Persistent Nitrogen-centered Free Radicals, N-(Arylthio)-3,5-di-t-butylphenylaminyls. Decomposition Reactions[1)]

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Synopsis.   N-(4-Chlorophenylthio)-3,5-di-t-butylphenyl-aminyl was decomposed in oxygen-free benzene, and the products were examined. On the basis of the results, the decomposition mechanism of the radical is described.

In a previous report[1)] we described how N-(arylthio)-3,5-di-t-butylphenylaminyls are very persistent radicals and that they can be isolated as dimers which dissociate into the orginal radicals, even at room temperature (K=[radical]^2[dimer]$^{-1}$=0.98 × 10^{-4}—4.59 × 10^{-4} mol l^{-1} in benzene at 27 °C). On standing in solution over a long period, however, the radicals gradually decompose. In order to elucidate the decomposition mechanism, N-(4-chlorophenylthio)-3,5-di-t-butylphenylaminyl (**1**), which is one of this family, was decomposed in oxygen-free benzene, and the products were examined. In this report the results will be described, and the decomposition mechanism of the radical will be presented.
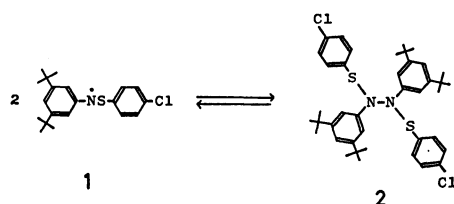
The dimer, **2**, was dissolved in 30 ml of benzene, and the resultant dark blue solution (λ_{max}: 602 nm), in which 0.498 mmol of **2** and 0.043 mmol of **1** were present,[2)] was allowed to stand under oxygen-free conditions (at ≈20 °C in the dark). After *ca.* three months, the solution turned orange, indicating the complete decomposition of **1** (and **2**). The orange solution was concentrated, and the residue was chromatographed on alumina. Elution with benzene–hexane (1 : 2) gave a mixture of five products, and the subsequent elution with benzene gave N-(4-chlorophenylthio)-3,5-di-t-butylaniline (**3**). The mixture was then run on a preparative TLC (silica gel; hexane) to give 1,3,5,7-tetra-t-butyl-

TABLE 1. PRODUCTS OF THE DECOMPOSITION OF THE DIMER, **2**[a,b)]

Product	Yield mg (mmol)
3	68 (0.195)
4	34 (0.084)
5	9 (0.031)
6	18 (0.026)
7	150 (0.306)
8	49 (0.121)
Total	328

a) These data are compiled from three experiments.
b) Dimer, 360 mg (0.519 mmol); benzene, 30 ml; ≈20 °C.

phenazine (**4**), bis(4-chlorophenyl) disulfide (**5**), Product **6**, N,N-bis(4-chlorophenylthio)-3,5-di-t-butyl-aniline (**7**), and 3,3′,5,5′-tetra-t-butylazobenzene (**8**). The results are listed in Table 1 and the yields in the table are determined by weight. Since **3** and **5** are the known compounds, they were identified by means of the melting points and by a comparison of the IR and NMR spectra with those of authentic samples. The structures of the other products were determined by means of the IR, NMR, and mass spectra and the elemental analyses. Also, Product **7** was prepared independently by the reaction of 3,5-di-t-butylaniline with two equivs of 4-chlorobenzenesulfenyl chloride in the presence of triethylamine. Interestingly, the substance, on photolysis with a high-pressure mercury lamp, gave **1** effectively.
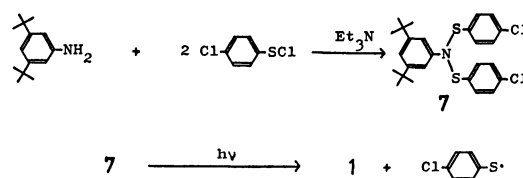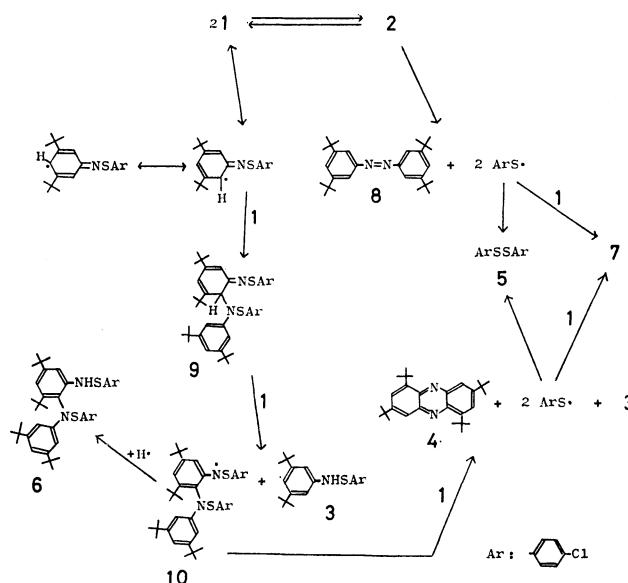

The major products of the decomposition are **3**,[3)] **4**, **7**, and **8**. In addition, small amounts of **5** and **6**[3)] were isolated. The sum of the products isolated is 328 mg, which corresponds to 91% of the starting material (360 mg). On the basis of the results shown in Table 1, we present a decomposition mechanism of **1** (and **2**) in Scheme 1. Product **3** is formed from **1** *via* hydrogen-atom abstractions, probably from **9** or an intermediate derived from **10** which finally gives the phenazine, **4**.

Scheme 1.

Product **7** is formed *via* the radical-coupling reaction between **1** and a thiyl radical. Also, **4** is derived from **10** with the loss of a hydrogen atom and two arylthiyl radicals, and **6** is formed from **10** *via* hydrogen-atom abstractions. On the other hand, the azo compound, **8**, is considered to be derived from the dimer, **2**, with the loss of two arylthiyl radicals. If this decomposition mechanism is reasonable, the mole quantity of **3** should be equal to twice that of **4** with respect to hydrogen atoms, and with arylthiyl radicals, the sum of the mole quantity of **5** and a half that of **7** should be equal to the sum of those of **4** and **8**. As can be seen in Table 1, these stoichiometric requirements are approximately satisfied.

Experimental

All the melting points were taken on a Yanaco Model melting-point apparatus and are uncorrected. The IR spectra were run on a JASCO Model IR-G spectrometer. The ^{1}H NMR spectra were recorded with a Hitachi Perkin Elmer R-20 spectrometer, with tetramethylsilane as the internal standard. The mass spectra were obtained on either a JEOL JMS-07 or a Hitachi M-60 mass spectrometer. The dimer, **2**[1] and 3,5-di-*t*-butylaniline[4] were obtained by the reported methods.

Decomposition of The Dimer.   The dimer, **2** (360 mg, 0.519 mmol), and benzene (30 ml) were placed in a glass tube, and the solution was degassed by three freeze-pump-thaw cycles and sealed under a vacuum. On standing for three months at $\approx$20 °C in the dark, the dark blue solution turned orange. The solvent was evaporated under reduced pressure, and the resultant residue was subjected to column chromatograph (alumina; E. Merck Art 1097; column-size: 3×30 cm). Elution with benzene–hexane (1 : 2) gave a mixture of 1,3,5,7-tetra-*t*-butylphenazine (**4**), bis(4-chlorophenyl) disulfide (**5**), Compound **6**, *N,N*-bis(4-chlorophenylthio)-3,5-di-*t*-butylaniline (**7**), and 3,3′,5,5′-tetra-*t*-butylazobenzene (**8**), and elution with benzene gave *N*-(4-chlorophenylthio)-3,5-di-*t*-butylaniline (**3**) (68 mg). The mixture was then run on a preparative TLC (silica gel; E. Merek Art 7730; eluent: hexane) to give **4** (34 mg), **5** (9 mg), **6** (18 mg), **7** (150 mg), and **8** (49 mg). The products were purified by recrystallization from the appropriate solvents or sublimation.

Product **3** was identified by means of its melting point.

Product 4.   Light yellow crystals; mp$>$305 °C (sublimation); ^{1}H NMR (CDCl$_3$): δ 1.48 (s, *t*-Bu, 18H), 1.74 (s, *t*-Bu, 18H), 7.64—7.82 (m, aromatic, 4H); MS (20 eV), *m/e* (rel intensity), 404 (5, M$^+$), 389 (21), 362 (19), 348 (29), 347 (94), 305 (20), 158 (40), 141 (20), 127 (26), 113 (33), 99 (42), 85 (94), 71 (100), 57 (90). Found: C, 82.63; H, 10.04; N,

6.80%. Calcd for C$_{28}$H$_{40}$N$_2$: C, 83.11; H, 9.97; N, 6.92%.

Product 6.   Colorless plates; mp 167—168 °C (ethanol); IR (KBr): 3400 (NH), 2950—2850 cm^{-1} (CH); ^{1}H NMR (CDCl$_3$): δ 1.24, 1.27, and 1.30 (s, *t*-Bu, 36H), 4.97 (s, NH, 1H), 6.70—7.54 (m, aromatic, 13H); MS (30 eV), *m/e* (rel intensity), 694 (6, M$^+$+2), 692 (6, M$^+$), 551 (27), 550 (25), 549 (27), 408 (16), 405 (19), 350 (59), 349 (100), 347 (42), 291 (19). Found: C, 69.11; H, 7.16; N, 4.31; Cl, 10.50; S, 9.21%. Calcd for C$_{40}$H$_{50}$Cl$_2$N$_2$S$_2$: C, 69.24; H, 7.26; N, 4.04; Cl, 10.22; S, 9.24%.

Product 7.   Colorless plates; mp 119—121°C(methanol); ^{1}H NMR (CDCl$_3$): δ 1.24 (s, *t*-Bu, 18H), 6.93—7.33 (m, aromatic, 11H); MS (20 eV), *m/e* (rel intensity), 489 (5, M$^+$), 406 (13), 349 (21), 348 (19), 347 (63), 332 (15), 311 (27), 290 (16), 288 (75), 287 (15), 286 (100), 205 (17), 204 (15), 189 (38), 144 (38), 143 (41). Found: C, 63.33; H, 5.85; N, 2.81%. Calcd for C$_{26}$H$_{29}$Cl$_2$NS$_2$: C, 63.66; H, 5.96; N, 2.86%.

Product 8.   Orange crystals; mp 210—212 °C (methanol); ^{1}H NMR (CDCl$_3$): δ 1.39 (s, *t*-Bu, 36H), 7.48—7.72 (m, aromatic, 6H); MS (75 eV), *m/e* (rel intensity), 406 (18, M$^+$), 363 (8), 190 (17), 189 (100), 147 (9), 133 (24), 91 (9), 57 (92). Found: C, 82.65; H, 10.88; N, 7.12%. Calcd for C$_{28}$H$_{42}$N$_2$: C, 82.70; H, 10.41; N, 6.89%.

Product **3** was identified by the melting point [148—150 °C (hexane), lit,[1] 150—151 °C] and its IR and NMR spectra, and Product **5**, by means of its IR spectrum.

Preparation of 7.   4-Chlorobenzenesulfenyl chloride, prepared by the treatment of 4-chlorobenzenethiol (1.72 g, 11.9 mmol) with chlorine in dry chloroform at 0—5 °C, was dissolved in 50 ml of dry ether, and the solution was added, drop by drop, to a stirred solution of 3,5-di-*t*-butylaniline (1.09 g, 5.32 mmol) and triethylamine (1.3 g, 13 mmol) in dry ether (200 ml) at 0—5 °C. After being stirred for 2 h at the same temperature, the reaction mixture was filtered, concentrated, and the residue was recrystallized from methanol to give colorless plates (119—120 °C) in a 17% yield (0.22 g).

References

1)   Part 15 in the series: "ESR Studies of Nitrogen-Centered Free Radicals." For Part 14, see: Y. Miura, A, Yamamoto, Y. Katsura, and M. Kinoshita, *J. Org. Chem.*, **45**, 3875 (1980).

2)   These values are derived from the equilibrium constant (*K*) at 20 °C (1.22×10^{-4} mol 1^{-1}).

3)   These products, like the other products, showed no detectable decomposition on standing in benzene at 20 °C for 2 months.

4)   N. L. Allinger, H. M. Blatter, L. A. Freiberg, and F. M. Karkowski, *J. Am. Chem. Soc.*, **88**, 2999 (1966).