Radical Switch Reaction. A Novel Reaction between Two Free Radicals in a Solvent Cage

Michio Kobayashi,* Michiko Gotoh, and Masato Yoshida
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University,
Fukazawa, Setagaya-ku, Tokyo 158
(Received July 10, 1986)

Studies on the thermal decomposition of t-butyl phenylazo sulfone suggested the occurrence of a radical switch reaction, a novel type of reaction between two radicals. A primary geminate radical pair, t-butanesulfonyl and phenyl radical pair, exchange sulfur dioxide to form a new radical pair consisting of t-butyl and benzenesulfonyl radicals. The generation of benzenesulfonyl radical was confirmed by its ESR spectrum and the isolation of products containing a benzenesulfonyl group.

The thermal decomposition of arylazo aryl sulfones (Ar-N=N-SO_2Ar') can be considered to be initiated by the homolytic cleavage of the S–N bond to give a diazenyl radical and a sulfonyl radical; the diazenyl radical further decomposes to an aryl radical and nitrogen.[1-5] In continuing studies on the decomposition mechanism of azo sulfones, we are interested in the decomposition of t-butyl phenylazo sulfone (Ph-N=N-SO_2-t-Bu 1). Since the 1,1-dimethylethanesulfonyl radical, which is expected to be generated by homolytic cleavage of the S–N bond of 1, is known to decompose readily to a t-butyl radical and sulfur dioxide,[6] the mechanism and products of the decomposition of 1 may be different from that of arylazo aryl sulfones. During the study of the decomposition mechanism of 1 by product analysis, chemically induced dynamic nuclear polarization (CIDNP) and ESR, we have observed the occurrence of a new type of reaction between two geminate radicals in a solvent cage. The results will be described in this paper.

Results and Discussion

The rate constant of the decomposition of the azo sulfone 1 was determined in benzene in the presence of 3 mol of pyridine per mol of 1; pyridine was added in order to suppress the autocatalyzed decomposition of 1 by acidic products.[2] The reaction was monitored by UV absorption at 296 nm. The rate was found to be first order in 1. The observed first order rate constants were 48.3 (65.2 °C), 23.3 (60.2 °C), 8.84 (55.2 °C), and

6.05×10^{-5} s^{-1} (50.8 °C). Activation parameters estimated from these value are $\Delta H^{\neq}$=133.7 kJ mol^{-1} and $\Delta S^{\neq}$=126.7 J K^{-1} mol^{-1}.

The products of decomposition of 1 under these conditions are summarized below.

Detection of biphenyl among the products suggested the generation of a phenyl free radical. This was further confirmed by the examination of the orientation in the phenylation of the aromatic ring in the thermal decomposition of 1 in nitrobenzene: The isomer ratio of the nitrobiphenyl produced was o-72.2%; m- 5.2%; p- 22.6%. The total yield of nitrobiphenyls amounted to 28%. The isomer distribution (o,p-orientation) is the characteristic of homolytic
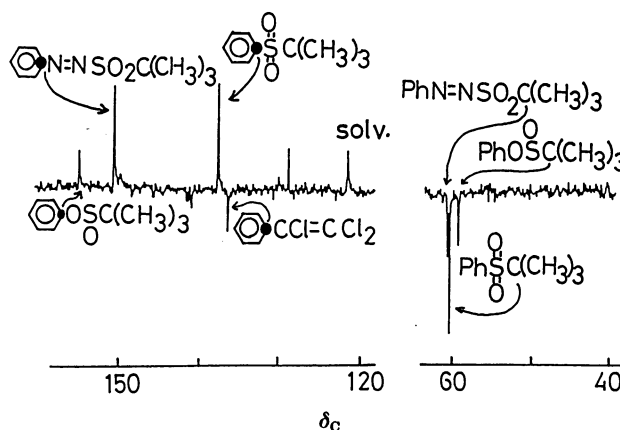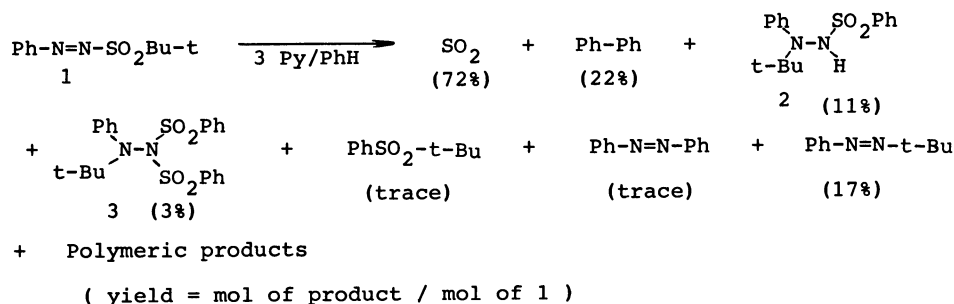

Fig. 1. The CIDNP spectra obtained in the thermal decomposition of azo sulfone 1 in tetrachloroethylene.

Scheme 1.

substitution by the phenyl radical.[7] The production of sulfur dioxide indicates the generation of the 1,1-dimethylethanesulfonyl radical followed by rapid decomposition to sulfur dioxide and a t-butyl radical.

We further examined the decomposition of azo sulfone 1 using the ^{13}C-CIDNP technique. When 1 was decomposed in tetrachloroethylene in a ^{13}C-NMR probe, several ^{13}C-CIDNP signals were observed as shown in Fig. 1. The enhanced absorption of C_1 and the emission signal of C_α of azo sulfone 1 itself indicates that the first step of the decomposition of 1 to give phenyldiazenyl-sulfonyl radical pair is reversible as shown in Eq. 1.

(1)
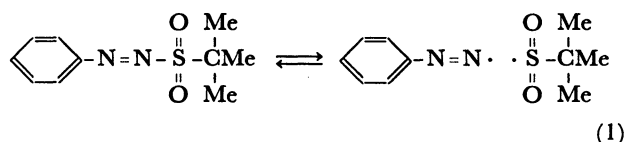
The mode of the CIDNP signals attributable to t-butyl phenyl sulfone and phenyl 1,1-dimethylethanesulfinate was also characteristic of the cage recombination products.[8] This suggests that in the second step, the primary geminate radical pair consisting of the phenyldiazenyl and 1,1-dimethylethanesulfonyl radicals decomposes to form a secondary radical pair consisting of phenyl and 1,1-dimethylethanesulfonyl radicals.

A considerable degree of a spin selection must occur in this radical pair before recombination or diffusion

out of the solvent cage. Since the sulfonyl radical is ambident, recombination of these radicals in the solvent cage may give both sulfone and sulfinic ester. Although phenyl 1,1-dimethylethanesulfinate is unstable and could not be isolated as such among the final products of the decomposition of 1, the ^{13}C-CIDNP spectrum shown in Fig. 1 cleary indicates that sulfinic ester is produced as the cage product during the thermal decomposition of 1. In the previous paper,[1] we reported that the arenesulfonyl radical was ambident and acted either as a S- or O-centered radical.[5] Now the 1,1-dimethylethanesulfonyl radical is also shown to behave as a S- and O-centered radical.

Although considerable amounts of t-butylbenzene and benzene were detected among the decomposition products, they did not exhibit the CIDNP signals. The formation of t-butylbenzene and benzene indicates that the 1,1-dimethylethanesulfonyl radical decomposes to a t-butyl radical and sulfur dioxide in the third step to give the t-butyl and phenyl radical pair in the solvent cage. This radical pair may give t-butylbenzene as a recombination product, and benzene and isobutene as disproportionation products. Failure to observe CIDNP signals due to t-butylbenzene or benzene may be explained by the small difference between the g values of the phenyl and t-butyl radicals. Results of CIDNP studies of the decomposition of 1 in tetrachloroethylene are summarized in Scheme 2.
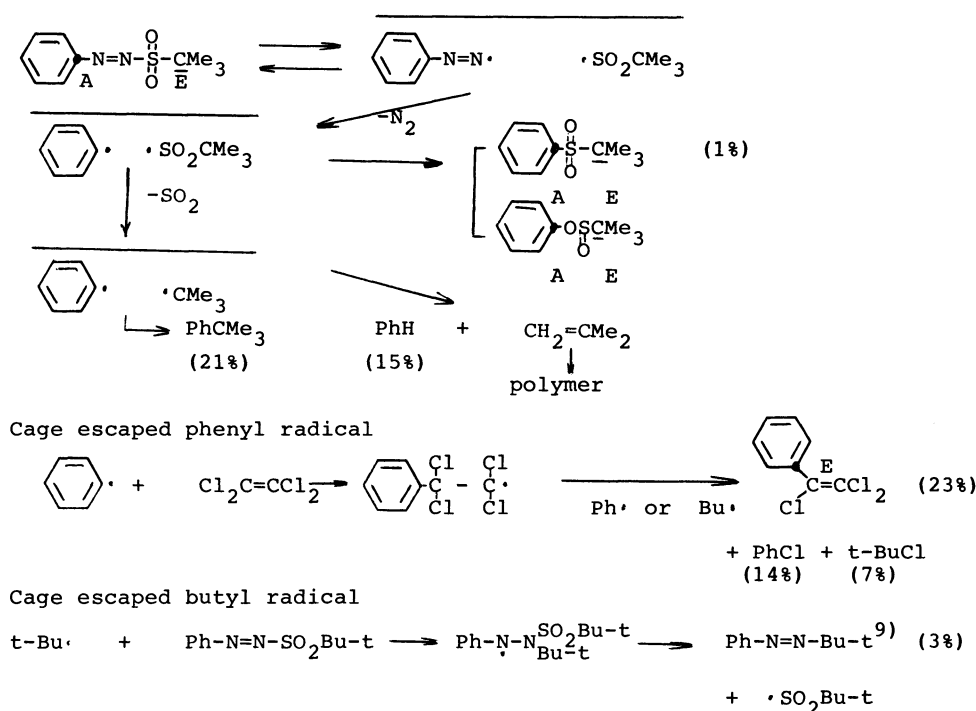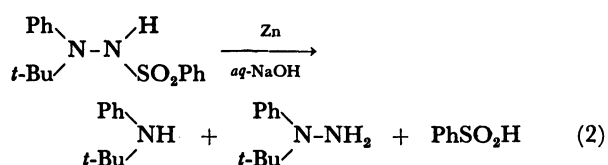
Compound 3 was also isolated in a yield of 1%.
· or — shows the polarized carbons. A: enhanced absorption, E: emission signal.

Scheme 2.

The above-mentioned results obtained by product analysis and CIDNP technique are those expected from the usual homolytic decomposition of an azo sulfone. A remarkable result was the isolation of some unexpected products, phenylsulfonylhydrazine **2** and **3**, in considerable yields. The products were characterized by ^{1}H, ^{13}C-NMR, IR, and MS spectra. In order further to confirm the structure of **2**, it was reduced by zinc dust in aq. NaOH. The production of N-(t-butyl)phenylamine and benzenesulfinic acid is consistent with the structure suggested by the spectral data.
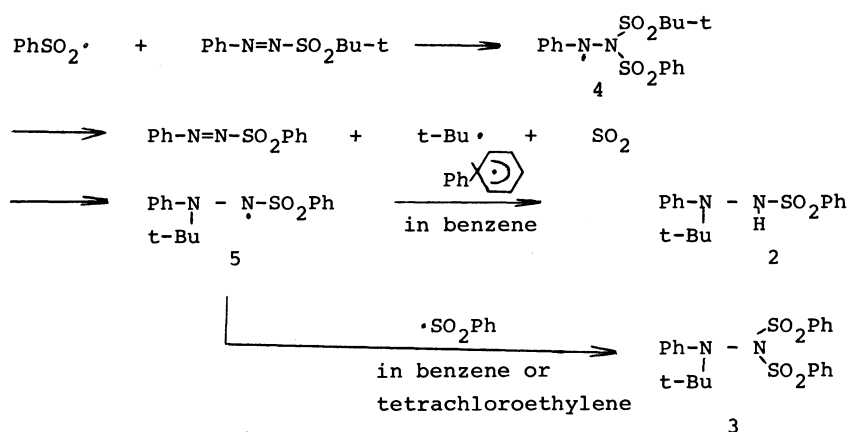
$$
\begin{array}{c}
\underset{t\text{-Bu}}{\overset{Ph}{\diagdown}}N-N\underset{\diagdown SO_2Ph}{\overset{\diagup H}{}} \quad \xrightarrow[aq\text{-NaOH}]{Zn} \\[2mm]
\underset{t\text{-Bu}}{\overset{Ph}{\diagdown}}NH \;+\; \underset{t\text{-Bu}}{\overset{Ph}{\diagdown}}N\text{-}NH_2 \;+\; PhSO_2H \qquad (2)
\end{array}
$$

Formation of these phenylsulfonylhydrazine indicates the generation of benzenesulfonyl radical (PhSO$_2\cdot$) during the decomposition of **1**. Once sulfur dioxide splits off from 1,1-dimethylethanesulfonyl radical and diffuses out of the cage, the likelyhood of an encounter with a phenyl radical must be very small. As a phenyl radical is very reactive, a cage escaped phenyl radical should react with solvent benzene to give biphenyl before an encounter with sulfur dioxide. Thus, the only chance for the generation of a benzenesulfonyl radical is the recombination of the geminate phenyl radical and sulfur dioxide within the solvent cage.
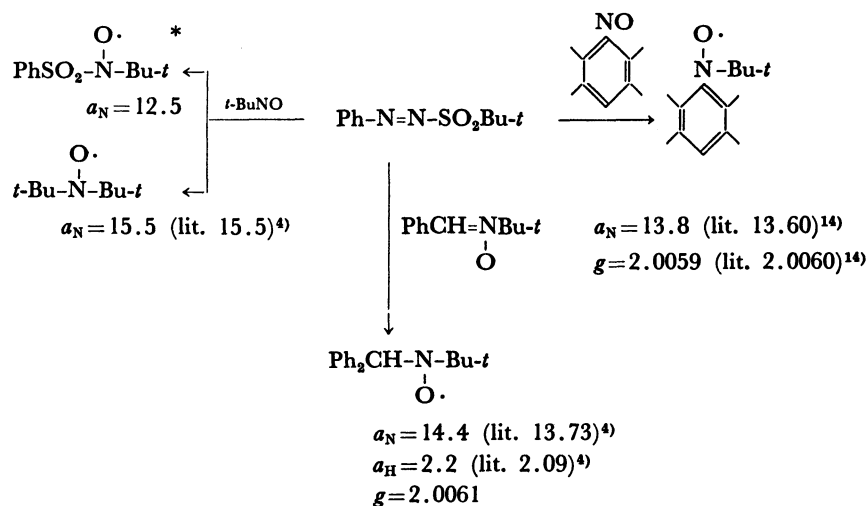
$$
Ph\cdot\;\cdot SO_2Bu\text{-}t \;\rightleftharpoons\; Ph\cdot\;SO_2\;\cdot Bu\text{-}t \;\longrightarrow\; PhSO_2\cdot\;\cdot Bu\text{-}t
$$

$$(3)$$
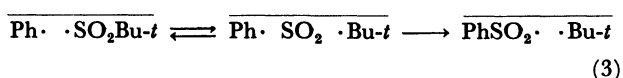
This exchange of sulfur dioxide between phenyl and 1,1-dimethylethanesulfonyl radicals to give benzenesulfonyl and t-butyl radical pair is a new type of reaction between two free radicals, which has no precedent. The driving force of this radical switch reaction must be the higher thermal stability of benzenesulfonyl radical than the 1,1-dimethylethanesulfonyl radical. The reaction of an aryl radical and sulfur dioxide to give a sulfonyl radical is well known, so the recombination of a phenyl radical and sulfur dioxide within the cage is plausible. Formation of **2** and **3** may be explained as shown in Scheme 3. The addition of a free radical to an N=N double bond to form a relatively stable hydrazyl radical ($>$N-$\overset{\cdot}{N}$-Ar) must be thermally an easy process, although it has received little attention.[5,10,11] The addition of a benzenesulfonyl radical to the N=N bond of azo sulfone **1** will give the hydrazyl radical **4**, which may decompose to afford phenylazo phenyl sulfone and a t-butyl radical. The t-butyl radical then further attacks the azo sulfone to give the radical **5**. The radical **5** substituted by both electron-donor and -acceptor groups is expected to be rather stable (captodative substituent effect).[12,13] The hydrazyl radical **5** may give hydrazine **2** and **3** in benzene; in tetrachloroethylene it will give **3**. The hydrogen source for the formation of **2** should be a cyclohexadienyl radical formed by the addition of a phenyl radical to the solvent benzene.

Phenyl, butyl, and benzenesulfonyl radicals escape from the solvent cage. These radicals could be trapped by spin trapping reagents such as nitrosodurene, 2-nitroso-2-methylpropane, or N-(t-butyl)-α-phenylnitrone to give nitroxide radicals which may be detected by ESR. As shown in Scheme 4, the formation of the benzenesulfonyl radical along with t-butyl and phenyl radicals was verified by spin trapping.

$$
PhSO_2\cdot \;+\; Ph\text{-}N\text{=}N\text{-}SO_2Bu\text{-}t \;\longrightarrow\; \underset{4}{Ph\text{-}\underset{\cdot}{N}\text{-}N\underset{\diagdown SO_2Ph}{\overset{\diagup SO_2Bu\text{-}t}{}}}
$$

$$
\longrightarrow\; Ph\text{-}N\text{=}N\text{-}SO_2Ph \;+\; t\text{-Bu}\cdot \;+\; SO_2
$$

$$
\longrightarrow\; \underset{5}{\underset{t\text{-Bu}}{Ph\text{-}\underset{\cdot}{N}}\text{-}N\text{-}SO_2Ph} \quad \xrightarrow[\text{in benzene}]{Ph\diagup\!\!\!\overset{\cdot}{\bigcirc}} \quad \underset{2}{\underset{t\text{-Bu}}{Ph\text{-}N}\text{-}\underset{H}{N\text{-}SO_2Ph}}
$$

$$
\xrightarrow[\substack{\text{in benzene or}\\ \text{tetrachloroethylene}}]{\cdot SO_2Ph} \quad \underset{3}{\underset{t\text{-Bu}}{Ph\text{-}N}\text{-}N\underset{\diagdown SO_2Ph}{\overset{\diagup SO_2Ph}{}}}
$$

Scheme 3.

$$
\begin{array}{c}
\text{O·} \qquad * \\
\text{PhSO}_2\text{-N-Bu-}t \;\leftarrow \\
a_N = 12.5 \qquad \overset{t\text{-BuNO}}{\longleftarrow} \quad \text{Ph-N=N-SO}_2\text{Bu-}t \\
\text{O·} \\
t\text{-Bu-N-Bu-}t \;\leftarrow \\
a_N = 15.5 \text{ (lit. 15.5)}^{4)}
\end{array}
$$

NO   O·
(ring structure) N–Bu-t

PhCH=NBu-t $a_N = 13.8$ (lit. 13.60)$^{14)}$
|
O $g = 2.0059$ (lit. 2.0060)$^{14)}$

Ph$_2$CH-N-Bu-t
|
O·

$a_N = 14.4$ (lit. 13.73)$^{4)}$
$a_H = 2.2$ (lit. 2.09)$^{4)}$
$g = 2.0061$

* The signal was assigned by the comparison with that obtained from benzene-sulfonyl iodide and 2-nitroso-2-methylpropane under photo-irradiation.

O·
|
PhSO$_2$I $\xrightarrow{h\nu/t\text{-BuNO}}$ PhSO$_2$-NBu-t
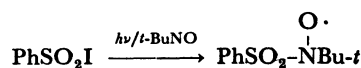
Scheme 4.

Experimental

Materials. Azo sulfone 1 was prepared from benzene-diazonium tetrafluoroborate and sodium 1,1-dimethyleth-anesulfinate in water and recrystallized from hexane-benzene. Mp 65—66 °C (decomp), ^{1}H-NMR (CDCl$_3$) $\delta_H = 1.63$ (9H, s), 7.32—7.90 (5H, m), Found: C, 52.98; H, 6.31; N, 12.43%. Calcd for C$_{10}$H$_{14}$N$_2$SO$_2$: C, 53.08; H, 6.24; N, 12.43%. t-Butyl phenyl sulfone was prepared by the oxidation with hydrogen peroxide of t-butyl phenyl sulfide which was synthesized from isobutene and thiophenol. ^{13}C-NMR (Cl$_2$C=CCl$_2$) $\delta_C = 23.0, 58.2, 127.6, 129.9, 132.0, 135.9.$

Product Analysis of Thermal Decomposition of 1 in Benzene. After the decomposition was completed, the reaction mixture was washed with water. The organic layer was dried over magnesium sulfate and evaporated to give the oily residue, which was subjected to column chromatography. Sulfur dioxide was determined by the iodometric titration with a standard sodium thiosulfate solution.

Product Analysis of Thermal Decomposition of 1 in Tetrachoroethylene. The yields of the products shown in Scheme 2 were determined by gas chromatography except the sulfone, yield of which was an isolated yield by column chromatography.
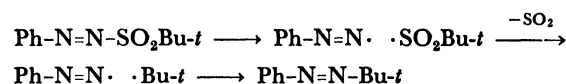
CIDNP Spectra. A solution of 1 (1 mmol) and pyridine (3 mmol) in 10 cm^3 tetrachloroethylene was inserted in an NMR probe which had been heated at 100 °C, and ^{13}C NMR was measured: pulse flipping angle 45°; data points 8192; accumulation 30, pulse interval 2 s. A JEOL Fx-60 FT NMR spectrometer was used. The CIDNP signals were assigned by comparison with the chemical shifts of the authentic samples. The chemical shifts of the sulfinate were estimated from the related compounds. The sign of the net polarization as calculated according to Kaptein's rule agreed with the observed one.[8]

Spectral Data of 2 and 3. 2: Mp 140 °C (decomp) ^{1}H-NMR (CDCl$_3$) $\delta = 1.10$ (s, 9H), 6.80—7.70 (m, 15H), ^{13}C-

NMR (CDCl$_3$) $\delta = 27.4, 59.8, 115.8, 116.3, 126.2, 128.3, 128.8, 132.7,$ IR 3240 (NH), 1323, 1160 cm^{-1} (SO$_2$), MS m/z 305, 304 (M$^+$), 163 (base), 107, 77, 57. Found: C, 63.06; H, 6.68; N, 9.19%. Calcd for C$_{16}$H$_{20}$SO$_2$N$_2$: C, 63.13; H, 6.62; N, 9.20%. 3: Mp 120 °C (decomp) ^{1}H-NMR (CDCl$_3$) $\delta = 1.38$ (s, 9H), 6.9—8.0 (m, 16H), ^{13}C-NMR (CDCl$_3$) $\delta = 29.7, 62.3, 125.0, 127.6, 127.8, 128.5, 129.4, 133.7, 139.9, 143.3,$ IR 1360, 1340, 1179, 1162 cm^{-1} (SO$_2$), MS m/z 444 (M$^+$), 303, 247, 163, 125, 105 (base), 77, 57. Found: C, 59.65; H, 5.41; N, 6.56%. Calcd. for C$_{22}$H$_{24}$S$_2$O$_4$N$_2$: C, 59.44; H, 5.44; N, 6.30%.

References

1) M. Kojima, H. Minato, and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, **45**, 2032 (1972).

2) M. Kobayashi, H. Minato, M. Kojima, and N. Kamigata, *Bull. Chem. Soc. Jpn.*, **44**, 2501 (1971).

3) M. Kobayashi, S. Fujii, and H. Minato, *Bull. Chem. Soc. Jpn.*, **45**, 2039 (1972).

4) M. Kobayashi, E. Akiyama, H. Minato, and N. Kito, *Bull. Chem. Soc. Jpn.*, **47**, 1504 (1974).

5) M. Yoshida, N. Furuta, and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, **54**, 2356 (1981).

6) R. T. van Aller, R. B. Scott, Jr., and E. L. Brockenbank, *J. Org. Chem.*, **31**, 2357 (1966).

7) M. J. Perkins, "Free Radicals," J. K. Kochi ed., Chap. 16, John Wiley & Sons, New York (1973).

8) R. Kaptein and J. Osterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969).

9) There is another plausible mechanism for the formation of Ph-N=N-Bu-t.

$$
\begin{array}{c}
\text{Ph-N=N-SO}_2\text{Bu-}t \longrightarrow \text{Ph-N=N· ·SO}_2\text{Bu-}t \xrightarrow{-SO_2} \\
\text{Ph-N=N· ·Bu-}t \longrightarrow \text{Ph-N=N-Bu-}t
\end{array}
$$

This cage recombination mechanism was rejected since in the decomposition of 1 in the presence of DPPH (2,2-

diphenyl-1-picryl hydrazyl: 1.5 mol per mol of **1**) as a radical scavenger, formation of Ph–N=N–Bu-*t* was completely suppressed.

10) J. L. Kice and R. S. Gabrielsen, *J. Org. Chem.*, **35**, 1004 (1970).

11) W. A. Pryor and H. Guard, *J. Am. Chem. Soc.*, **86**, 1150 (1964).

12) H. G. Viehe, R. Merenyi, L. Stella, and Z. Janousek, *Angew. Chem. Int. Ed. Engl.*, **18**, 917 (1979). H. G. Viehe, Z. Janousek, R. Merenyi, and L. Stella, *Acc. Chem. Res.*, **18**, 148 (1985).

13) D. Kost, M. Raban, and K. Aviram, *J. Chem. Soc., Chem. Commun.*, **1986**, 346.

14) S. Terabe, K. Kuruma, and R. Konaka, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 1252.