Chemistry of *N*-Thiosulfinylanilines. I. Reactions of Sterically Hindered Anilines with Sulfur Chlorides. Preparation of *N*-Thiosulfinylanilines

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Reaction of 2,4-di-*t*-butyl-6-methylaniline (**3**) with disulfur dichloride afforded 2,4-di-*t*-butyl-6-methyl-*N*-thiosulfinylaniline (**4**) as a stable compound in 80% yield. Reaction of 2,4,6-tri-*t*-butylaniline (**1**) with disulfur dichloride gave in 70% yield 2,4,6-tri-*t*-butyl-7,8-dithia-9-azabicyclo[4.3.0]nona-2,4,9-triene, which in solution, exists as a tautomeric mixture with 2,4,6-tri-*t*-butyl-*N*-thiosulfinylaniline (**2b**) as a minor component. In the reactions with 2,4-di-*t*-butyl-6-isopropyl- or 2,4,6-trimethylaniline, *N*-thiosulfinylanilines obtained were unstable at ambient temperature. Aniline **1** reacted with sulfur dichloride to give **2** and the corresponding sulfur diimide and *N*-sulfinylaniline. The reaction of **4** with the dichloride afforded **4** and the corresponding sulfur diimide.

p-Dimethylamino-*N*-thiosulfinylaniline has been the only compound that has thiosulfinylamino group.[1] However, the reported yield in the reaction of *p*-dimethylaminonitrosobenzene or *p*-dimethylamino-*N*-sulfinylaniline with phosphorus pentasulfide was poor (15 or 1% respectively). Moreover, this compound could not be purified by chromatography, and appeared to be air-sensitive.[2]

Protection of a reactive group by bulky substituents often stabilizes the compounds and has an advantage over stabilization brought about by introduction of a strongly electron-donating or -withdrawing group, since the nature of a functional group to be studied is electronically less perturbed. As part of our study on poly-*t*-butylbenzene derivatives,[3] we undertook an investigation on steric protection of thiosulfinylamino group and a stable thiosulfinylamino compound was obtained in a high yield by a reaction of disulfur dichloride with a sterically hindered aniline. Although the reaction of disulfur dichloride with aniline leading to the formation of 1,2,3-benzodithiazol-2-ium chloride (Herz compound) is known as the Herz reaction[4] and has been extensively studied, there has been no report on the reaction of S_2Cl_2 with anilines bearing two ortho substituents. This paper describes the results of the reaction with such hindered anilines.

Results and Discussion

Reaction of 2,4,6-tri-*t*-butylaniline (**1**) with disulfur dichloride (S_2Cl_2) in the presence of triethylamine in ether at 0 °C for 1 h afforded a compound with a molecular formula $C_{18}H_{29}NS_2$ in 70% yield; the molecular weight was determined by mass spectrometry (M^+: *m/e* 323) and vapor pressure osmometry in benzene at 39.4 °C (323). In solution, this compound was found to be a mixture of two isomers (**2a** and **2b**) on the following basis.

1) The compound is yellow crystalline material but reddish in solution: a very weak absorption at 535 nm was observed in a fairly concentrated solution (*ca.* 2.5×10^{-2} M). This absorption around 540 nm is considered to be characteristic of the *N*-thiosulfinylanilines (see Ref. 1 and the data listed in Table 1).

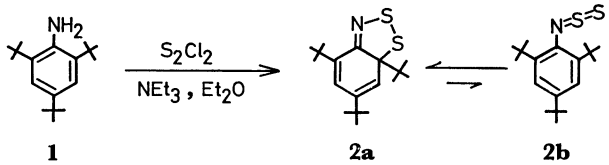
2) The NMR spectrum shows the presence of two compounds; the major one (**2a**) has three singlets due to nonequivalent *t*-butyl groups at δ 0.83, 1.18, and 1.38, and two pairs of doublet due to nonequivalent olefinic protons at 5.87 and 6.39, while the minor one (**2b**) has two singlets due to *t*-butyl groups at δ 1.31 (2 and 6 positions) and 1.34 (4 position), and a singlet due to the two equivalent aromatic protons. The molar ratio of the two species was calculated based on the NMR signal intensities of the two olefinic protons of **2a** and the two aromatic protons of **2b** and found to vary reversibly with temperature. The typical results are shown in Table 2. The compound (**2**) exists only as a monomer in the solid state and the structure of **2a** was confirmed by X-ray crystallographic analysis.[5]

Table 1. Electronic spectra of *N*-thiosulfinylanilines

Compound	Solvent	λ_{max} nm, (ε)
2a+**2b**	hexane	268(2610), 292(2580), 340(2050), 410(3480), 535(weak)
4	hexane	270 sh(1470), 310 sh(1940), 343(5590), 476(2190), 536 sh(1190)
8	pentane	272 sh(2060), 305 sh(2330), 343(6960), 483(1810), 542 sh(1130)
10	pentane	336(5700), 462(1900), 540 sh(870)

Table 2. Equilibrium constant in CD_2Cl_2 (0.48 M)

Temp	[**2a**]/[**2b**]	ΔG(kcal/mol)
35 °C	14.2	1.62
0 °C	33.7	1.91



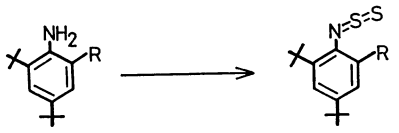
1 **2a** **2b**

Unlike the case of **1**, a similar reaction with 2,4-di-*t*-butyl-6-methylaniline (**3**) gave the corresponding *N*-thiosulfinylaniline (**4**) in 80% yield, which was deep purple crystals and stable at ambient temperature. The electronic spectra are tabulated in Tables 1 and 3; the visible part of the spectra did not show any appre-

Table 3. Solvent effect on electronic spectra of **4**

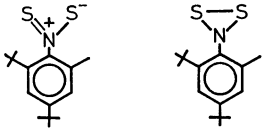
Solvent	λ_{max} nm, (ε)		
Hexane	343(5590),	476(2190),	536 sh(1190)
CCl_4	345(5830),	480(2230),	548 sh(1280)
EtOH	343(6000),	478(2170),	544 sh(1260)

ciable solvent effect (Table 3). No evidence for the ring-chain tautomerism as observed for **2** was obtained for this compound. X-Ray analysis established the structure (**4**),[5]



3: R=Me **4**: R=Me
7: R=*i*-Pr **8**: R=*i*-Pr

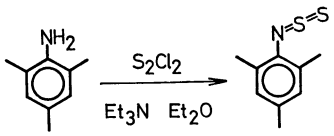
thus eliminating other possible structures, *i.e.*, (dithionitro)benzene (**5**) or dithiaziridine (**6**).



5 **6**

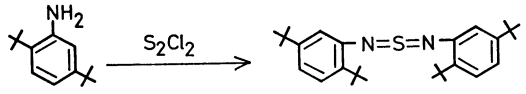
A similar reaction of 2,4-di-*t*-butyl-6-isopropylaniline (**7**) gave the corresponding *N*-thiosulfinylaniline (**8**) as a purple oil (14%), which decomposed slowly at room temperature. The electronic spectrum is listed in Table 1. The isolation of analytically pure specimen was difficult because of its instability. The fact that more sterically hindered *N*-thiosulfinylaniline (**7**) was less stable than **4** is noteworthy and this point will be discussed in the accompanying paper[8] in connection with the thermolysis of these *N*-thiosulfinylanilines.

The reaction of 2,4,6-trimethylaniline (**9**) with disulfur dichloride under similar conditions gave no *N*-thiosulfinylaniline. However, lowering of both reaction temperature (−78 °C, 2 h) and work-up temperature (−2 °C) enabled us to isolate **10** in 2% yield as a reddish purple oil (see Table 1 for the electronic spectrum), although satisfactory analytical data could not be obtained because of its instability.



9 **10**

Unlike both aforementioned reactions and the Herz reaction, the reaction of 2,5-di-*t*-butylaniline (**11**) with disulfur dichloride under conditions similar to those for the reaction of **1** gave *N*,*N*′-bis(2,5-di-*t*-butylphenyl)sulfur diimide (**12**) in 70% yield as orange crystals.



11 **12**

The above results indicate that the reactions of disulfur dichloride with anilines substituted at both ortho positions gave *N*-thiosulfinylanilines, although they are fairly unstable in the absence of bulky substituents. Therefore, existence of a highly electron-donating group (as in *p*-dimethylamino-*N*-thiosulfinylaniline)[1] is not essential for preparation of a thiosulfinylamino compound.

N-Thiosulfinylanilines were obtained also by the reactions of **1** and **3** with sulfur dichloride (SCl_2). In these cases, considerable amounts of the sulfur diimides were obtained. The *N*-sulfinylaniline (**15**) was formed as well.

$$\mathbf{1} \xrightarrow[Et_3N,\ Et_2O]{SCl_2} \mathbf{2}\ (23.7\%) + Ar^1\text{-}N{=}S{=}N\text{-}Ar^1\ (12.6\%)\ \mathbf{14} + Ar^1\text{-}N{=}S{=}O\ (11.9\%)\ \mathbf{15} + \mathbf{1}\ (45\%)$$

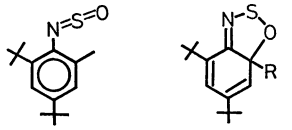
$Ar^1 = 2,4,6\text{-}(t\text{-}Bu)_3C_6H_2$

$$\mathbf{3} \xrightarrow[Et_3N,\ Et_2O]{SCl_2} \mathbf{4}\ (16.9\%) + Ar^2\text{-}N{=}S{=}N\text{-}Ar^2\ (50.1\%) + \mathbf{3}\ (26.3\%)$$

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

Formation of **2** or **4** may be ascribed to the reactions of **1** or **3** with disulfur dichloride, because sulfur dichloride is known to dissociate partly into disulfur dichloride and chlorine molecule.[6]

Reactions of **1** and **3** with thionyl chloride gave *N*-sulfinylanilines **15** (83.0%) and **16** (72.3%), respectively. These *N*-sulfinylanilines showed no tendency to undergo intramolecular cyclization into **17** unlike the case of **2**.



16 **17** R=Me or *t*-Bu

Experimental

All melting points were uncorrected. The IR and UV spectra were recorded with Hitachi EPI-G2 and Hitachi EPS-3 spectrophotometers, respectively. The NMR spectra were measured with a Hitachi R-20B spectrometer using tetramethylsilane as an internal standard. The mass spectra were recorded with a Hitachi RMU-6L mass spectrometer. Molecular weights were determined with a Hitachi 117 Molecular Weight Apparatus. Reactions were performed under nitrogen, and chromatographic separations were carried out by dry column chromatography (Woelm silica gel for dry column chromatography).

*Reaction of 2,4,6-Tri-t-butylaniline (**1**) with S_2Cl_2.* A solution of S_2Cl_2 (261 mg, 1.94 mmol) in ether (1.7 ml) was added dropwise to a solution of 2,4,6-tri-*t*-butylaniline[7] (500 mg, 1.91 mmol) and triethylamine (399 mg, 3.95 mmol) in ether (20 ml) with stirring at 0 °C. After being stirred for 1 h, the reaction mixture was washed with water, and dried ($MgSO_4$). Removal of the solvent gave a brown tarry material, which was chromatographed on silica gel with hexane. The first fraction gave 16 mg of sulfur. The second fraction afforded 434 mg (1.34 mmol, 70.2%) of 2,4,6-tri-*t*-butyl-7,8-dithia-9-azabicyclo[4.3.0]nona-2,4,9-triene (**2a**) as yellow crystals (mp 92.5—94 °C), which were recrystallized three times from ethanol; mp 96—97 °C; IR (KBr):

2950, 1625, 1475, 1455, 1385, 1360, 1255, 835, 665, and 638 cm^{-1}; NMR (CCl_4): the major component (**2a**) δ 0.83 (s, 9H), 1.18 (s, 9H), 1.38 (s, 9H), 5.87 (d, J=2 Hz, 1H), and 6.39 (d, J=2 Hz, 1H); the minor component (**2b**): 1.31 (s, 18H), 1.34 (s, 9H), 7.34 (s, 2H); λ_{max}^{hexane} (ε): 240 sh (4720), 268 (2610), 292 (2580), 340 (2050), 410 nm (3480), and 535 sh (very weak); *m/e* 323 (M^+, trace), 291 (4.4%), 266 (72), 251 (49), 244 (100), and 236 (49): mol wt (vapor pressure osmometry in benzene, 39.4 °C); 322.9 (Calcd: 323.55).

Found: C, 66.64; H, 8.96; N, 4.08; S, 19.72%. Calcd for $C_{18}H_{29}NS_2$: C, 66.84; H, 9.04; N, 4.33; S, 19.79%.

The third fraction gave 10 mg of orange crystals, which were identified as *N,N'*-bis(2,4,6-tri-*t*-butylphenyl)sulfur diimide (**14**)[8] by the IR spectrum and TLC. From the last fraction aniline (**1**) (52 mg, 10.4%) was recovered.

Reaction of 2,4-Di-t-butyl-6-methylaniline (3) with S_2Cl_2. A solution of S_2Cl_2 (624 mg, 4.62 mmol) in ether (4.2 ml) was added dropwise to a solution of **3**[7] (993 mg, 4.52 mmol) and triethylamine (839 mg, 8.3 mmol) in ether (40 ml) with stirring at 0 °C. After being stirred for 1 h, the reaction mixture was poured into water, and the organic layer was dried ($MgSO_4$). Removal of the solvent gave a dark purple tar, which was subjected to chromatographic separation (silica gel, hexane). The first fraction gave 27 mg of sulfur. The second purple fraction gave 1.021 g (80.1%) of 2,4-di-*t*-butyl-6-methyl-*N*-thiosulfinylaniline (**4**) as a dark purple tar, which crystallized on standing (mp 53—54 °C). Repetitive recrystallizations from aq methanol afforded analytically pure specimen, mp 67—68 °C; IR (KBr): 2950, 1590, 1455, 1360, 1222, 1169, 995, 940, 870, 780, 760, 690, 650, and 620 cm^{-1}; NMR (CCl_4): δ 1.33 (s, 18H), 2.02 (s, 3H), and 7.22 (ABq, $\Delta\delta$=0.22, J=2 Hz, 2H); λ_{max}^{hexane} (ε): 270 sh (1270), 310 (1940), 343 (5590), 476 (2190), and 536 sh nm (1190); *m/e*: 281 (M^+, 0.5%), 266 (20), 224 (100), 217 (18), 209 (18), and 204 (20); mol wt (vapor pressure osmometry in benzene at 39.4 °C): 295. Found: C, 64.01; H, 8.46; N, 5.10; S, 22.97%. Calcd for $C_{15}H_{23}NS_2$: C, 64.01; H, 8.24; N, 4.98; S, 22.78%.

The third fraction gave 86 mg of orange tar, which was treated with preparative TLC (silica gel, benzene) to give 28 mg (2.6%) of *N,N'*-bis(2,4-di-*t*-butyl-6-methylphenyl)-sulfur diimide (**13**), which was identified by comparison of the NMR, IR, and mass spectra with those of an authentic sample obtained by photolysis of **4**.[9] The fourth fraction gave 49 mg (4.9%) of **3**.

This reaction was performed in a larger scale using 20 g of **3**, where conventional column chromatography was used to separate **4** from the reaction mixture for the purpose of preparative convenience. Hexane could also be used as reaction solvent instead of ether.

Reaction of 2,4-Di-t-butyl-6-isopropylaniline (7) with S_2Cl_2. To an ice-cold solution of **7**[10] (517 mg, 2.09 mmol) and triethylamine (460 mg, 4.55 mmol) in ether (30 ml), a solution of S_2Cl_2 (294 mg, 2.18 mmol) in ether (10 ml) was added dropwise with stirring. After additional stirring for 45 min at 0 °C and then usual work up, the resulting residue was chromatographed (silica gel, pentane). A red purple part of the column was eluted with pentane to give a red purple solution, which was used for measurement of an electronic spectrum. Removal of the solvent gave 93 mg (14.4%) of 2,4-di-*t*-butyl-6-isopropyl-*N*-thiosulfinylaniline (**8**) as a purple oil. IR (neat): 1595, 1360, 1128, and 1000 cm^{-1}; NMR (CCl_4): δ 1.12 (d, J=6.5 Hz, 6H), 1.34 (s, 9H), 1.36 (s, 9H), 2.58 (sep, J=6.5 Hz, 1H), and 7.27 (ABq, $\Delta\delta$=0.13, J=2 Hz); $\lambda_{max}^{pentane}$ (ε): 272 sh (2060), 305 sh (2330), 343 (6960), 483 (1810), and 542 sh nm (1130).

Reaction of 2,4,6-Trimethylaniline (9) with S_2Cl_2. To a solution of **9** (998 mg, 7.38 mmol) and triethylamine (1.495 g, 14.8 mmol) in ether (50 ml), a solution of S_2Cl_2 (1.247 g, 9.24 mmol) in ether (30 ml) was added dropwise with stirring at −78 °C. After additional stirring for 40 min at −78 °C, an insoluble part was filtered off at −78 °C. The red-purple filtrate was condensed under reduced pressure at −10 °C. The residue was chromatographed (silica gel, pentane) at −2 °C. A red-purple fraction which contained 2,4,6-trimethyl-*N*-thiosulfinylaniline (**10**) was eluted with pentane at −2 °C to give a red solution (100 ml), which was immediately used for measurement of an electronic spectrum. The concentration of the solution was determined to be 0.3 g/l on the basis of the weight of the residue from a 5 ml-portion of the eluted solution. Thus the yield of **10** was 30 mg (2%). Removal of the solvent at −10 °C afforded a red purple oil, which was immediately subjected to NMR measurement in carbon tetrachloride. **10**; NMR (CCl_4, at 0 °C): δ 2.01 (s, 6H), 2.31 (s, 3H), and 6.90 (s, 2H); $\lambda_{max}^{pentane}$ (ε): 336 (5700), 462 (1900), and 540 sh nm (870).

The pentane solution of **10** obtained as above was decolorized by none of the following reagents suggesting no reaction: dimethyl acetylenedicarboxylate, *N*-phenylmaleimide, cyclohexene, or norbornadiene.

Reaction of 2,5-Di-t-butylaniline (11) with S_2Cl_2. A solution of S_2Cl_2 (1.001 g, 7.49 mmol) in ether (10 ml) was added to a solution of **11**[12] (996 mg, 4.85 mmol) and triethylamine (1.59 g, 15.7 mmol) in ether (50 ml) dropwise with stirring at 0 °C. After stirring for 1 h and usual work-up, the residue was chromatographed on silica gel with hexane. The first effluent (50 ml) gave 35 mg of sulfur. A red fraction gave 749 mg (70.4%) of *N,N'*-bis(2,5-di-*t*-butylphenyl)sulfur diimide (**12**) as a red tarry material, which was purified by TLC (silica gel, hexane) to give vermilion crystals, which were recrystallized three times from acetone; mp 86—87 °C; IR (KBr): 2960, 1475, 1385, 1355, 1280, 1095, and 822 cm^{-1}; NMR (CCl_4): δ 0.87 (s, 18H), 1.46 (s, 18H), 6.36 (d, J=2 Hz, 2H), 6.89 (dd, J=8 and 2 Hz, 2H), and 7.16 (d, J=8 Hz, 2H); λ_{max}^{hexane} (ε): 241.5 nm (14300), 252 sh (12900), 392 (9350); *m/e*: 438 (M^+, 13.7%), 381 (21), 203 (100), 188 (32), 146 (30), and 132 (39). Found: C, 76.96; H, 9.86; N, 6.38; S, 7.38%. Calcd for $C_{28}H_{42}N_2S$: C, 76.66; H, 9.65; N, 6.38; S, 7.31%. Aniline **11** (104 mg, 10.4%) was also recovered.

Reaction of 2,4-Di-t-butyl-6-methylaniline (3) with Sulfur Dichloride. To an ice-cold solution of **3** (908 mg, 4.14 mmol) and triethylamine (1.041 g, 10.31 mmol) in ether (40 ml), a solution of SCl_2 (432 mg, 4.19 mmol) in ether (10 ml) was added dropwise with stirring. After additional stirring for 1.5 h and usual work-up, the residue was chromatographed on silica gel with hexane. A red purple fraction gave 197 mg (16.9%) of 2,4-di-*t*-butyl-6-methyl-*N*-thiosulfinylaniline (**4**) as dark purple crystals (identified by IR and NMR). An orange fraction gave 484 mg (50.1%) of *N,N'*-bis(2,4-di-*t*-butyl-6-methylphenyl)sulfur diimide (**13**) as orange crystals (identified by IR and NMR).[8] From the subsequent fraction 239 mg (26.3%) of **3** was recovered.

Reaction of 2,4,6-Tri-t-butylaniline (1) with SCl_2. To an ice-cold solution of **1** (1.605 g, 6.15 mmol) and triethylamine (1.26 g, 12.5 mmol) in ether (40 ml), a solution of SCl_2 (640 mg, 6.21 mmol) in ether (10 ml) was added dropwise with stirring, and the mixture was stirred for 1.25 h at 0 °C. After usual work-up, the residue was chromatographed on silica gel with hexane. The first fraction gave 471 mg (23.7%) of **2**. The second fraction was rechromatographed (silica gel, hexane) to give 213 mg (12.6%) of *N,N'*-bis(2,4,6-tri-*t*-butylphenyl)sulfur diimide (**14**) and 224 mg (11.9%) of

2,4,6-tri-*t*-butyl-*N*-sulfinylaniline. From the third fraction, 722.4 mg (45%) of **1** was recovered.

14; mp 202.5—203.5 °C; IR (KBr): 2960, 1590, 1470, 1405, 1385, 1360, 1265, 1235, 1130, 875, and 770 cm^{-1}; NMR (CCl_4): δ 1.31 (s, 18H), 1.38 (s, 36H), and 7.26 (s, 4H); λ_{max}^{hexane} (ε): 332 (7650) and 414 nm (4960); *m/e* 550 (M^+, 3.8%), 291 (100), 259 (58), and 244 (48).

Found: C, 78.45; H, 10.37; N, 4.80; S, 6.04%. Calcd for $C_{36}H_{58}N_2S$: C, 78.49; H, 10.61; N, 5.08; S, 5.82%.

*Preparation of 2,4-Di-t-butyl-6-methyl-N-sulfinylaniline (**16**).* To an ice-cold solution of 2,4-di-*t*-butyl-6-methylaniline (**3**) (5.01 g, 22.9 mmol) and triethylamine (5.08 g, 50.3 mmol) in hexane (250 ml), a solution of thionyl chloride (2.97 g, 25 mmol) in hexane (50 ml) was added dropwise with stirring. After additional stirring for 70 min, the reaction mixture was washed with water, and dried ($MgSO_4$). Removal of the solvent afforded orange crystals, which were recrystallized once from aq. methanol to give 4.39 g (72.3%) of **16** (mp 54—55.5 °C), which was recrystallized three times from aq. methanol for an analytical specimen; mp 55.5—56.5 °C; IR (KBr): 1272 and 1182 cm^{-1} (NSO); NMR (CCl_4): δ 1.31 (s, 9H), 1.43 (s, 9H), 2.25 (s, 3H), and 7.20 (ABq, $\Delta\delta$= 0.13, J=2 Hz, 2H); λ_{max}^{hexane} (ε): 226 (10100), 255 (5390), 282 sh (2700), and 392 nm (2590); *m/e* 265 (M^+, 23%), 250 (77), 209 (42), 208 (81), 202 (32), and 57 (100). Found: C, 67.92; H, 8.92; N, 5.52; S, 11.95%. Calcd for $C_{15}H_{23}NOS$: C, 67.88; H, 8.73; N, 5.28; S, 12.08%.

*Preparation of 2,4,6-Tri-t-butyl-N-sulfinylaniline (**15**).* To an ice-cold solution of 2,4,6-tri-*t*-butylaniline (5.33 g, 20.4 mmol) and triethylamine (5.04 g, 49.9 mmol) in hexane (170 ml), a solution of thionyl chloride (2.70 g, 22.7 mmol) in hexane (30 ml) was added dropwise with stirring. After additional stirring for 40 min at 0 °C, usual work-up afforded 6.13 g (97.7%) of 2,4,6-tri-*t*-butyl-*N*-sulfinylaniline (**15**), which was recrystallized once from aq ethanol to give 5.21 g (83.0%) of **15** as orange crystals: mp 120.5—122 °C; IR (KBr): 1295 and 1180 cm^{-1} (NSO); NMR (CCl_4) δ 1.27 (s, 9H), 1.38 (s, 18H), and 7.28 (s, 2H); λ_{max}^{hexane} (ε): 230.5 (12400) and 410 nm (350); *m/e*: 307 (M^+, 13%), 292 (65), 251 (100), and 245 (90). Found: C, 70.61; H, 9.61; N, 4.86; S, 10.53%. Calcd for $C_{18}H_{29}NOS$: C 70.31; H, 9.51; N, 4.56; S, 10.43%.

References

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