

Efficient Additions of an Electronically Stabilized Persistent Aminyl Radical to Conjugated Alkenes¹⁾

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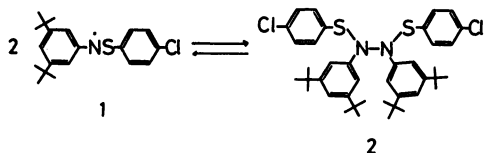
(Received January 9, 1985)

It has been found that an electronically stabilized persistent *N*-(4-chlorophenylthio)-3,5-di-*t*-butylphenylaminyl radical (**1**) adds to conjugated alkenes to afford 1:2 adducts of the alkenes and **1** in fair to excellent yields, along with small amounts of 1:1 adducts of the alkenes and **1**.

In contrast to the very large number of studies of the additions of carbon-centered free radicals to alkenes, reports in the literature concerning the additions of nitrogen-centered free radicals to alkenes are rare.^{2–10} Therefore, there is much less information regarding the additions of nitrogen-centered free radicals to alkenes, and the addition reactions are not yet well enough understood.

It has been reported that some aminyl radicals, including $\dot{\text{N}}\text{H}_2$ and dialkylamino radicals, add to alkenes to give 1:1 and 1:2 adducts of the alkenes and the radicals in low yields. For instance, the photolysis of a solution of tetramethyltetrazene and isopropenylbenzene in cyclohexane affords a 1:2 adduct of the alkene and the dimethylamino radical in a 10% yield, along with a minor formation of 1:1 adducts.⁹⁾

We have recently found that *N*-(4-chlorophenylthio)-3,5-di-*t*-butylphenylaminyl radical (**1**) adds to some conjugated alkenes to give 1:2 adducts of the alkenes and **1** in fair to excellent yields. Radical **1** is quite persistent, even in the presence of air, and can be isolated as the hydrazine-type dimer **2**, which, upon dissolution into ordinary solvents, dissociates into **1** with a relatively large dissociation constant.¹¹⁾ The efficient additions of such an electronically stabilized aminyl radical to conjugated alkenes are rather surprising and considerably interesting. We wish to report herein the products derived from the additions of **1** to conjugated alkenes; the mechanism of the formation of the adducts are also briefly described.



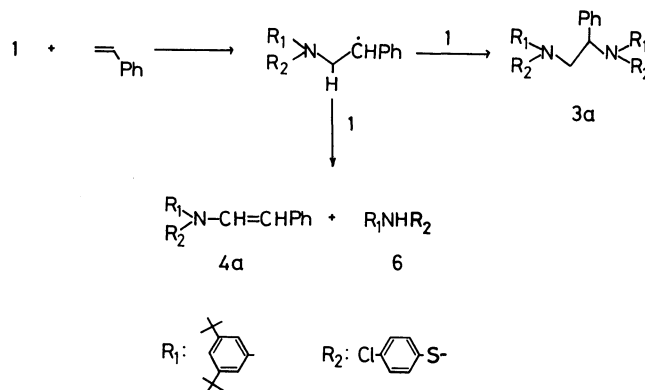
Results and Discussion

The reactions of **1** with alkenes were carried out in degassed benzene at 50°C. When mixtures of **1** and alkenes (excess) were heated to 50°C for 0.3–60 h, the dark blue color attributable to **1** disappeared almost completely, and the mixture became orange or red. The mixtures, after column chromatography, afforded 1:2 adducts of the alkenes and **1** in fair to excellent yields, along with small amounts of 1:1 adducts of alkenes and **1**. The results of the reactions are sum-

marized in Table 1; the yields in the Table are averaged over at least three runs in most cases.

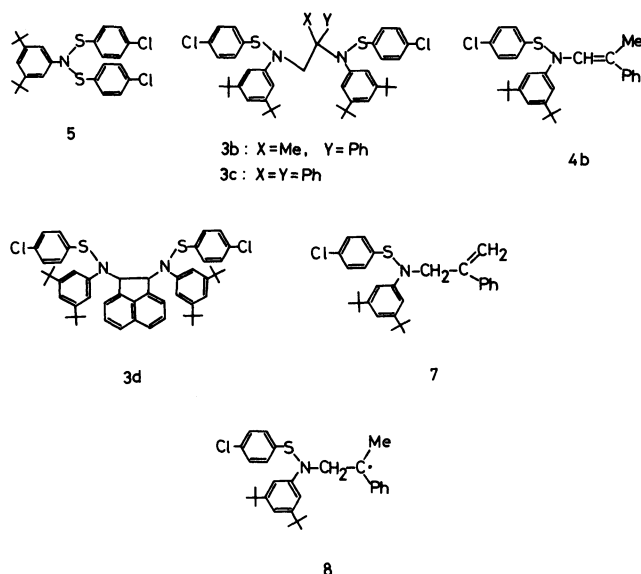
The reaction with styrene yielded, after heating for 14 h, two products (**3a** and **4a**) derived from styrene, along with **5** (11%) and **6** (41%), which do not contain the styrene moiety. Since the latter two products have been found to be formed *via* the self-decomposition of **1** (and **2**),¹²⁾ considerable parts of the products seem to be generated by this reaction. In the former two products, **3a**, which is a 1:2 adduct of styrene and **1**, is the major product (31%), while the minor product, **4a**, which is a 1:1 adduct of styrene and **1**, is formed in a 12% yield. It is almost certain that these products are formed by the routes shown in Scheme 1. Furthermore, the predominant formation of **3a** shows that the intermediate radical, which is derived from the addition of **1** to styrene, is predominantly captured by another molecule of **1** to give **3a**, while hydrogen-atom abstraction from the intermediate radical, probably by **1**, is less important. Therefore, we believe that **1** is not highly active in hydrogen-atom abstraction.

The reaction with isopropenylbenzene afforded three products (**3b**, **4b**, and **7**) derived from the alkene, along with **5** (8.1%) and **6** (27%). The major product **3b**, which is formed in a 40% yield, is a 1:2 adduct of the alkene and **1**, much as in the case of styrene. On the other hand, two minor products, **4b** and **7**, are formed in 3.9 and 6.6% yields respectively. For the formation of **4b**, hydrogen-atom abstraction from the intermediate radical **8** is most likely. On the other hand, for the formation of **7** there are two possible routes: one is hydrogen-atom abstraction from the methyl group of **8**, and the second is first hydrogen-atom abstraction from



Scheme 1.

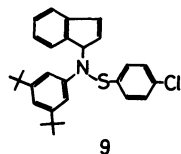
the methyl group of isopropenylbenzene, followed by the combination of the resultant intermediate radical with **1**. Although we can not determine unequivocally which route is predominant, we favor the former route, since **1** does not seem to be so active as to abstract a hydrogen atom from the methyl group of isopropenylbenzene.



The reaction with 1,1-diphenylethylene afforded **3c** in an 88% yield, while the reaction with acenaphthylene gave **3d** in a 38% yield. In neither case could a 1:1 adduct corresponding to **4a** or **4b** be isolated from the reaction mixtures.

The reactions with 1-octene and (E)-1,2-diphenylethylene gave neither 1:2 nor 1:1 adducts; even when the mixture of **1** and the alkenes were heated at 50°C for 60 h, the only products isolated were **5** and **6**.

The reaction with indene was complete within only 0.3 h and gave **9** in a 37% yield, instead of the corresponding 1:2 adduct. Although the TLC of the reaction mixture showed a spot suggesting the formation of trace amounts of the 1:2 adduct, it could not be isolated because they were only trace amounts. It is



most likely that this product is formed by the first abstraction of the allylic hydrogen of indene, probably by **1**, followed by combination of the resultant intermediate radical with **1**. Therefore, the hydrogen-atom abstraction is predominant over the addition of **1** to the double bond of indene; this is in accord with the highly reactive allylic hydrogens of indene.

As can be seen from Table 1, the total yields of the 1:1 and 1:2 adducts increase in the following order: 1-octene $\approx$ (E)-1,2-diphenylethylene < acenaphthylene < styrene < isopropenylbenzene < 1,1-diphenylethylene.

TABLE 1. RESULTS OF THE REACTIONS OF **1** WITH ALKENES^{a-c}

Alkene ^{d)}	Time ^{e)}		Products (%) ^{f)}
	h		
1-Octene	60	g)	
Styrene	14	3a (31), 4a (12)	
Isopropenylbenzene	11	3b (40), 4b (3.9), 7 (6.6)	
1,1-Diphenylethylene	7	3c (88)	
(<i>E</i>)-1,2-Diphenylethylene	60	g)	
Acenaphthylene	5	3d (38)	
Indene	0.3	9 (37)	

a) Dimer **2**: 0.577 mmol. b) Temperature: 50°C. c) Solvent: benzene 10 cm³. d) Alkene: 7.7 mmol. e) Time required for the complete reaction of **1**. f) Isolated yield based on **1**. g) No formation of adducts was revealed by a TLC inspection of the reaction mixture.

This order is parallel to the stabilities of the intermediate radicals resulting from the addition of **1** to the alkenes. The only exception is (E)-1,2-diphenylethylene. In this case no formation of adducts can be reasonably explained in terms of the steric inhibition in the addition reaction.

Experimental

The melting point were taken on a Yanagimoto micro-melting point apparatus and are uncorrected. The IR spectra were run on a JASCO A-200 spectrometer as KBr pellets. The ¹H NMR spectra were measured with a JEOL PS-100 spectrometer, using TMS as the internal standard.

Styrene, isopropenylbenzene, 1,1-diphenylethylene, and indene were, after column chromatography on alumina (Merck art 1097; column size, 3×10 cm; eluant, hexane), distilled under reduced pressure prior to use, while acenaphthylene was purified by recrystallization (ethanol) and sublimation. *N,N'*-Bis(4-chlorophenylthio)-*N,N'*-bis(3,5-di-*t*-butylphenyl)hydrazine (**2**) was prepared by our previously reported method.¹⁰

General Procedure for Reactions of 1 with Alkenes. Dimer **2** (400 mg, 0.577 mmol), alkene (7.7 mmol), and benzene (10 cm³) were placed in a glass tube, the content was degassed by three freeze-pump-thaw cycles, and the tube was sealed off from the vacuum system. The tube was then immersed in a water-bath heated to 50°C, and the precipitate, **2**, in the solution was dissolved with occasional shaking. When the blue color of the reaction mixture had been changed to orange or red, the tube was broken and the mixture was evaporated under reduced pressure. Column chromatography of the residue on silica gel (Wako gel C-200, column size, 3×45 cm) at 3–5°C gave products, **3–7** and **9**.

Reaction with Styrene. After being heated for 14 h, the reaction mixture (orange) was evaporated; subsequent column chromatography of the residue, with 1:7 benzene-hexane as the eluant, gave the following products: **5**, 30 mg (0.061 mmol), which was identified by its melting point [118–119°C (from methanol) (lit.¹² 119–121°C)] and by comparing its IR spectrum with that of an authentic sample. **4a**: 60 mg (0.13 mmol, 12%); colorless needles; mp 131–132°C (from methanol); IR 2950–2850 (C–H of *t*-Bu) and 1640 cm⁻¹ (vinyl); NMR (CDCl₃) δ =1.30 (s, *t*-Bu, 18H), 6.37 (d, *J*=15 Hz, vinylic, 1H), and 7.20–7.38 (m, aromatic, 12H, and vinylic, 1H). Found: C, 74.93; H, 7.05; N, 2.90%. Calcd

for $C_{28}H_{32}ClNS$: C, 74.72; H, 7.17; N, 3.11%. **3a**: 141 mg (0.177 mmol, 31%); colorless prisms; mp 179.5–180.5°C (from methanol–benzene); NMR ($CDCl_3$) δ =1.13 and 1.23 (each s, *t*-Bu, 36H), 4.24 (dd, J =5 and 15 Hz, $\underline{CHH}$ -N, 1H), 4.52 (dd, J =7 and 15 Hz, $\underline{CHH}$ -N, 1H), 5.68 (dd, J =5 and 7 Hz, $\underline{CH}$ -N, 1H), and 6.76–7.29 (m, aromatic, 19H). Found: C, 72.16; H, 7.59; N, 3.64%. Calcd for $C_{48}H_{58}Cl_2N_2S_2$: C, 72.24; H, 7.33; N, 3.51%. **6**: 163 mg (0.468 mmol), which was identified by its melting point [151–152°C (from hexane) (lit.¹¹ 150–151°C)] and by comparing its IR spectrum with that of an authentic sample.

Reaction with Isopropenylbenzene. After being heated for 11 h, the reaction mixture (orange) was evaporated; subsequent column chromatography of the residue, with 1:7 benzene–hexane as the eluant, gave the following five products: **5**, 23 mg (0.047 mmol), which was identified by its melting point [118–119°C (from methanol)] (lit.¹² 119–121°C] and by comparing its IR spectrum with that of an authentic sample. **4b**: 21 mg (0.045 mmol, 3.9%); colorless prisms; mp 96–97°C (from methanol); IR 2950–2850 (C–H of *t*-Bu) and 1620 cm^{-1} (vinyl); NMR ($CDCl_3$) δ =1.28 (s, *t*-Bu, 18H), 1.97 (d, J =1.2 Hz, $\underline{CH_3}$, 3H), 6.59 (q, J =1.2 Hz, vinylic, 1H), and 7.01–7.18 (m, aromatic, 12H). Found: C, 75.33; H, 7.29; N, 3.10%. Calcd for $C_{29}H_{34}ClNS$: C, 75.05; H, 7.38; N, 3.02%. **7**: 36 mg (0.078 mmol, 6.6%); colorless needles; mp 119–120°C (from methanol); IR 2950–2850 (C–H of *t*-Bu) and 1630 cm^{-1} (vinyl); NMR ($CDCl_3$) δ =1.26 (s, *t*-Bu, 18H), 4.72 (s, $\underline{CH_2}$, 2H), 5.22 (s, vinylic, 1H), 5.46 (s, vinylic, 1H), and 6.97–7.37 (m, aromatic, 12H). Found: C, 75.64; H, 7.51; N, 2.64%. Calcd for $C_{29}H_{34}ClNS$: C, 75.05; H, 7.38; N, 3.02%. **3b**: 186 mg (0.229 mmol, 40%); colorless prisms; mp 159–161°C (from methanol–benzene); NMR (CCl_4) δ =1.12 and 1.20 (each s, *t*-Bu, 36H), 1.80 (s, $\underline{CH_3}$, 3H), 4.31 (d, J =15 Hz, $\underline{CHH}$ -N, 1H), 4.56 (d, J =15 Hz, $\underline{CHH}$ -N, 1H), and 6.63–7.28 (m, aromatic, 19H). Found: C, 72.37; H, 7.37; N, 3.45%. Calcd for $C_{49}H_{60}Cl_2N_2S_2$: C, 72.47; H, 7.45; N, 3.45%. **6**: 108 mg (0.310 mmol), which was identified by its melting point [151–152°C (from hexane) (lit.¹¹ 150–151°C)] and by comparing its IR spectrum with that of an authentic sample.

Reaction with 1,1-Diphenylethylene. After being heated for 7 h, the reaction mixture (orange) was evaporated; subsequent column chromatography of the residue, with 1:5 benzene–hexane as the eluant, gave 445 mg (0.509 mmol, 88%) of **3c**: colorless needles; mp 116–117°C (from methanol–benzene); NMR (CCl_4) δ =1.18 and 1.20 (each s, *t*-Bu, 36H), 4.62 (s, $\underline{CH_2}$, 2H), and 6.46–7.50 (m, aromatic, 24H). Found: C, 74.05; H, 7.14; N, 3.31%. Calcd for $C_{54}H_{62}Cl_2N_2S_2$: C,

74.20; H, 7.15; N, 3.21%.

Reaction with Acenaphthylene. After being heated for 5 h, the reaction mixture (red) was evaporated; subsequent column chromatography of the residue, with 1:5 benzene–hexane as the eluant, gave 184 mg (0.217 mmol, 38%) of **3d**: colorless needles; mp 206–209°C (decomp) (from methanol–benzene); NMR (CCl_4) δ =1.15 (s, *t*-Bu, 36H), 6.25 (s, $\underline{CH}$, 2H), and 6.75–7.73 (m, aromatic, 20H). Found: C, 74.11; H, 6.88; N, 3.36%. Calcd for $C_{52}H_{58}Cl_2N_2S_2$: C, 73.82; H, 6.91; N, 3.31%.

Reaction with Indene. After being heated for 0.3 h, the reaction mixture (light orange) was evaporated; subsequent column chromatography of the residue, with 1:7 benzene–hexane as the eluant, gave 147 mg (0.423 mmol, 37%) of **9**: colorless needles; mp 149.5–150.5°C (from methanol); NMR (CCl_4) δ =1.19 (s, *t*-Bu, 18H), 5.52 (dd, J =1.8 and 2.2 Hz, $\underline{CH}$, 1H), 6.38 (dd, J =1.8 and 5.7 Hz, olefinic, 1H), 6.78 (dd, J =2.2 and 5.7 Hz, olefinic, 1H), and 6.84–7.40 (m, aromatic, 11H). Found: C, 75.13; H, 7.11; N, 3.27%. Calcd for $C_{29}H_{32}ClNS$: C, 75.37; H, 6.98; N, 3.03%.

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