January, 1990] © 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 57—63 (1990) 57

Addition of a Sulfonamidyl Radical to Unsaturated Aromatic and Aliphatic Hydrocarbons[1)]

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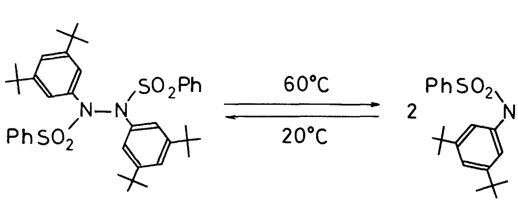
(Received May 29, 1989)

The reaction of *N*-phenylsulfonyl-3,5-di-*t*-butylphenylaminyl radical (**2**) with unsaturated aromatic and aliphatic hydrocarbons has been carried out in degassed benzene at 75 °C. The reactions of **2** with unsaturated aromatic hydrocarbons gave 1:1, 1:2, and 2:1 adducts of **2** and the hydrocarbons in fair to good yields. On the other hand, in the reactions of **2** with unsaturated aliphatic hydrocarbons, hydrogen-abstraction by **2** from the hydrocarbons was the major reaction. In the reaction with 2-methylpropene, a product indicating the addition of **2** to 2-methylpropene was isolated in a 16% yield. On the basis of these results the reactivity of **2** is discussed and compared with that of structurally related *N*-(4-chlorophenylthio)-3,5-di-*t*-butylphenylaminyl radical.

Sulfonamidyls ($RSO_2\dot{N}R'$) are interesting radicals in connection with carboxyamidyl radicals ($RCO\dot{N}R'$).[2)] A variety of ESR spectroscopic investigations of sulfonamidyls have been undertaken; the results obtained have been indicative of a π-electronic ground state for them.[3)] However, in contrast to the deep understanding of the electronic structures of sulfonamidyls, there are still few data regarding their chemical reactivities (e.g., the hydrogen-atom abstraction and the addition to double bonds).[4)]

It was previously reported that the photolytic rearrangement of *t*-$BuNXSO_2R$ (X=Cl, Br) and the photolytic addition of $MeNClSO_2R$ to unsaturated hydrocarbons proceeded via a free-radical-chain process involving sulfonamidyl radicals as intermediates.[5—7)] However, the above reactions were light-induced reactions, and the influence of the halogens generated during photolysis can not be ignored. For this reason, we have searched for a better method for the generation of sulfonamidyl radicals. It has been found that the hydrazine-like dimer (**1**) of sulfonamidyl **2** dissociates, upon heating to above 60 °C, into **2**.[8)] By this method one can easily and cleanly generate **2** without the irradiation of light and the evolution of halogens. In the present work we have carried out the reactions of **2** with unsaturated aromatic and aliphatic hydrocarbons in order to understand the chemical reactivities of **2**.



1 2

Results

The reactions of **2** with unsaturated hydrocarbons were carried out by heating a mixture of **1** and an unsaturated hydrocarbon in degassed benzene at 75 °C for 16 h. After heating, the reaction mixtures were analyzed on thin-layer chromatoplates, and the products formed were separated by column chromatography. The results of the reactions are summarized in Table 1.

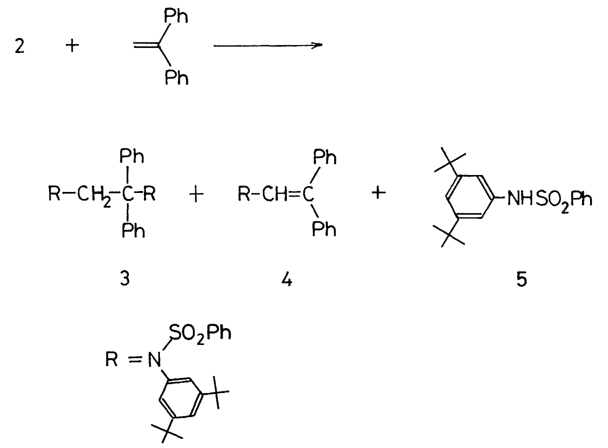
The reaction of **2** with 1,1-diphenylethylene which is one of the most reactive unsaturated hydrocarbons for free radical additions was first examined. When **2** was allowed to react with 0.66 equiv of 1,1-diphenylethylene, the resulting reaction mixture gave **3**, **4**, and

Table 1. Results of the Reactions of **2** with Unsaturated Hydrocarbons[a)]

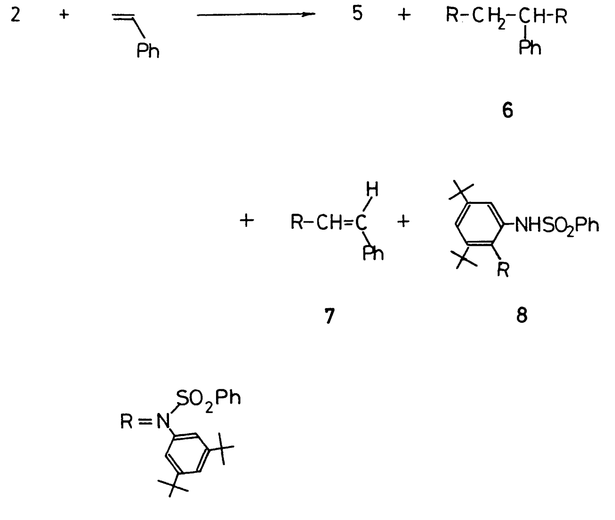
Entry	Hydrocarbon	mmol	Molar ratio of hydrocarbon/**2**	Products (%)[b)]
1	1,1-Diphenylethylene	0.38	0.66	**3** (76), **4** (11), **5** (12)
2	1,1-Diphenylethylene	5.5	9.5	**3** (71), **4** (14), **5** (15)
3	Styrene	0.43	0.71	**5** (27), **6** (37), **7** (12), **8** (8)
4	Isopropenylbenzene	0.38	0.66	**5** (38), **9** (20), **10** (7.5)
5	Isopropenylbenzene	6.2	10.6	**5** (49), **9** (8.2), **11** (26)
6	Acenaphthylene	0.38	0.66	**5** (36), *trans*-**13** (31), *cis*-**13** (14)
7	Cyclohexene	0.40	0.68	**5** (60), **8** (13), **14** (20)
8	Cyclohexene	9.9	17	**5** (76), **14** (23)
9	1-Butene	5.5	9.5	**5** (54)
10	2-Methylpropene	6.1	11	**5** (56), **8** (15), **15** (16), **16** (10)

a) Reaction conditions: **1** 0.290 mmol (**2** 0.580 mmol); temperature, 75 °C; time, 16 h. b) Isolated yields based on **2**.

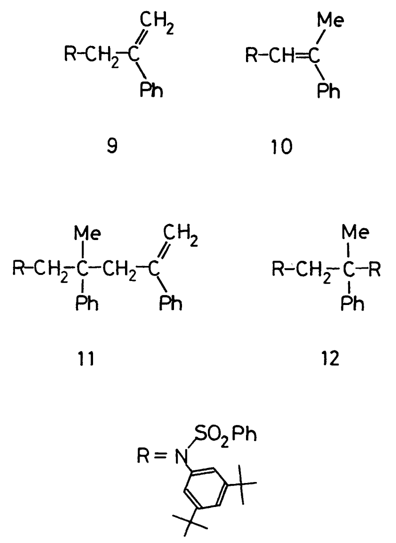
5 in 76, 11, and 12% yields respectively. Products **3** and **4** are 2:1 and 1:1 adducts of **2** and 1,1-diphenylethylene respectively, while **5** is a product derived from hydrogen-atom abstraction by **2**. Although **2** was also treated with a large excess (9.5 equiv) of 1,1-diphenylethylene, the results were almost the same as above (see Table 1).



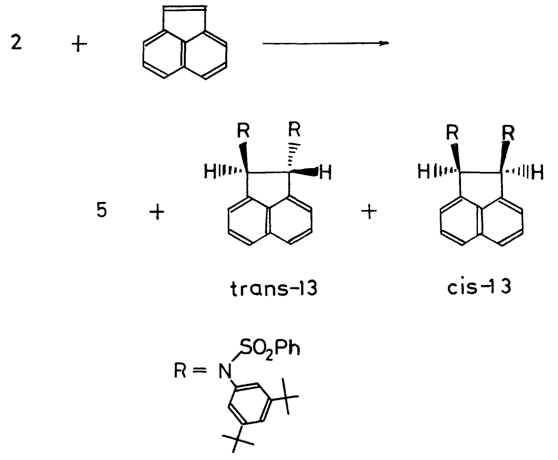
The reaction of **2** with styrene (styrene/**2**=0.71) gave **5** (27%), **6** (37%), **7** (12%), and **8** (8%). As has previously been reported,[8] the formation of **8** involves an attack of a **2** radical on the ortho position of the anilino group of another **2** radical. When **2** was treated with a large excess of styrene, the polymerization of styrene took place and no adduct could be isolated from the reaction mixture.



The reaction of **2** with isopropenylbenzene gave somewhat different results. When **2** was allowed to react with 0.66 equiv of isopropenylbenzene, the resulting reaction mixture gave **9** (20%), and **10** (7.5%) as 1:1 adducts of **2** and isopropenylbenzene, along with **5** (38%). On the other hand, when **2** was treated with a large excess (10.6 equiv) of isopropenylbenzene, the resulting reaction mixture gave **9** (8.2%) and **11** (26%), along with **5** (49%). Product **11** is a 1:2 adduct of **2** and isopropenylbenzene, as is shown by its structure. No corresponding 1:2 adduct was found to be formed in the reactions of **2** with the other unsaturated hydrocarbons. Furthermore, we observed, in the reaction of **2** with isopropenylbenzene, no formation of a 2:1 adduct (**12**).

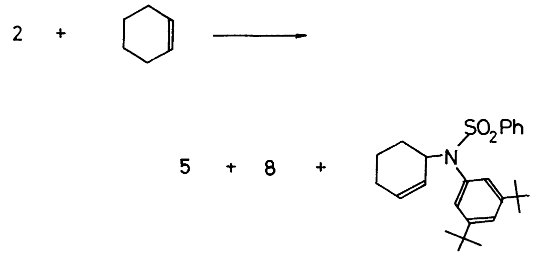


The reaction of **2** with acenaphthylene gave two kinds of 2:1 adducts (**13**) of **2** and acenaphthylene in 31 and 14% yields respectively. In the ^{1}H NMR spectrum of the major adduct, the two methine protons are magnetically equivalent (δ 6.43), while in that of the minor adduct, the two methine protons are magnetically unequivalent and are absorbed at δ 5.65 and 5.81 as a singlet. From the NMR results, we assigned the major adduct to a trans-isomer (*trans*-**13**) and the minor adduct to a cis-isomer (*cis*-**13**), because steric repulsions between the two bulky R groups seemed to be bigger in the cis-isomer than in the trans-isomer.



As unsaturated aliphatic hydrocarbons, cyclohexene, 1-butene, and 2-methylpropene were examined.

When **2** was treated with 0.68 equiv of cyclohexene, the resulting reaction mixture gave **5**, **8**, and **14** in 60, 13, and 20% yields respectively. On the other hand, when a large excess (17 equiv) of cyclohexene was employed in the above reaction, the resulting reaction mixture gave **5** and **14** in 76 and 23% yields respectively.



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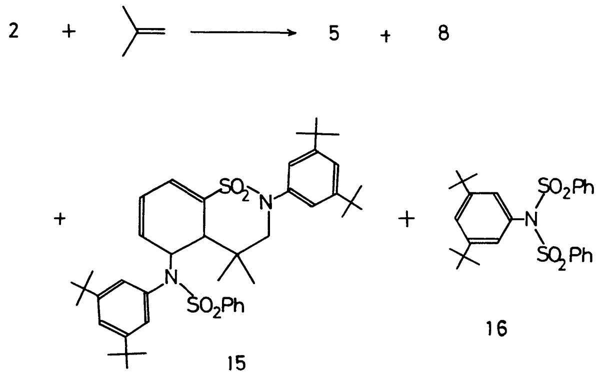
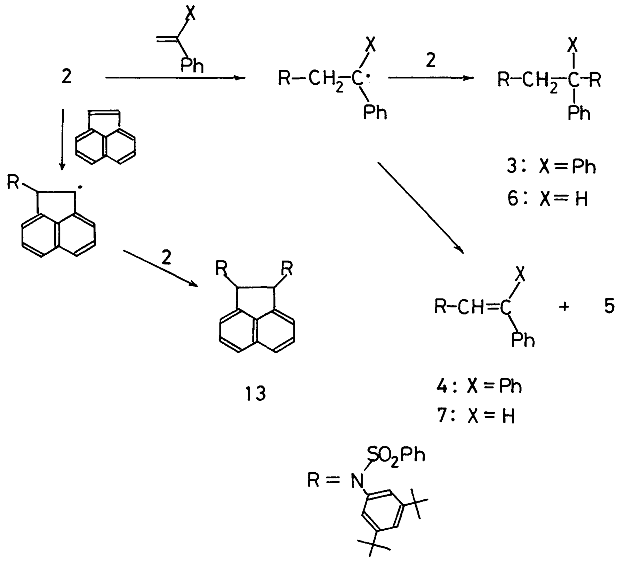
The reaction of **2** with 1-butene gave **5** (54%) as the only isolable product. The TLC analysis of the reaction mixture gave two major spots. After the column-chromatographic separation, one component was found to be **5**, while the other (oil) was shown by the ^{1}H NMR spectrum to be a mixture of **8** and an unknown compound. Since the unknown compound could not be isolated, further experiments were not done.

The reaction of **2** with 2-methylpropene afforded an interesting product, **15**. When **2** was allowed to react with a large excess of 2-methylpropene, the resulting reaction mixture gave **15** in a 16% yield, besides **5** (56%), **8** (15%), and **16** (10%). The formation of **15** can be accounted for as being derived from an intermediate radical formed by the addition of **2** to the double bond of 2-methylpropene, as will be described below (see Scheme 4). The complex structure was established on the basis of the IR, mass, and ^{1}H and ^{13}C NMR spectra. In the IR spectrum, no N–H absorption was found around 3200 cm^{-1} and the mass spectrum gave a peak due to M^{+} at 744. The ^{1}H NMR spectrum indicated the presence of two di-*t*-butylanilino groups in different surroundings, one phenylsulfonyl group, two magnetically unequivalent methyl groups [δ 1.02 (s), 1.30 (s)], two magnetically unequivalent methylene protons [δ 2.99 (d), 3.95 (d), J=13.2 Hz], and three olefinic protons [δ 5.93 (dd), J=5.3 and 9.3 Hz; δ 6.00 (dd), J=5.6 and 9.3 Hz; δ 6.32 (d), J=5.6 Hz]. The ^{13}C NMR spectrum gave signals for 26 different carbons (s 9, d 12, t 1, q 4) and supported the results from the ^{1}H NMR spectrum. Finally, the position to which the *N*-phenylsulfonyl-3,5-di-*t*-butylanilino group links was unequivocally determined by the ^{1}H–^{1}H and ^{1}H–^{13}C spin-decoupling experiments, and the structure was finally determined to be **15** (for the full assignments, see Experimental section).

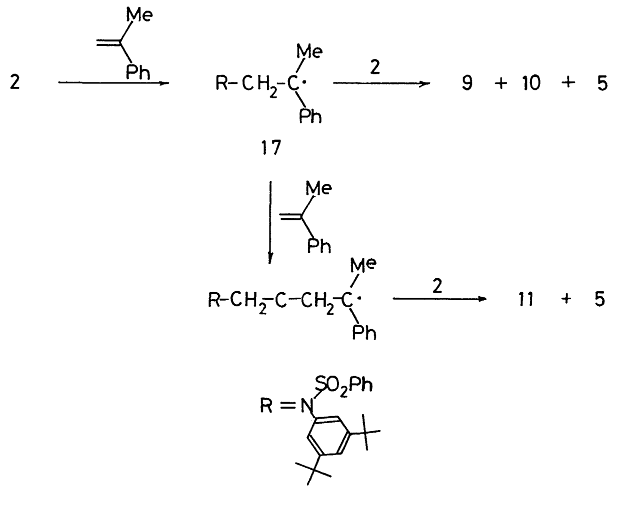


Discussion

The reactions of **2** with unsaturated aromatic hydrocarbons gave 1:1, 1:2, and 2:1 adducts of **2** and the hydrocarbons in fair to good yields; particularly, in the reaction with 1,1-diphenylethylene the total yield



Scheme 1.



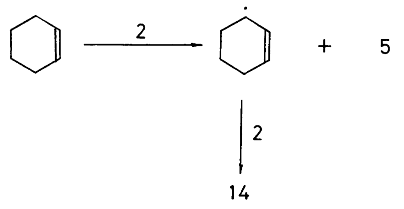
Scheme 2.

of 1:1 and 2:1 adducts attained to 85—87%. A general mechanism accounting for the formation of the adducts from the reactions of **2** with unsaturated aromatic hydrocarbons is outlined in Schemes 1 and 2. In any case, no formation of any adducts expected from the addition of **2** to the substituted (head) end of the double bonds was found.

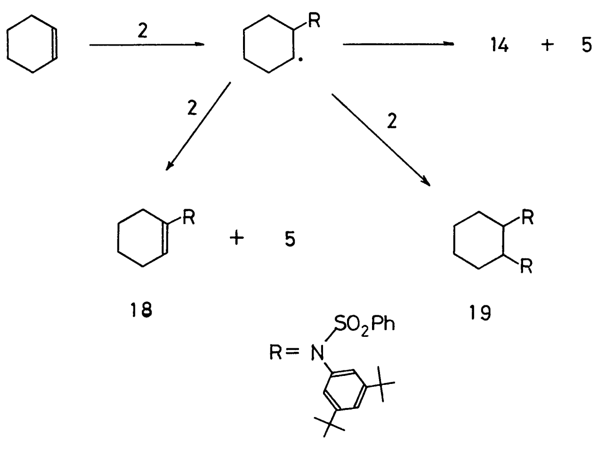
The reaction of **2** with isopropenylbenzene gave somewhat different results, as has been mentioned. The reaction of **2** with 0.66 equiv of isopropenylbenzene gave only 1:1 adducts (**9** and **10**) of **2** and isopropenylbenzene, while the reaction of **2** with a large excess of isopropenylbenzene gave a 1:2 adduct (**11**) of **2** and isopropenylbenzene, besides the 1:1 adduct **9**. If the intermediate radical **17** reacts with **2**, **9**, and **10** will be formed, but if it reacts with isopropenylbenzene, **11** will be formed. The above results thus indicate that, in the latter reaction, **17** reacted predominantly with isopropenylbenzene rather than with **2**.

The reaction of **2** with unsaturated aliphatic hydrocarbons gave high yields (54—76%) of **5**, indicating that hydrogen-abstraction by **2**, probably from the hydrocarbons, was the major reaction. However, in the reaction with cyclohexene and 2-methylpropene, compounds (**14** and **15**) containing a *N*-phenylsulfonyl-3,5-di-*t*-butylanilino group were isolated from the reaction mixtures.

For the formation of **14**, there are two possible mechanisms (see Schemes 3a and b). If **14** is formed via the pathways shown in Scheme 3b, the formation of **18** and **19** can also be expected, besides **14**. A careful inspection of the reaction mixture by TLC, however, did not indicate the formation of such compounds. Accordingly, we favor Scheme 3a as the mechanism to account for the formation of **14**.

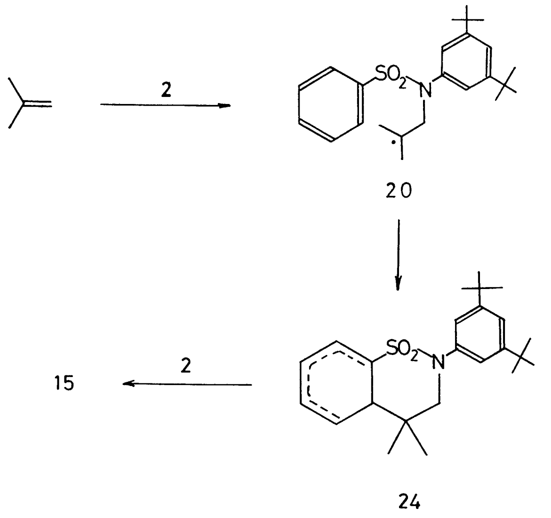


Scheme 3a.



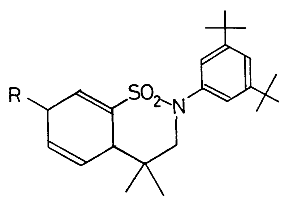
Scheme 3b.

The isolation of **15** is worthy of note. The formation can be accounted for as being derived from an intermediate radical **20** formed by the addition of **2** to 2-methylpropene (see Scheme 4); this indicates that



Scheme 4.

2 possesses the ability to add to some unsaturated aliphatic hydrocarbons. Besides **15**, the compounds **5**, **8**, and **16** were also isolated from the reaction mixture. However, the compounds **21** and **22**, which are isomers of **15**, and the compound **23**, which is expected to be formed from the aromatization of **24**, were not found in the reaction mixture. We assume that, although these compounds might also be formed, their yields were too low for them to be isolated. At present, though, we can not clearly explain why only **15** was formed in a relatively high yield.



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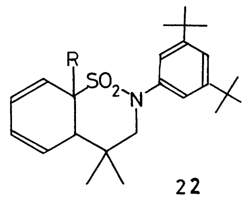

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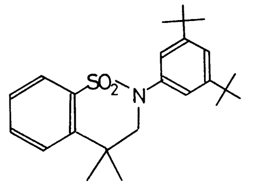

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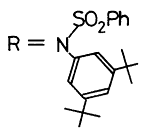
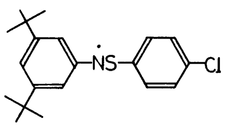


Comparison of Reactivity with 25. The aminyl radical **25** is structurally very similar to **2**. We previously reported the addition reactions of **25** to unsaturated aromatic and aliphatic hydrocarbons,



25

such as 1,1-diphenylethylene, styrene, isopropenylbenzene, acenaphthylene, and 1-butene.[9] The aminyl **25** is highly stabilized by the conjugative delocalization of the unpaired electron from the nitrogen to the sulfur $(-\dot{N}-\ddot{S}- \leftrightarrow -\ddot{N}^{-}-\dot{S}^{+}-)$[10] Thus, the hydrazine-like dimer of **25** dissociates into **25** even at room temperature. In contrast, **2** is not so highly stabilized because of the inability of SO_2 to delocalize the unapired electron.[11] Thus, the dimer **1** showed no dissociation into **2** at room temperature (it does dissociate above 60 °C, as has been mentioned above). Accordingly, it is likely that **2** is much more reactive than **25**. However, a previous work showed that **25**, like **2**, added efficiently to unsaturated aromatic hydrocarbons.[9] For example, the reaction with 1,1-diphenylethylene gave a 2:1 adduct of **25** and diphenylethylene in an 88% yield, while the reaction with styrene gave 2:1 and 1:1 adducts of **25** and styrene in 33 and 12% yields. From these results, we can say that there is no essential difference between **2** and **25** regarding the addition to unsaturated aromatic hydrocarbons.

A remarkable difference was, however, found in the reactions with unsaturated aliphatic hydrocarbons. As has been mentioned above, we isolated a product (**11**) indicating the addition of **2** to the double bond of 2-methylpropene. However, the reactions of **25** with unsaturated hydrocarbons gave no evidence suggesting the addition of **25** to unsaturated aliphatic hydrocarbons.[12] We assume that **25** is too highly stabilized to add to unsaturated aliphatic hydrocarbons.

On the basis of the products formed in the reactions of **2** with unsaturated hydrocarbons, we can conclude that **2** possesses the ability to add to unsaturated aliphatic hydrocarbons, as well as to unsaturated aromatic hydrocarbons.

Experimental

The melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. The IR spectra were run on a JASCO A-202 spectrophotometer. The ^1H NMR spectra were taken with a JEOL PS-100 (100 MHz) or JEOL GX-400 spectrometer (400 MHz), while the ^{13}C NMR spectra were recorded with a JEOL FX-100 spectrometer (25 MHz). The chemical shifts are expressed in ppm values (δ) using Me_4Si as the internal reference. The EI-mass spectra were taken by direct insertion on a JEOL D-300 or JEOL HX-100 spectrometer.

The dimer **1** was prepared by a previously reported method.[8] Styrene, isopropenylbenzene, 1,1-diphenylethylene, acenaphthylene, and cyclohexene were purified by the usual method prior to use.[9] 2-Methylpropene and 1-butene were purified by trap-to-trap distillation. The column chromatography (column size, 3.5×45 cm unless otherwise noted) was performed on silica gel (Wako-gel C-200, 100—200 mesh), using benzene as the eluent. The TLC analyses were performed on Merck silica gel 60 F_{254} (eluent, benzene) and Merck aluminium oxide 60 F_{254} plates (eluent, 1:1 benzene–hexane).

General Procedure for Reactions of 2 with Unsaturated Hydrocarbons. A solution of the dimer **1** (200 mg, 0.290 mmol) and an unsaturated hydrocarbon (0.38—12 mmol) in benzene (5.0 ml) was degassed by three freeze-pump-thaw cycles and sealed in a glass tube. The sealed tube was then immersed in a water-bath heated to 75 °C for 16 h. The reaction mixture was evaporated under reduced pressure, and the resulting residue was chromatographed. In the case of 1,1-diphenylethylene, the product **3** was isolated by adding hexane (ca. 10 ml) to the residue. After the collection of **3** by filtration, the filtrate was concentrated and the residue was chromatographed to give **4** and **5**. Compounds **5** and **8** were identified by means of their melting points and their IR and ^1H NMR spectra.[3c,8]

Reaction with 1,1-Diphenylethylene. A reaction with 69 mg (0.38 mmol) of 1,1-diphenylethylene gave 191 mg (0.22 mmol, 76%) of **3**, 33 mg (0.063 mmol, 11%) of **4**, and 24 mg (0.070 mmol, 12%) of **5**. Also, a reaction with 1.00 g (5.5 mmol) of 1,1-diphenylethylene gave 180 mg (0.207 mmol, 71%) of **3**, 42 mg (0.080 mmol, 14%) of **4**, and 29 mg (0.084 mmol, 14%) of **5**. The melting points and spectral data for **3** and **4** were reported in a previous paper.[8]

Reaction with Styrene. A reaction with 43 mg (0.41 mmol) of styrene gave 31 mg (0.070 mmol, 12%) of **7**, 16 mg (0.023 mmol, 8%) of **8**, 85 mg (0.107 mmol, 37%) of **6**, and 54 mg (0.16 mmol, 27%) of **5**.

***N*,*N*′-Bis(3,5-di-*t*-butylphenyl)-*N*,*N*′-bis(phenylsulfonyl)-1-phenylethylenediamine (6):** colorless prisms; mp 183—185 °C (crystallized from methanol); IR (KBr) 2950—2850 (*t*-Bu), 1350 and 1165 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ=1.11 (s, *t*-Bu, 18H), 1.18 (s, *t*-Bu, 18H), 3.80 (dd, *J*=6 and 13 Hz, N-C$\underline{H}$H, 1H), 4.21 (dd, *J*=10 and 13 Hz, N-C$\underline{H}$H, 1H), 5.20 (dd, *J*=6 and 10 Hz, N-CH, 1H), 6.25—7.58 (m, aromatic, 21H). Found: C, 72.58; H, 7.61; N, 3.59%. Calcd for $C_{48}H_{60}N_2O_4S_2$: C, 72.69; H, 7.63; N, 3.53%.

***N*-(3,5-Di-*t*-butylphenyl)-*N*-(phenylsulfonyl)-2-phenylethenamine (7):** colorless prisms; mp 130—132 °C (crystallized from hexane); IR (KBr) 2950—2850 (*t*-Bu), 1630 (C=C), 1355 and 1170 cm^{-1} (SO_2); MS (30 eV) *m/z* (%) 447 (38, M$^+$), 306 (100); ^1H NMR ($CDCl_3$) δ=1.26 (s, *t*-Bu, 18H), 5.29 (d, *J*=13 Hz, olefinic, 1H), 6.74—7.84 (m, olefinic and aromatic, 12H). Found: C, 75.58; H, 7.70; N, 2.97%. Calcd for $C_{28}H_{33}NO_2S$: C, 75.13; H, 7.43; N, 3.13%.

Reaction with Isopropenylbenzene. A reaction with 44.8 mg (0.38 mmol) of isoproenylbenzene gave 20 mg (0.044 mmol, 7.5%) of **10**, 55 mg (0.118 mmol, 20%) of **9**, and 77 mg (0.223 mmol, 38%) of **5**, while a reaction with 727 mg (6.15 mmol) of isopropenylbenzene gave 102 mg of **9** and **11** (mixture) and 98 mg (0.28 mmol, 49%) of **5**, along with 22 mg of an unknown compound (not pure). The molar ratio of **11**/**9** in the mixture was determined to be 5.0 from the integrated ^{1}H NMR spectrum of the mixture. This indicates that there were 14 mg (0.030 mmol, 5.2%) of **9** and 88 mg (0.15 mmol, 26%) of **11** in the mixture. The crystallization of the mixture from methanol gave pure crystals of **11**.

***N*-(3,5-Di-*t*-butylphenyl)-*N*-(phenylsulfonyl)-2-phenyl-2-propenamine (9):** colorless needles; mp 109—110 °C (crystallized from hexane); IR (KBr) 2950—2850 (*t*-Bu), 1630 (C=C), 1350 and 1165 cm^{-1} (SO$_2$); MS (30 eV) *m/z* (%) 461 (100, M$^+$), 358 (54), 320 (62); ^{1}H NMR (CDCl$_3$) δ=1.12 (s, *t*-Bu, 18H), 4.60 (s, CH$_2$, 2H), 4.97 (s, olefinic, 1H), 5.18 (s, olefinic, 1H), 6.44—7.52 (m, aromatic, 13H). Found: C, 75.19; H, 7.60; N, 3.30%. Calcd for $\mathrm{C_{29}H_{35}NO_2S}$: C, 75.45; H, 7.64; N, 3.03%.

***N*-(3,5-Di-*t*-butylphenyl)-*N*-(phenylsulfonyl)-2-phenylpropenamine (10).** This compound was isolated as a viscous oil and did not crystallize from any solvent used. IR (neat) 2950—2850 (*t*-Bu), 1635 (C=C), 1350 and 1160 cm^{-1} (SO$_2$); ^{1}H NMR (CDCl$_3$) δ=1.13 (s, *t*-Bu, 18H), 1.88 (d, *J*=1.5 Hz, Me, 3H), 6.44 (q, *J*=1.5 Hz, olefinic, 1H), 6.88—7.61 (m, aromatic, 13H).

***N*-(3,5-Di-*t*-butylphenyl)-*N*-(phenylsulfonyl)-2,4-diphenyl-2-methyl-4-pentenamine (11):** colorless prisms; mp 117—119 °C; IR (KBr) 2950—2850 (*t*-Bu), 1620 (C=C), 1340 and 1160 cm^{-1} (SO$_2$); ^{1}H NMR (CDCl$_3$) δ=1.10 (s, *t*-Bu, 18H), 1.29 (s, Me, 3H), 2.73 (d, *J*=14 Hz, $\mathrm{C\underline{H}H}$, 1H), 2.90 (d, *J*=14 Hz, $\mathrm{C\underline{H}H}$, 1H), 3.65 (d, *J*=14 Hz, $\mathrm{C\underline{H}H}$, 1H), 3.89 (d, *J*=14 Hz, $\mathrm{C\underline{H}H}$, 1H), 4.68 (br. s, olefinic, 1H), 5.06 (d, *J*=2 Hz, olefinic, 1H), 6.41—7.33 (m, aromatic, 18H); ^{13}C NMR (CDCl$_3$) δ=22.4 (q), 31.2 (q), 34.6 (s), 44.0 (s), 46.9 (t), 61.5 (t), 117.7 (t), 121.1 (d), 123.5 (d), 125.7 (d), 126.6 (d), 126.9 (d), 127.5 (d), 127.8 (d), 128.2 (d), 128.5 (d), 132.2 (d), 138.4 (s), 139.7 (s), 143.6 (s), 144.5 (s), 145.7 (s), 150.6 (s). Found: C, 78.54; H, 7.65; N, 2.65%. Calcd for $\mathrm{C_{38}H_{45}NO_2S}$: C, 78.71; H, 7.82; N, 2.42%.

Reaction with Acenaphthylene. A reaction with 57 mg (0.38 mmol) of acenaphthylene gave 73 mg (0.087 mmol, 31%) of *trans*-**13**, 35 mg (0.042 mmol, 14%) of *cis*-**13**, 72 mg (0.21 mmol, 36%) of **5**, and 24 mg of an unknown compound.

***trans*-*N*,*N*′-Bis(3,5-di-*t*-butylphenyl)-*N*,*N*′-bis(phenylsulfonyl)-1,2-diaminoacenaphthene (*trans*-13):** colorless plates; mp 233—236 °C (decomp) (crystallized from benzene-hexane); IR (KBr) 2950—2850 (*t*-Bu), 1350 and 1160 cm^{-1} (SO$_2$); ^{1}H NMR (CDCl$_3$) δ=1.03 (s, *t*-Bu, 36H), 6.43 (s, N-CH, 2H), 6.84—7.99 (m, aromatic, 22H). Found: C, 74.17; H, 7.16; N, 3.36%. Calcd for $\mathrm{C_{52}H_{60}N_2O_4S_2}$: C, 74.25; H, 7.19; N, 3.33%.

***cis*-*N*,*N*′-Bis(3,5-di-*t*-butylphenyl)-*N*,*N*′-bis(phenylsulfonyl)-1,2-diaminoacenaphthene (*cis*-13):** slightly yellowish plates; mp 163—165 °C (decomp) (crystallized from hexane); IR (KBr) 2950—2850 (*t*-Bu), 1350 and 1160 cm^{-1} (SO$_2$); ^{1}H NMR (CDCl$_3$) δ=1.04 (s, *t*-Bu, 36H), 5.65 (br s, N-CH, 1H), 5.81 (br s, N-CH, 1H), 6.32—7.83 (m, aromatic, 22H). Found: C, 74.14; H, 7.31; N, 3.31%. Calcd for $\mathrm{C_{52}H_{60}N_2O_4S_2}$: C, 74.25; H, 7.19; N, 3.33%.

The Unknown Compound: slightly yellowish microneedles; mp 215—217 °C (decomp) (crystallized from hexane); IR (KBr) 3400 (NH), 2950—2850 (*t*-Bu), 1340 and 1170 cm^{-1} (SO$_2$). Found: C, 79.06; H, 7.83; N, 3.95%. In an acidic CHCl$_3$ solution this compound turned into a red compound with a mp of 181—183 °C.

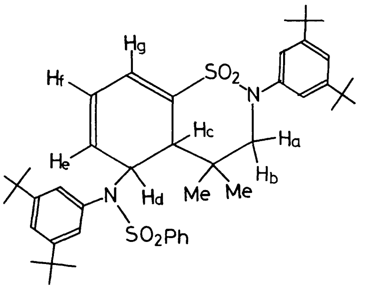
Reaction with Cyclohexene. A reaction with 811 mg (9.9 mmol) of cyclohexene gave 57 mg (0.134 mmol, 23%) of **14** and 152 mg (0.440 mmol, 76%) of **5**, while a reaction with 33 mg (0.40 mmol) of cyclohexene gave 75 mg of **8** and **14** (mixture) and 120 mg (0.347 mmol, 60%) of **5** (column size, 3.5×10 cm). The molar ratio of **14**/**8** in the mixture was determined to be 3.0 from the integrated ^{1}H NMR spectrum of the mixture. From this value, the amounts of **8** and **14** were calculated to be 26 mg (0.038 mmol, 13%) and 49 mg (0.12 mmol, 20%) respectively.

***N*-(3,5-Di-*t*-butylphenyl)-*N*-(phenylsulfonyl)-2-cyclohexenylamine (14):** colorless needles; mp 134.5—136 °C (crystallized from hexane); IR (KBr) 2950—2850 (*t*-Bu), 1645 (C=C), 1340 and 1165 cm^{-1} (SO$_2$); ^{1}H NMR (CDCl$_3$) δ=1.21 (s, *t*-Bu, 18H), 1.43—1.71 [m, (CH$_2$)$_3$, 6H], 4.96 (br s, N-CH, 1H), 5.56 (br d, *J*=11 Hz, olefinic, 1H), 5.61 (br d, *J*=11 Hz, olefinic, 1H), 6.77—7.77 (m, aromatic, 8H). Found: C, 73.12; H, 8.16; N, 3.51%. Calcd for $\mathrm{C_{26}H_{35}NO_2S}$: C, 73.37; H, 8.29; N, 3.29%.

Reaction with 1-Butene. A reaction with 310 mg (5.5 mmol) of 1-butene gave 109 mg (0.315 mmol, 54%) of **5** as an isolable product.

Reaction with 2-Methylpropene. A reaction with 340 mg (6.1 mmol) of 2-methylpropene gave 15 mg (0.030 mmol, 10%) of **16**, 30 mg (0.044 mmol, 15%) of **8**, 34 mg (0.046 mmol, 16%) of **15**, and 112 mg (0.323 mmol, 56%) of **5**.

2-(3,5-Di-*t*-butylphenyl)-5-[*N*-(3,5-di-*t*-butylphenyl)-*N*-phenylsulfonyl]amino-4,4-dimethyl-3,4,4a,5-tetrahydro-2*H*-benzo[*e*]thiazine 1,1-Dioxide (15): colorless needles; mp 196—197 °C (crystallized from methanol); IR (KBr) 2950—2850 (*t*-Bu), 1160 cm^{-1} (SO$_2$); EI-MS (70 eV) *m/z* (%) 744 (M$^+$, 1) 399 (100), 345 (80), 330 (80), 217 (72), 57 (45); ^{1}H NMR (CDCl$_3$) δ=1.02 (s, Me, 3H), 1.21 (s, *t*-Bu, 18H), 1.28 (s, *t*-Bu, 18H), 1.30 (s, Me, 3H), 2.99 (d, *J*=13.2 Hz, $\mathrm{H_a}$ or $\mathrm{H_b}$, 1H), 3.38 (br s, $\mathrm{H_c}$, 1H), 3.95 (d, *J*=13.2 Hz, $\mathrm{H_a}$ or $\mathrm{H_b}$, 1H), 5.31 (dd, *J*=1.5 and 5.3 Hz, $\mathrm{H_d}$, 1H), 5.93 (dd, *J*=5.3 and 9.3 Hz, $\mathrm{H_e}$, 1H), 6.00 (dd, *J*=5.6 and 9.3 Hz, $\mathrm{H_f}$, 1H), 6.32 (d, *J*=5.6 Hz, $\mathrm{H_g}$, 1H), 6.77 (d, *J*=2.0 Hz, *o*-H of the anilino group, 2H), 7.03 (d, *J*=2.0 Hz, *o*-H of the anilino group, 2H), 7.28—7.30 (m, *p*-H of the anilino group, 2H), 7.44—7.72 (m, SO$_2$Ph, 5H); ^{13}C NMR (CDCl$_3$) δ=19.2 (q), 23.9 (q), 31.2 (q), 31.4 (q), 34.7 (s), 34.9 (s), 40.7 (s), 49.9 (d, $\mathrm{CH_c}$), 52.8 (d, $\mathrm{CH_d}$), 64.9 (t, $\mathrm{CH_aH_b}$), 121.0 (d), 121.5 (d), 122.8 (d), 123.2 (d), 124.4 (d), 126.5 (d), 127.7 (d), 128.7 (d), 128.9 (d), 132.7 (d), 133.9 (s), 135.5 (s), 139.8 (s), 140.9 (s), 150.9 (s), 151.7 (s). Found: C, 70.89; H, 8.12; N, 3.70%. Calcd for $\mathrm{C_{44}H_{60}N_2S_2O_4}$: C, 70.93; H, 8.12; N, 3.76%.



***N*,*N*-Bis(phenylsulfonyl)-3,5-di-*t*-butylaniline (16):** colorless needles; mp 160—162 °C (crystallized from hexane); IR (KBr) 2950—2850 (*t*-Bu), 1380 and 1170 cm^{-1} (SO$_2$); MS

(30 eV) m/z (%) 485 (M^+, 52), 470 (21), 358 (18), 344 (20), 288 (62), 125 (100); ^{1}H NMR ($CDCl_3$) δ=1.22 (s, *t*-Bu, 18H), 6.74—8.01 (m, aromatic, 13H). Found: C, 64.17; H, 6.44; N, 2.54%. Calcd for $C_{26}H_{31}NO_4S_2$: C, 64.30; H, 6.43; N, 2.88%.

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12) Beside 1-octene, we also examined the reaction of **25** with unsaturated aliphatic hydrocarbons, including cyclohexene and 2-methylpropene.