$$\mathbf{4} \xrightarrow{\text{P(OMe)}_3} \text{Ar}^1\text{NHP(O)(OMe)}_2 \qquad \mathbf{8}$$

$$\text{Ar}^1 = 2,4,6\text{-}(t\text{-Bu})_3\text{C}_6\text{H}_2$$

The reactivity of the *N*-thiosulfinylanilines is in striking contrast to that of *N*-sulfinylanilines, which do not react with trivalent phosphorus compounds; for example, 2,4,6-tri-*t*-butyl-*N*-sulfinylaniline (**7**) reacted with neither triphenylphosphine nor trimethyl phosphite.

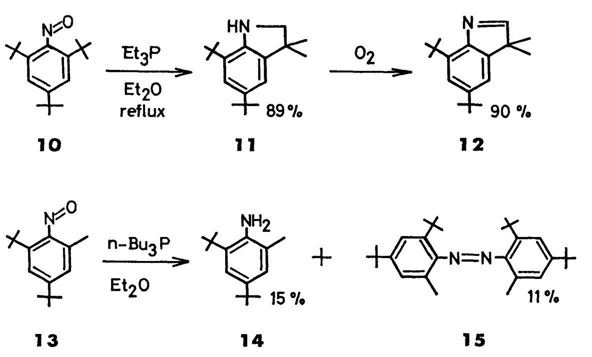
When the reaction of **4** with triphenylphosphine was carried out under a stream of oxygen, the sulfur diimide (**6**) was not produced, but the yield of the *N*-sulfinylaniline (**7**) increased up to 38.6% instead. Since **4** did not react with oxygen under the reaction conditions, this result suggests

$$\mathbf{4} \xrightarrow[-78\,^\circ\text{C}]{\text{Ph}_3\text{P, O}_2} \text{Ar}^1\text{-NH}_2 + \text{Ar}^1\text{-N=S=O}$$
$$\mathbf{5},\ 35.4\% \qquad \mathbf{7},\ 38.6\%$$

that the sulfur diimide (**6**) and the *N*-sulfinylaniline

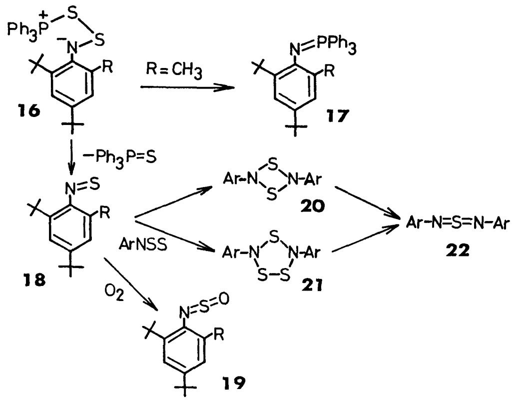
(**7**) were produced *via* a common intermediate, thionitrosobenzene (**9**) (Ar^1–N=S), which could be trapped by oxygen.

Reactions of sterically hindered nitrosobenzenes (**10** and **13**) with trialkylphosphines afford products which are considered to be formed *via* nitrene[10,11] (Scheme 3).



Scheme 3.

Absence of **11** or **15** in the prodcuts obtained by the reaction of **1** or **4** with triphenylphosphine excludes the nitrene formation. Therefore, the probable reaction mechanism can be depicted as in Scheme 4. Nucleophilic attack of triphenylphosphine on **1** or **4** affords zwitterion **16**, which gives the iminophosphorane **17** when R is methyl. When R is more bulky *t*-butyl, elimination of triphenylphosphine sulfide from **16** to give the thionitrosobenzene (**18**) is a predominant pathway. The thionitroso derivative gives **22** *via* cyclization into **20** or **21** followed by extrusion of sulfur. Formation mechanism of 2,4,6-tri-*t*-butylaniline (**5**) is not clear but one possible route is hydrolysis of the zwitterion **16**.



Scheme 4.

Reactions with Amines. A sulfinyl group of a sulfinylamine has been reported to be transferred to a primary amine.[12]

$$R\text{-}N{=}S{=}O + R'\text{-}NH_2 \longrightarrow R\text{-}NH_2 + R'\text{-}N{=}S{=}O$$

In the hope that a similar transfer might occur in the case of thiosulfinylamino compounds, the reactions of the *N*-thiosulfinylaniline (**1**) with amines were attempted. Reactions of **1** with alkylamines afforded 2,4-di-*t*-butyl-6-methylaniline (**14**) together with other products which could not be identified because of difficulty in purification. The results are summarized in Table (see also Experimental).

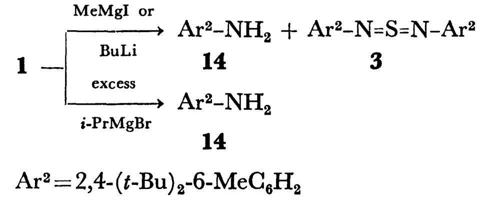
TABLE 1. YIELDS OF **14**

$R\text{-}NH_2$	Reaction time	Solvent	Molar ratio $R\text{-}NH_2/$**1**	Yield of **14** %
n-$BuNH_2$	88 h	EtOH	1.08	41.1
t-$BuNH_2$	22 h	Et_2O	1.39	30.6
1-$AdNH_2$[a]	11 days	CH_2Cl_2	1.01	81.1
$PhNH_2$	1 week	Et_2O	0.94	no reaction
Pyrr.[b]	2.5 h	CH_2Cl_2	2.23	63.7

a) 1-Ad denotes 1-adamantyl. b) Pyrr. stands for pyrrolidine.

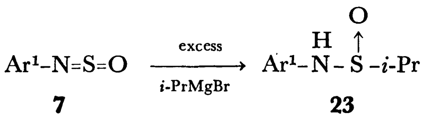
Similar reduction of **1** also took place with thiourea in ethanol for a day at room temperature in 87.7% yield.

Reactions with Organometallic Compounds. Reaction of **1** with an equimolar amount of methylmagnesium iodide afforded the aniline (**14**) (65.2%) and the sulfur diimide (**3**) (8.5%). In the reaction with an equimolar amount of butyllithium the products were also **14** (54.1%) and **3** (23.6%). Reaction of **1** with excess isopropylmagnesium bromide gave **14** in 59.6% yield. These reactions proceeded smoothly and **1** was almost completely consumed. In contrast to these reactions, reactions of 2,4,6-tri-*t*-butyl-*N*-sulfinylaniline (**7**) with isopropylmagnesium bromide afforded 63.0% of *N*-(2,4,6-tri-*t*-butylphenyl)-1-methylethanesulfinamide (**23**),



$$\mathbf{1} \begin{cases} \xrightarrow[\text{BuLi}]{\text{MeMgI or}} \underset{\mathbf{14}}{Ar^2\text{-}NH_2} + \underset{\mathbf{3}}{Ar^2\text{-}N{=}S{=}N\text{-}Ar^2} \\ \xrightarrow[i\text{-PrMgBr}]{\text{excess}} \underset{\mathbf{14}}{Ar^2\text{-}NH_2} \end{cases}$$

$Ar^2 = 2,4\text{-}(t\text{-}Bu)_2\text{-}6\text{-}MeC_6H_2$



$$\underset{\mathbf{7}}{Ar^1\text{-}N{=}S{=}O} \xrightarrow[i\text{-PrMgBr}]{\text{excess}} \underset{\mathbf{23}}{Ar^1\text{-}\overset{H}{N}\text{-}\overset{\overset{O}{\uparrow}}{S}\text{-}i\text{-}Pr}$$

the structure of which was established by hydrolysis giving the aniline (**5**) as well as its spectral and analytical data.

Reaction with an Enamine. Reaction of **1** with 1-(1-pyrrolidinyl)cyclopentene was carried out in the hope of obtaining 1 : 1 cycloadduct. Although the reaction proceeded immediately even at −78 °C to give the aniline (**14**) (57.7%), the reaction mechanism is not clear at present. Absence of the cycloadduct may be attributable to steric hindrance around the nitrogen atom of **1** and to lability of the N–S bond against nucleophilic attack.[13]

Reaction with Hydrogen Sulfide. Reaction of **1** with hydrogen sulfide in benzene followed by chromatographic treatment on silica gel afforded 50.8% of the aniline (**14**) and another compound which was unstable to decompose into **14** on further chromatographic treatment on alumina.

Conclusion. In all these reactions described above, 1:1 adducts appeared too unstable to be isolated. Since any product containing sulfur atom(s) could not be isolated except for the case of triphenylphosphine, the detailed reaction mechanism remains to be determined. However, it is clear that the thiosulfinylamino group has thiotransfer ability judging from the formation of the corresponding reduced compounds.

Experimental

All melting points were uncorrected. The IR and UV spectra were recorded with Hitachi EPI-G2 and EPS-3 spectrophotometers, respectively. The NMR spectra were measured with a Hitachi R-20B (60 MHz) spectrometer using tetramethylsilane as an internal standard. The mass spectra were recorded with a Hitachi RMU-6L mass spectrometer (70 eV). Chromatographic treatment was carried out using dry column chromatography (Woelm silica gel for dry column chromatography) unless otherwise stated.

*Reaction of 2,4-Di-*t*-butyl-6-methyl-*N*-(thiosufinyl)aniline (**1**) with Triphenylphosphine.* To an ethereal solution (25 ml) of **1** (634 mg, 1.90 mmol)[14] was added an ethereal solution (15 ml) of triphenylphosphine (498 mg, 1.90 mmol) at −78 °C under nitrogen. After the mixture was stirred for 4 h at −78 °C, the temperature was raised gradually up to −5 °C over a 13.5 h period. Removal of the solvent followed by treatment with hexane gave white precipitates. They were recrystallized once from ethanol to give triphenylphosphine sulfide (mp 166.5—167.0 °C), which was identified by means of IR. Hexane-soluble part was subjected to dry column chromatography (DCC) (silica gel, hexane) to give three fractions. From the first fraction was recovered 287 mg (53.7%) of **1**. The second fraction gave 51 mg of orange tar, which was purified by DCC to give 43 mg (21.0% based on consumed **1**) of bis(2,4-di-*t*-butyl-6-methylphenyl)sulfur diimide (**3**) (NMR and IR).[9] The third fraction afforded 278 mg (66.0% based on consumed **1**) of (2,4-di-*t*-butyl-6-methylphenylimino)triphenylphosphorane (**2**) as pale yellow crystals, which were recrystallized five times from hexane to give colorless crystals, mp 171—172.5 °C; IR (KBr): 1110 (P–Ph) cm^{-1}; NMR (CCl_4): δ 1.24 (s, 9H), 1.31 (s, 9H), 1.61 (s, 3H), 6.6 (broad, 1H), 7.01 (broad, 1H), and 7.13—7.93 (m, 15H); MS: *m/e* 479 (M^+, 31.5%), 464 (43.5), 262 ($Ph_3P^{+\cdot}$, 50.0), 252 (45.4), and 185 (Ph_2P^+, 100). Found: C, 82.42; H, 8.14; N, 2.84%. Calcd for $C_{33}H_{38}NP$: C, 82.64; H, 7.99; N, 2.92%.

*Reaction of 2,4,6-Tri-*t*-butyl-7,8-dithia-9-azabicyclo[4.3.0]nona-2,4,9-triene (**4**) with Triphenylphosphine.* To an ethereal solution (20 ml) of **4** (426 mg, 1.32 mmol)[14] was added an ethereal solution (12 ml) of triphenylphosphine (351 mg, 1.34 mmol) at −78 °C under nitrogen. The mixture was stirred for 1.5 h at −78 °C, for 2 h at 0 °C, and 3 h at room temperature. Removal of the solvent followed by treatment with hexane afforded triphenylphosphine sulfide (mp 161—163 °C), which was identifical by means of IR. The hexane-soluble part was chromatographed (silica gel, hexane) to give four fractions. The first fraction afforded recovered **4** (225 mg, 52.8%). The second fraction was rechromatographed (silica gel, CCl_4) to give 59 mg (34.4% based on consumed **4**) of bis(2,4,6-tri-*t*-butylphenyl)sulfur diimide (**6**) and 21 mg (11.0% based on consumed **4**) of *N*-sulfinyl-2,4,6-tri-*t*-butylaniline (**7**). These products were identified by comparing the IR and NMR spectra with those of authentic samples.[9] The third fraction gave 63 mg (38.6% based on consumed **4**) of 2,4,6-tri-*t*-butylaniline (**5**) which was identified by IR and NMR. The fourth fraction gave 21 mg of pale yellow tarry material, which could not be purified.

*Reaction of **4** with Triphenylphosphine under a Stream of Oxygen.* After oxygen was bubbled into 40 ml of ether at −78 °C for 30 min, 804 mg (2.49 mmol) of **4** was dissolved. To this solution was added an ethereal solution (39 ml) of triphenylphosphine (652 mg, 2.49 mmol). The reaction mixture was stirred under an oxygen stream for 5 h at −78 °C, for 2 h at 0 °C, and similar work-up to the preceding experiment gave **4** (409 mg, 50.9% recovery), **7** (145 mg, 38.6% based on consumed **4**) and **5** (113 mg, 35.4% based on consumed **4**).

*Reaction of **4** with Trimethyl Phosphite.* A solution of **4** (560 mg, 1.73 mmol) and trimethyl phosphite (332 mg, 8.04 mmol) in ether (45 ml) was stirred for 3 days at room temperature. After ether and excess trimethyl phosphite were removed under reduced pressure, the resulting residue was treated with hexane to give 357 mg (56%) of *O,O*-dimethyl *N*-(2,4,6-tri-*t*-butylphenyl)phosphoramidate (**8**) as colorless needles, which were recrystallized six times from hexane and once from methanol, mp 182 °C; IR (KBr): 3170 (broad, NH), 1140 (PO), and 825 cm^{-1} ($POCH_3$); NMR (CCl_4): δ 1.31 (s, 9H), 1.52 (s, 18H), 3.56 (d, *J*=11 Hz, 6H), 4.35 (broad, 1H), and 7.33 (s, 2H); MS: *m/e* 369 (M^+, 20.6%), 298 (41.3), 242 (40.0), 57 (100), and 41 (87.0). Found: C, 64.74; H, 10.03; N, 3.73%. Calcd for $C_{20}H_{36}NO_3P$: C, 65.02; H, 9.82; N, 3.79%.

*Reaction of 2,4,6-Tri-*t*-butylnitrosobenzene (**10**) with Triethylphosphine.* To an ethereal solution (50 ml) of **10**[15] (8.43 g, 27 mmol), was added triethylphosphine (6.4 g, 54 mmol) dissolved in 50 ml of ether under nitrogen. The solution was then refluxed for 18 h. The solvent and the remaining triethylphosphine were removed under reduced pressure. Crude 3,3-dimethyl-5,7-di-*t*-butylindoline (**11**) was obtained by DCC on silica gel. The yield was 6.2 g (89%). The crude material dissolved in petroleum ether was shaken with aq hydrochloric acid. The precipitated hydrochloride salt was washed with petroleum ether. The free indoline (**11**) was obtained by treatment of the salt with aq sodium carbonate. The above purification was repeated four times to yield pure **11** (2.6 g, 34%), mp 100—102 °C; NMR (CCl_4): δ 1.25 and 1.31 (24H), 3.20 (2s, H), 3.69 (br, 1H), 6.77 (d, *J*=4 Hz, 1H), and 6.92 (d, *J*=4 Hz, 1H); IR (KBr): 3300 cm^{-1} (NH). Found: C, 83.10; H, 11.43; N, 5.50%. Calcd for $C_{18}H_{29}N$: C, 83.33; H, 11.27; N, 5.40%. This compound was also purified by recrystallization from ethanol. The dihydroindole (**11**) (0.41 g, 1.6 mmol) dissolved in 25 ml of 90% ethanol was heated at reflux for 11 h in the presence of active charcoal (1 g) under a stream of oxygen. The active charcoal was filtered off from the warm solution and then the crude 3*H*-indole (**12**) (0.36 g, 90%) was obtained by removal of the solvent. The pure material was obtained by repeated recrystallization from 80% ethanol. The yield was 0.2 g (50%), mp 128—129 °C; NMR (CCl_4): δ 1.29 and 1.35 (s, 15H), 1.50 (s, 9H), 7.04 (d, *J*=4 Hz, 1H), 7.17 (d, *J*=4 Hz, 1H), and 7.77 (s, 1H); IR (KBr): 1590 cm^{-1} (C=N); UV$_{max}$ (C_2H_5OH): 224 (log ε 4.2), 231 (4.1), and 266 nm (3.9). Found: C, 83.86; H, 10.51; N, 5.28%. M^+ 257. Calcd for $C_{18}H_{27}N$: C, 83.99; H, 10.57; N, 5.44%. M^+ 257.

*Reaction of 2,4-Di-*t*-butyl-6-methylnitrosobenzene (**13**) with Tributylphosphine.* To an ethereal solution (20 ml) of tributylphosphine (2 g, 9.9 mmol) was added an ethereal solution (15 ml) of **13** (0.996 g, 4.27 mmol).[15] The mixture was stirred for 70 min at room temperature, and then stirred with sulfur (170 mg) for 40 min. After removal of the solvent, the residue was chromatographed on silica gel. Elution with benzene afforded a red fraction (Fraction A) and a yellow one (Fraction B). Fraction A was chromatographed on silica gel with CCl_4 as eluent to afford 97.5 mg (0.224 mmol, 10.5%) of 2,2′,4,4′-tetra-*t*-butyl-6,6′-dimethylazobenzene (**15**), which was recrystallized from aq methanol; mp 156—158 °C. NMR (CCl_4): δ 1.37 (s, 36H), 2.24 (s, 6H), 7.04 (d, J=2 Hz, 2H), and 7.32 (d, J=2 Hz, 2H); UV_{max} (hexane): 238 (ε 9040), 247 (sh) (8570), 312 (15650), and 486 nm (1750); MS: *m/e* 434 (M^+, 5.4%), 217 (35), and 57 (100).

Fraction B was chromatographed on alumina with hexane as eluent to give 140 mg (0.638 mmol, 15.0%) of 2,4-di-*t*-butyl-6-methylaniline (**14**).

Reactions of 1 with Amines. Reactions were carried out under nitrogen or argon.

Reaction with Butylamine: A mixture of **1** (400 mg, 1.42 mmol) and butylamine (112 mg, 1.53 mmol) in 10 ml of ethanol was stirred for 88 h at room temperature. The reaction mixture was filtered to give 62 mg of colorless crystals, which melted at 107.5—108.5 °C after twice recrystallization from ethanol; IR (KBr): 3420, 870, 725, 605, and 590 cm^{-1}; NMR (CCl_4): δ 1.27 (s, 9H), 1.48 (s, 9H), 2.42 (s, 3H), and 7.05 (ABq, J=2 Hz, $\Delta\delta$=0.09, 2H); MS: *m/e* 267 (3.6%), 233 (3.6), 225 (17.2), 220 (17.5), and 205 (100). Found: C, 59.90; H, 8.44; N, 4.54; S, 26.58%, which requires $C_{15.4}H_{25.8}NS_{2.6}$, but the structure was not determined.

The filtrate was treated with DCC (silica gel, CCl_4). A reddish fraction gave 116 mg of tarry mixture, which could not be purified and identified; IR (neat): 3430 and 3340 cm^{-1} (broad); NMR (CCl_4): δ 1.26 (s, *ca.* 18H), 1.44 (s, 18H), 2.35 (s, *ca.* 3H), 2.41 (broad s, *ca.* 3H), 5.24 (broad, 1H), 5.37 (broad, 1H), 6.92 (m, 2H), and 7.07 (m, 2H). A colorless fraction gave 128 mg (41.1%) of **14**.

Reaction with t-*Butylamine*: A mixture of **1** (399 mg, 1.42 mmol) and *t*-butylamine (145 mg, 1.98 mmol) in 5 ml of ether was stirred for 22 h at room temperature. Removal of the solvent followed by treatment with hexane afforded 62 mg of colorless precipitates; IR (KBr): 2600—2500 (broad band), 1200, 1110, and 640 cm^{-1}; NMR ($CDCl_3$): δ 1.31 (s, 9H), 1.47 (s, 18H), 2.50 (s, 3H), 5.62 (broad s, 1H), 6.05 (broad s, 4H), 7.15 (m, 1H), and 7.33 (m, 1H). The hexane-soluble part was treated with DCC (silica gel, hexane) to give 117 mg (29.3%) of **1**, 116 mg of tarry mixture, which could not be purified, and 95 mg (30.6%) of **14**.

Reaction with 1-Adamantylamine: A solution of **1** (565 mg, 2.01 mmol), 380 mg (2.03 mmol) of 1-adamantylammonium chloride, and triethylamine (255 mg, 2.52 mmol) in dichloromethane (15 ml) was stirred for 11 days at room temperature. The reaction mixture was washed with water and dried over $MgSO_4$. Removal of the solvent followed by treatment with pentane afforded 110 mg of sparingly soluble colorless powder, which sublimed at 315—350 °C; IR (KBr): 3345 (NH), 3250—2500 (broad band), 1210, 1190, 1025, and 640 cm^{-1}; NMR (acetone-d_6): δ 1.55—1.92 (m) and 2.00—2.25 (m), the intensity ratio was 12:3; MS: *m/e* 264 (2.6%), 330 (1.1), 307 (1.1), 297 (0.9), 284 (0.9), 213 (2.2), 204 (4.8), 197 (3.0), 151 (1-$AdNH_2^{+\cdot}$, 100), 135 (Ad^+, 62), and 108 (32).

Found (recrystallized once from acetone): C, 52.00; H, 7.15; N, 5.82; S, 22.31%, which requires $C_{10.4}H_{17.0}N_{1.0}O_{1.9}S_{1.7}$, but the structure could not be identified.

The pentane-soluble part was treated with DCC (silica gel, hexane) to give 72 mg (12.7%) of **1** in a purple fraction, and 357 mg (81.1%) of **14**. The other products could not be isolated, but a tarry mixture (104 mg) obtained from a fraction next to an orange-yellow fraction exhibited following spectral data; IR (neat): 3410 (sharp), 3475, and 3300 cm^{-1} (broad); NMR (CCl_4): δ 1.18 (s, 9H), 1.38 (s, 9H), 1.46—1.88 (m, 11—12H), 1.82—2.20 (m, 3H), 2.36 (s, 3H), 3.46 (broad, 1H), 5.40 (broad, 1H), 6.39 (d, J=2 Hz, 1H), and 7.15 (d, J=2 Hz, 1H); MS: *m/e* 380 (trace), 352 (trace), 330 (trace), 262 (trace), 247 (6.6%), 232 (23.8), 219 (18.9), 204 (100), 151 (13.9), 148 (7.8), 94 (86.9), and 64 (75.4).

Reaction with Pyrrolidine: A solution of **1** (302 mg, 1.07 mmol) and pyrrolidine (170 mg, 2.39 mmol) in dichloromethane (5 ml) was stirred for 2.5 h at room temperature to give a yellowish orange solution, which was washed with water and dried over $MgSO_4$. Removal of the solvent followed by DCC (silica gel, hexane) gave 150 mg (63.7%) of **14**. The other products could not be isolated.

Reaction of 1 with Thiourea. Ethanol solution (10 ml) of 404 mg (1.44 mmol) of **1** and 109 mg (1.44 mmol) of thiourea was stirred for 24 h at room temperature. The reaction mixture was filtered to give 83 mg (2.58 mg-atom) of sulfur and reddish brown solution. After removal of the solvent, the residue was treated with hexane to give colorless crystals which seemed to be a mixture containing thiourea mainly on the basis of the IR spectrum, but could not be purified. The hexane-soluble part was subjected to DCC (silica gel, hexane) to give 276 mg (87.7%) of **14**.

Reaction of 1 with Organometallic Compounds. Reactions were carried out under nitrogen. Concentration of organometallic reagents were determined by titration with 2-butanol in xylene using 1,10-phenanthroline as an indicator.[16)]

Reaction of 1 with Methylmagnesium Iodide. To an ethereal solution (10 ml) of **1** (440 mg, 1.56 mmol) cooled to *ca.* 0 °C was added an ethereal solution (1.63 ml) of CH_3MgI (0.98 M). After being stirred for 30 min at 0 °C, the reaction mixture was treated with aq NH_4Cl (5 ml) to give orange solution, which was washed with water and dried over $MgSO_4$. Removal of the solvent followed by DCC (silica gel, hexane) afforded 23 mg (5.3% recovery) of **1** in a purple fraction. The subsequent fraction gave 25 mg of slightly colored tarry material, which partly decomposed into purple substance (probably **1**) on treatment with TLC (silica gel). This tarry material afforded following spectral data; IR (neat): 3420 cm^{-1}; NMR (CCl_4): δ 1.28 (s, 9H), 1.49 (s, 9H), 1.94 (s, 3H), 5.46 (broad s, 1H), 7.00 (d, J=2 Hz, 1H), and 7.15 (d, J=2 Hz, 1H); MS: *m/e* 247 (3%), 232 (13), 219 (19), and 204 (100).

The orange fraction gave 118 mg of orange crystalline material, which was recrystallized once from acetone to give 31 mg (8.5%) of the sulfur diimide **3**.

The most polar fraction gave 224 mg (65.2%) of **14**.

Reaction of 1 with Isopropylmagnesium Bromide. To an ethereal solution of the Grignard reagent prepared from 871 mg (7.08 mmol) of isopropyl bromide and cooled with an ice bath, 160 mg (6.59 mmol) of magnesium, and 11 ml of ether, was added an ethereal solution (11 ml) of **1** (198 mg, 0.703 mmol) dropwise over a period of 10 min. After being stirred for 1 h at 0 °C, the reaction mixture was hydrolyzed by aq NH_4Cl. After the usual work up, the residue was treated with DCC (silica gel, hexane) to give 32 mg of orange tar, which gave 15 mg of **14** on purification by TLC (silica gel, CCl_4–hexane; 4:1), and 112 mg of pale yellow tar, which was treated with DCC (silica gel, CCl_4). From a colorless fraction, 77 mg of **14** was obtained. Thus the yield of **14** was 92 mg (59.6%).

Reaction of 1 with Butyllithium. To a pentane solution (5 ml) of **1** (501 mg, 1.78 mmol) was added 1.15 ml of hexane solution of butyllithium (1.55 M) at 0 °C over a 5 min period. After being stirred for 1 h at 0 °C, the reaction mixture was hydrolyzed by 5 ml of aq NH_4Cl, washed with water, dried over $MgSO_4$. After the solvent was removed, the residual orange tar was washed with 3 ml of methanol to give 98 mg (23.6%) of **3** as orange crystals. The methanol-soluble part was treated with DCC (silica gel, hexane) to give 211 mg (54.1%) of **14**.

*Reaction of 2,4,6-Tri-*t*-butyl-*N*-sulfinylaniline (7) with Isopropylmagnesium Bromide.* To the Grignard reagent prepared from 391 mg (16.1 mmol) of magnesium, 2.00 g (16.3 mmol) of isopropyl bromide, and 25 ml of ether and cooled with an ice bath, was added an ethereal solution (10 ml) of **7** (501 mg, 1.63 mmol) dropwise with stirring. After additional stirring for 40 min, the reaction mixture was hydrolyzed by aq NH_4Cl, washed with water, and dried over $MgSO_4$. Removal of the solvent gave 569 mg of colorless crystals, which were recrystallized once from aq methanol to give 261 mg (63.0%) of the sulfinamide **23** (mp 100.5—101 °C (dec)), which was recrystallized three times from hexane to give colorless needles, mp 101 °C (dec); IR (KBr): 3290 (broad, νNH) and 1075 cm^{-1} (νSO); NMR ($CDCl_3$): δ 1.33 (s, 9H), 1.45 (d, $J=7$ Hz, 6H), 1.50 (s, 18H), 3.21 (sep, $J=7$ Hz, 1H), 6.12 (broad s, 1H), and 7.39 (s, 2H); MS: m/e 261 ($M^+ - (CH_3)_2C{=}S{=}O$, 16.3%) and 246 (100). Found: C, 71.87; H, 10.84; N, 3.92; S, 8.94%. Calcd for $C_{21}H_{37}NOS$: C, 71.74; H, 10.61; N, 3.98; S, 9.12%.

A solution of **23** (42 mg, 0.12 mmol) in 10 ml of methanol containing 1 drop of trifluoroacetic acid was allowed to stand for 3 days at room temperature. Removal of the solvent followed by preparative TLC purification (silica gel, CCl_4) gave 17 mg (54%) of **14**.

Reaction of 1 with 1-(1-Pyrrolidinyl)cyclopentene. To a CH_2Cl_2 solution (15 ml) of **1** (880 mg, 3.13 mmol) was added a solution of the enamine[12] (4.38 mg, 3.19 mmol) in 10 ml of CH_2Cl_2 at −78 °C. The color of **1** (red-purple) disappeared immediately. After removal of the solvent, the residue was chromatographed on silica gel. Elution with benzene afforded 396 mg (57.7%) of **14**.

Reaction of 1 with Hydrogen Sulfide. Hydrogen sulfide was bubbled into a benzene solution (15 ml) of **1** (306 mg, 1.09 mmol) at *ca.* 10 °C for 3.5 h. Removal of the solvent followed by preparative TLC (silica gel, CCl_4) gave two fractions. The first fraction was rechromatographed (TLC, silica gel, hexane) to give 131 mg of brown tar, which gave **14** (57 mg) on treatment with TLC (alumina, hexane). The second fraction gave 121 mg (50.8%) of **14** (mp 33.5—35.5 °C).

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10) Under similar conditions, such reagents as triethyl phosphite, triphenylphosphine, and phosphorus trichloride did not react with **10**. When **10** and an excess amount of triethylphosphine were mixed in ether under nitrogen at 0 °C, the solution gradually turned red with concomitant appearance of a set of persistent ESR signals ($g=2.004$, $a_N=9.7$ G, $a_H(2)=2.2$ G; a triplet of triplet). When the solution was shaken under air, the red color as well as the ESR signals disappeared with concurrent recovery of the green color due to **10**. The same phenomena were observed when tributylphosphine was used in place of triethylphosphine. When the nitrosobenzene **13** was allowed to react with tributylphosphine, strong ESR signals were also observed, albeit they were less stable than that observed for **10**, bearing much complex features presumably due to the presence of some species.

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