Synthesis and Properties of Sterically Hindered Cycloalkenes Carrying Two *tert*-Butyls in Cis Orientation. 2,3-Di-*tert*-butylbicyclo[2.2.2]oct-2-ene Derivatives

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Abstract: 3,4-Di-*tert*-butylthiophene 1,1-dioxide (**2**), a cheletropic Diels–Alder reagent, reacts with 2 molecules of maleic anhydride to give the endo–endo bisadduct **4a** (73%) and endo–exo bisadduct **4b** (23%), which have a highly hindered double bond incorporated in a bicyclo[2.2.2]oct-2-ene ring system. The reaction of **2** with 2 equiv of PTAD affords the bisadduct **7** (87%), which is directly converted to 4,5-di-*tert*-butylpyridazine in 80% yield by treatment with KOH/MeOH followed by air oxidation and nitrogen extrusion. The reaction of **2** with phenyl vinyl sulfone affords *o*-di-*tert*-butylbenzene in 89% yield with loss of sulfur dioxide and benzenesulfinic acid. Reduction of **4a** and **4b** with $LiAlH_4$ followed by treatment of the resulting tetrols with *p*-toluenesulfonic acid affords the ether derivatives **15a** and **15b**, respectively, in good overall yields. The double bond of these hindered cycloalkenes is inert to hydroboration, peracid oxidation, and singlet oxygen, but both **15a** and **15b** react with bromine to give yellow, unstable crystalline 1:1 adducts to which we propose the polymeric ether–bromine adduct structure **19** rather than the bromonium bromide structure **18**.

We have recently reported a convenient synthesis of an overcrowded molecule 3,4-di-*tert*-butylthiophene (**1**) and its oxidative conversion to the corresponding sulfone **2** in high yield.[1] The cyclic sulfone **2** undergoes a cheletropic Diels–Alder reaction with a series of acetylenes and their synthetic equivalent to provide a high yield synthesis of *o*-di-*tert*-butylbenzene (**3**) and its derivatives (Scheme I).[2] Here we report that the successive Diels–Alder reaction of **2** with 2 molecules of suitably activated alkenes leads to highly crowded molecules possessing a framework of 2,3-di-*tert*-butylbicyclo[2.2.2]oct-2-ene (**4**) in which two adjacent *tert*-butyls are in cis orientation. Also reported are the chemical properties of these hindered cycloalkenes.

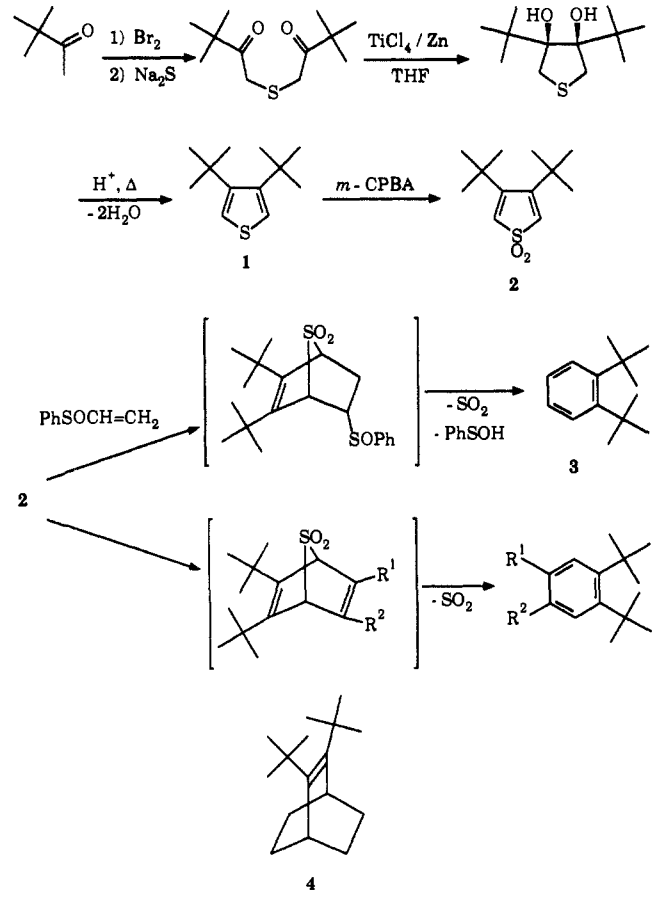
Results and Discussion

Diels–Alder Reaction of the Cyclic Sulfone 2 with Alkenes and Related Compounds. Heating the sulfone **2** with 2 equiv of maleic anhydride in refluxing *o*-dichlorobenzene afforded two isomeric bisadducts in 73% and 25% yields. The structure of the major isomer, whose two succinic anhydride moieties are equivalent in ^1H and ^{13}C NMR spectra, was tentatively determined as the endo–endo isomer **4a** at this point of time. Although the exo–exo isomer **4c** is also compatible with the above NMR data, a molecular model analysis shows that the formation of this adduct is least possible because two acid anhydride moieties in this molecule exist in close proximity and therefore the transition state leading to it is highly unfavorable because of dipole–dipole repulsion. The structure of the minor isomer, whose two succinic anhydride moieties are nonequivalent in NMR spectra, was unambiguously determined as the endo–exo isomer **4b**.

The reaction of **2** with 2 equiv of *N*-phenylmaleimide also afforded two isomeric bisadducts **5a** and **5b** in 58% and 40% isolated yields, respectively. Even the use of 1 equiv of the dienophiles did not allow the isolation of monoadducts **6** (Scheme II).

The reaction of **2** with 2 equiv of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) in refluxing toluene affords the bisadduct **7** in 87% yield. The completion of the reaction could be easily monitored by disappearance of the red due to PTAD. Treatment of **7** with KOH/MeOH followed by usual workup unexpectedly furnished 4,5-di-*tert*-butylpyridazine (**8**) directly in 80% yield (Scheme III).[3] The hydrazo compound **9** cannot be isolated even when the reaction was carried out under nitrogen because during workup it is easily oxidized to the corresponding azo compound, which spontaneously loses nitrogen to give **8**. The present method provides a simple synthesis of the highly crowded pyridazine **8** in which two *tert*-butyls occupy an adjacent position.[4]

Scheme 1



(1) Nakayama, J.; Yamaoka, S.; Hoshino, M. *Tetrahedron Lett.* **1988**, *29*, 1161–1164. See also: Nakayama, J.; Machida, H.; Saito, R.; Hoshino, M. *Tetrahedron Lett.* **1985**, *26*, 1983, 1984.

(2) Nakayama, J.; Yamaoka, S.; Nakanishi, T.; Hoshino, M. *J. Am. Chem. Soc.* **1988**, *110*, 6598, 6599.

(3) Preparation of **8** was preliminarily reported: Nakayama, J.; Hirashima, A. *Heterocycles* **1989**, *29*, 1241, 1242.

(4) Phosphorus derivatives of 3,4,5-tri-*tert*-butylpyridazines are the only reported pyridazines possessing two *tert*-butyls at adjacent positions: Eisenbarth, P.; Regitz, M. *Chem. Ber.* **1984**, *117*, 445–454. For other diazines having two *tert*-butyls at adjacent positions, see: (a) de Groot, A.; Wynberg, H. *J. Org. Chem.* **1966**, *31*, 3954–3958. (b) Visser, G. V.; Vos, A.; de Groot, A.; Wynberg, H. *J. Am. Chem. Soc.* **1968**, *90*, 3253, 3254.

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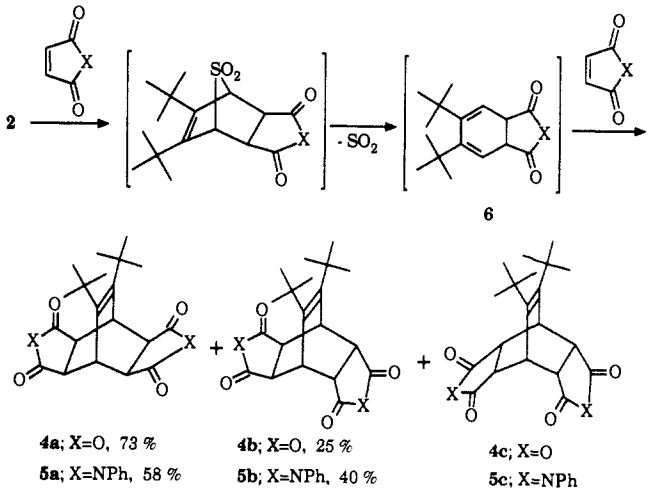
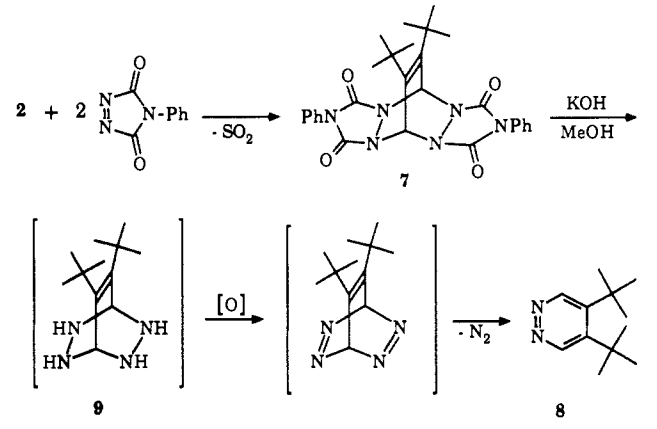
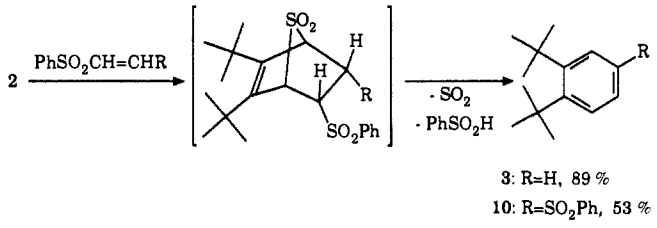
Scheme II



Scheme III

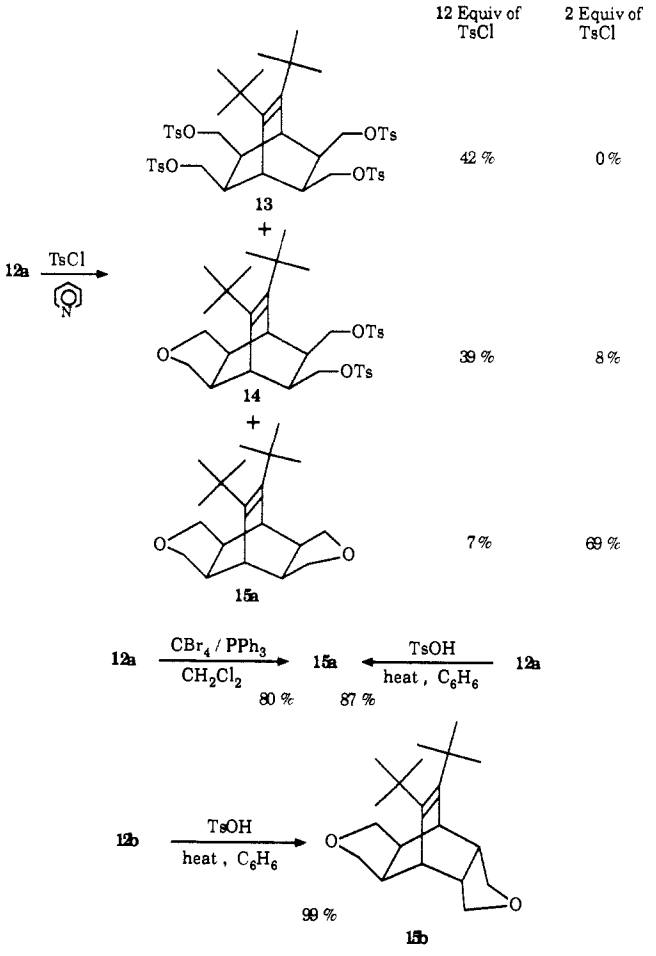


Scheme IV

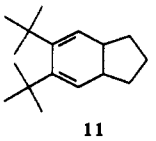


The reaction of **2** with excess phenyl vinyl sulfone[5] (3 equiv) in refluxing *o*-chlorotoluene afforded *o*-di-*tert*-butylbenzene (**3**) in 89% yield. No expected bisadduct was formed because the initial adduct loses both sulfur dioxide and benzenesulfinic acid under the applied conditions. The present synthesis of **3** is far superior to those reported previously,[6] including the reaction of **2** with phenyl vinyl sulfoxide.[2] In the present synthesis benzenesulfinic acid formed can be easily removed, while in the synthesis with phenyl vinyl sulfoxide benzenesulfenic acid formed turns to secondary products such as diphenyl disulfide, separation of which from **3** requires careful chromatographic workup. The same reaction of **2** with *cis*-1,2-bis(phenylsulfonyl)ethylene[7] resulted in the formation of the *o*-di-*tert*-butylbenzene derivative **10** in 53% yield (Scheme IV).

Scheme V



The reaction of **2** with excess cyclopentene under forced conditions afforded the cyclohexadiene **11** in low yield. Further



11

reaction of **11** with cyclopentene did not occur. Attempted reactions of **2** with 1,3-dithiole-2-thione[8] and 1,4-benzodithiin 1,1,4,4-tetroxide[9] afforded complex mixtures from which any pure identifiable products could not be isolated. In general, **2** is less reactive toward dienophiles than any other usual thiophene 1,1-dioxides because of steric hindrance.[10] It is thermally stable and does not undergo [4+2] dimerization even when heated at higher temperatures.

Transformations of 4a and 4b to Less Functionalized Derivatives. Compounds **4** and **5** possess a highly hindered and strained double bond incorporated in a bicyclo[2.2.2]oct-2-ene ring system. Unfortunately, however, they are too heavily functionalized to investigate the reactivities of the double bond. We therefore examined the conversion of **4a** and **4b** to less functionalized derivatives.

Treatment of **4a** with excess $LiAlH_4$ afforded the tetrol **12a** in 81% yield. The X-ray crystal structure analysis showed that

(5) (a) Carr, R. V. C.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 853-855. (b) Carr, R. V. C.; Williams, R. V.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 4976-4986.

(6) (a) Hoogzand, C.; Hübel, W. *Angew. Chem.* **1961**, *73*, 680. (b) Arnett, E. M.; Strem, M. E. *Chem. Ind. (London)* **1961**, 2008, 2009. (c) Barclay, L. R. C.; Milligan, C. E.; Hall, N. D. *Can. J. Chem.* **1962**, *40*, 1664-1671. (d) Burgstahler, A. W.; Abdel-Rahman, M. O. *J. Am. Chem. Soc.* **1963**, *85*, 173-180. For preparation of derivatives of **3**, see: (e) Viehe, H. G.; Merenyi, R.; Oth, J. F. M.; Valange, P. *Angew. Chem.* **1964**, *76*, 885. (f) Viehe, H. G. *Angew. Chem.* **1965**, *77*, 768-773. (g) Hoozgand, C.; Hübel, W. *Tetrahedron Lett.* **1961**, 637-643. (h) Arnett, E. M.; Strem, M. E.; Friedel, R. A. *Tetrahedron Lett.* **1961**, 658-662. (i) Krebs, A.; Franken, E.; Müller, S. *Tetrahedron Lett.* **1981**, *22*, 1675-1678.

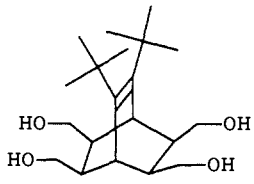
(7) DeLucchi, O.; Modena, G. *J. Chem. Soc., Chem. Commun.* **1982**, 914, 915.

(8) Klingsberg, E. *J. Am. Chem. Soc.* **1964**, *86*, 5290-5292.

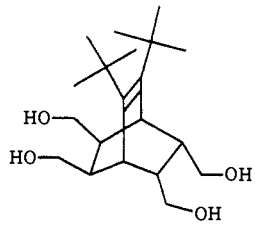
(9) (a) Nakayama, J.; Nakamura, Y.; Hoshino, M. *Heterocycles* **1985**, *23*, 1119-1122. (b) Parham, W. E.; Roder, T. M.; Hasek, W. R. *J. Am. Chem. Soc.* **1953**, *75*, 1647-1951.

(10) Rajappa, S. In *Comprehensive Heterocyclic Chemistry*; Bird, C. W., Cheeseman, G. W. H., Eds.; Pergamon: New York, 1978; Chapter 3.14.

four hydroxymethyls of **12a** all occupy the endo position.[11] Thus,



12a



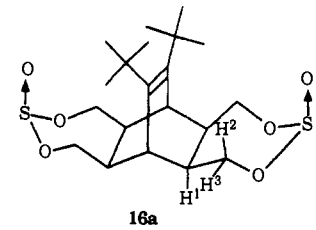
12b

the endo–endo structure of **4a** was rigidly established. Reduction of **4b** with $LiAlH_4$ also afforded the tetrol **12b** in 75% yield. Treatment of **12a** with excess tosyl chloride in pyridine afforded the expected tetratosylate **13** in 42% yield along with compounds **14** (39%) and **15a** (7%). The use of 2 equiv of tosyl chloride gave **15a** in 69% yield (Scheme V). Attempted reduction of **13** with $LiAlH_4$ was sluggish and afforded a complex mixture on a prolonged reaction in refluxing tetrahydrofuran; no expected tetramethyl derivative was formed in any amount. The steric crowdedness of **13** must be responsible for the failure in the expected reduction.[12]

The failure in the preparation of the tetramethyl derivative prompted us to develop a simpler synthesis of the ether derivative **15a** as an alternative to the former. Thus, the synthesis of **15a** could be attained in 80% yield by treatment of **12a** with CBr_4/PPh_3[13] and more conveniently in 87% yield by treating **12a** with *p*-toluenesulfonic acid (TsOH) in refluxing benzene. The isomeric ether **15b** was also obtained nearly quantitatively from **12b** by the latter method.

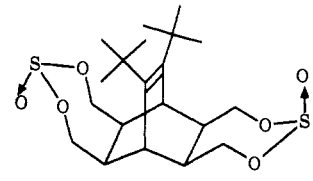
The reaction of **12a** with thionyl chloride in pyridine afforded three cyclic sulfites. In the seven-membered cyclic sulfites such as the commercial insecticide Thiodan, the oxygen atom on the sulfur is preferentially in the thermodynamically favorable axial orientation probably both in the solid state and in solution.[14,15] We therefore propose the axial structures **16a** (17%), **16b** (27%), and **16c** (9%) for these sulfites. The unsymmetrical isomer **16b** could be easily discriminated from symmetrical ones **16a** and **16c**. A decoupling experiment in ^1H NMR enables the determination of the coupling constant values between the exo hydrogen and the methylene ones. One symmetrical isomer that shows the coupling constant values of $J_{1,2}$ = 8.0 Hz and $J_{1,3}$ = 3.1 Hz is consistent with structure **16a**. The other isomer having the coupling constant values of $J_{1,2}$ = 7.6 Hz and $J_{1,3} \approx 0$ Hz is compatible with structure **16c** in which the dihedral angle H^1CCH^3 is nearly 90°. In the IR spectra determined in CCl_4, **16b** shows two absorptions due to the S=O stretching at 1190 and 1223 cm^{-1}, while **16a** and **16c** show one strong absorption at 1190 and 1223 cm^{-1}, respectively.[14]

Chemical Reactivities of 15a and 15b. Effort was then made to examine the chemical properties of the double bonds of **15a** and **15b**, which are considered a kind of "tied-back" derivative of hitherto unknown (*Z*)-1,2-di-*tert*-butyl-1,2-diisopropylethylene. The most hindered alkene prepared to date seems to be (*E*)-1,2-di-*tert*-butyl-1,2-diisopropylethylene.[16] Although the double bond of the present compounds is expected to be highly activated by nonbonded repulsion and angle strain, it would be more kinetically deactivated by steric hindrance. Actually, both **15a** and **15b** are inert to BH_3 under the conditions in which usual tetraalkyl-substituted alkenes easily undergo hydroboration.[17] The

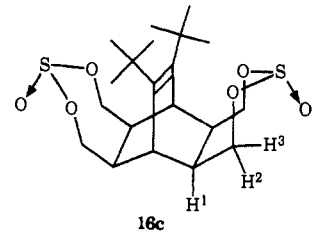


16a

$J_{1,2}$ = 8.0 Hz
$J_{1,3}$ = 3.1 Hz
$J_{2,3}$ = 11.8 Hz



16b



16c

$J_{1,2}$ = 7.6 Hz
$J_{1,3} \approx 0$ Hz
$J_{2,3}$ = 12.9 Hz

two compounds are also inert to oxidation with *m*-chloroperbenzoic acid (*m*-CPBA). Even trifluoroperacetic acid could not epoxidize **15a**. Singlet oxygen, produced by methylene-blue-sensitized irradiation, is also inert toward **15a** and **15b** under the conditions in which adamantylideneadamantane is efficiently converted to the corresponding dioxetane.[18]

The reaction of **15a** and **15b** with bromine is of particular interest. Standing an equimolar mixture of **15a** and bromine in CCl_4 in the dark brings about the formation of a yellow crystalline solid. Microanalysis, though it is not exact enough because of the instability of the material, shows that it is a 1:1 adduct of **15a** and bromine. The use of 2 equiv of bromine affords the same 1:1 adduct but not the 1:2 adduct. The adduct easily loses bromine when briefly heated or kept in vacuo. Its mass spectrum shows only peaks derived from **15a**. In CCl_4 it undergoes irreversible transfer of bromine to tetramethylethylene to give a 1:1 mixture of **15a** and 2,3-dibromo-2,3-dimethylbutane. In 1969, Wynberg and co-workers reported that the reaction of adamantylideneadamantane with bromine in CCl_4 affords a yellow solid having an empirical formula and properties compatible with the bromonium tribromide salt **17**,[19] whose structure was recently established by single-crystal X-ray analysis.[20] The properties of the present adduct described earlier fairly resemble those of **17**, though it is less stable. **17** is stable enough in $(CD_2Cl)_2$ to obtain an ^1H NMR spectrum, though it regenerates adamantylideneadamantane on attempted recrystallization from polar solvents.[20,21] The present adduct dissociates into **15a** and bromine in $CDCl_3$, and therefore its ^1H and ^{13}C NMR spectra are essentially identical with those of **15a**. On the basis of these observations, the bromonium bromide structure **18a**, in which the rearside attack by nucleophiles is strictly inhibited by steric hindrance, emerges as one of probable structures of the present adduct. In this case, the neighboring participation by the ether oxygen may be partly

(11) The X-ray analysis was performed by Professor F. Iwasaki of the University of Electro-Communications and will be reported elsewhere in detail.

(12) The approach of the hydride to the reactive site from the *tert*-butyl side is sterically least possible, and the approach from the open side increases the repulsion between *tert*-butyl and tosyl and/or the repulsion between tosyls at the S_N2 transition state.

(13) (a) Erickson, G. W.; Fry, J. L. *J. Org. Chem.* **1980**, *45*, 970–972. (b) Barry, C. N.; Evans, S. A., Jr. *J. Org. Chem.* **1981**, *46*, 3361–3364.

(14) (a) Forman, S. E.; Durbetaki, A. J.; Cohen, M. V.; Olofson, R. A. *J. Org. Chem.* **1965**, *30*, 169–175. (b) Byrn, S. R.; Siew, P. Y. *J. Chem. Soc., Perkin Trans. 2* **1977**, 144–149.

(15) Faucher, H.; Guimaraes, A.; Robert, J. B. *Tetrahedron Lett.* **1977**, 1743–1746.

(16) Lenoir, D. *Synthesis* **1989**, 883–897.

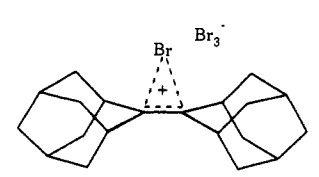
(17) Brown, H. C. *Organic Syntheses via Boranes*; John Wiley; New York, 1975.

(18) Wieringa, J. H.; Strating, J.; Wynberg, H. *Tetrahedron Lett.* **1972**, 169–172. For reactions of $^1O_2$ with hindered alkenes, see: Schaap, A. P.; Zaklika, K. A. In *Singlet Oxygen*; Wasserman, H. H., Ed.; Academic Press: New York, 1979; p 174.

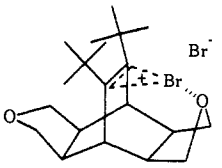
(19) Strating, J.; Wieringa, J. H.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1969**, 907.

(20) Slebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4504–4508.

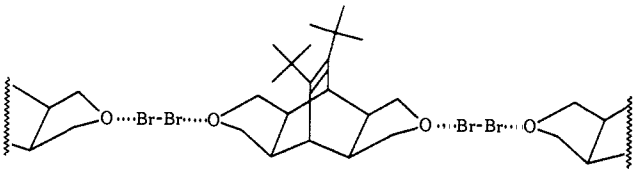
(21) Bellucci, G.; Bianchini, R.; Chiappe, C.; Marioni, F.; Ambrosetti, R.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1989**, *111*, 2640–2647.



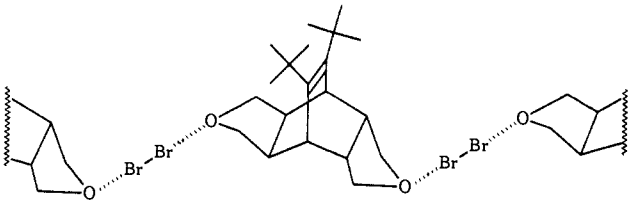
17



18a



19a



19b

responsible for the stabilization of **18a**. However, ethers are known to form weakly bonded complexes with halogens.[22] A notable example is the adduct of 1,4-dioxane and bromine, which acts as a bromine-transfer agent.[23] Therefore, the polymeric ether–bromine adduct structure **19a**[22] can also explain the properties of the present adduct. Actually, in the IR spectra (KBr), the strong absorption of **15a** at 922 cm^{-1}, which is probably associated with the ether bond, shifted to 878 cm^{-1} in the adduct along with many small changes of the position of other absorptions. The absorption of **15a** due to the C=C stretching, which is too weak to be observed, did not provide any information about the nature of the unsaturated part in the adduct. Furthermore, some hindered alkenes are known to be inert to bromine.[24] These facts indicate that structure **19a** is more probable than **18a** as the structure of the adduct. We are currently trying to prepare the more simple derivatives that do not contain the ether linkage in order to investigate the adduct formation with bromine.

The reaction of **15b** with bromine also affords a yellow, thermally unstable, 1:1 crystalline adduct. The properties of the adduct, to which we propose the ether–bromine adduct structure **19b**, are very similar to those of the adduct of **15a** and bromine.

Although the double bond of **15a** seems to be sterically more hindered than that of **15b**, differences in their reactivities were not appreciable in the present investigation.

Experimental Section

Melting points were determined on a MEL-TEMP capillary tube apparatus and are uncorrected. ^1H NMR spectra were measured at 400 or 90 MHz and ^{13}C NMR at 100.6 or 22.5 MHz. Mass spectra were determined at 70 eV in the EI mode unless otherwise stated. IR spectra of **16a–c** in solution were determined by FT-IR. Column chromatography utilized silica gel 60 (70–230 mesh, Merck). Solutions were dried with anhydrous $MgSO_4$. 3,4-Di-*tert*-butylthiophene 1,1-dioxide (**2**) was prepared by the literature method.[1] Dienophiles are from commercial sources except for 1,4-benzodithiin 1,1,4,4-tetroxide.[9] Microanalyses were performed by the Analytical Center of Saitama University.

Reaction of 2 with Maleic Anhydride. A mixture of 2.29 g (10 mmol) of **2** and 2.09 g (21 mmol) of maleic anhydride in 25 mL of *o*-dichlorobenzene was heated under reflux for 4 h. The mixture was cooled, and the resulting white crystalline precipitate was collected by filtration, washed with 10 mL of benzene, and dried to give 2.63 g (73%) of pure **4a**. The filtrate and washings were combined and evaporated under reduced pressure to give a solid residue, which was triturated with 20 mL of hexane to give 0.90 g (25%) of nearly pure **4b**.

4a: mp 357 °C dec (from 1,2-dichloroethane); IR (KBr) 2958, 1853, 1780, 1401, 1370, 1344, 1314, 1226, 1103, 1040, 926, 748, 730, 618 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (s, 18 H), 3.10 (m, 4 H), 4.40 (m, 2 H); ^{13}C NMR (DMSO-d_6) δ 32.44 (q), 35.04 (s), 36.94 (d), 43.38 (d), 144.42 (s), 172.97 (s); MS (FAB) m/z 361 (M + 1). Anal. Calcd for $C_{20}H_{24}O_6$: C, 66.65; H, 6.71. Found: C, 66.45; H, 6.63.

4b: mp 220 °C dec (from $CHCl_3$); IR 2966, 1865, 1779, 1398, 1368, 1225, 1096, 1038, 999, 927, 849, 824 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (S, 18 H), 3.15 (m, 4 H), 4.18 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 33.69 (q), 36.53 (s), 37.05 (d), 40.73 (d), 45.01 (d), 145.64 (s), 169.13 (s), 170.61 (s); MS (FAB) m/z 361 (M + 1). Anal. Found: C, 66.25; H, 6.78.

Reaction of 2 with *N*-Phenylmaleimide. A mixture of 228 mg (1 mmol) of **2** and 381 mg (2.2 mmol) of *N*-phenylmaleimide in 3 mL of *o*-dichlorobenzene was heated at reflux for 4.5 h. The mixture was cooled, and the resulting precipitate was collected by filtration and washed with 5 mL of benzene to give 164 mg (32%) of pure **5a**. The filtrate and washings were combined and evaporated under reduced pressure. The solid residue was chromatographed on a column of silica gel (40 g). Elution with CH_2Cl_2 gave 133 mg (26%) of **5a** and 205 mg (40%) of **5b**.

5a: mp 363–365 °C dec (from benzene); IR (KBr) 2954, 1772, 1704, 1597, 1496, 1458, 1370, 1317, 1191, 1124, 801, 746, 685, 614 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (s, 18 H), 3.04 (m, 4 H), 4.49 (m, 2 H), 7.23–7.47 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 33.17 (q), 35.78 (s), 37.18 (d), 43.79 (d), 126.03 (d), 128.63 (d), 129.12 (d), 131.66 (s), 143.69 (s), 176.14 (s); MS (FAB) m/z 511 (M + 1). Anal. Calcd for $C_{32}H_{34}N_2O_4$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.18; H, 6.82; N, 5.54.

5b: mp 264–265 °C dec (from cyclohexane); IR (KBr) 2960, 1773, 1716, 1597, 1499, 1376, 1185, 755, 723, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (s, 18 H), 3.01 (m, 2 H), 3.02 (m, 2 H), 4.27 (m, 2 H), 7.17–7.52 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 33.07 (q) 36.37 (s), 37.73 (d), 39.95 (d), 44.82 (d), 126.14 (d), 128.82 (d), 129.22 (d), 131.45 (s), 144.93 (s), 175.81 (s), 176.19 (s); MS (FAB) m/z 511 (M + 1).

Reaction of 2 with PTAD. A mixture of 0.69 g (3 mmol) of **2** and 1.09 g (6.2 mmol) of PTAD in 20 mL of toluene was refluxed for 5 h, during which the mixture turned from red to yellow. The resulting mixture was cooled, and the crystalline precipitate was collected by filtration and dried to give 894 mg (58%) of **7**. The filtrate was evaporated under reduced pressure, and the residue was recrystallized from benzene to give a further amount (442 mg, 29%) of **7**: mp 220 °C dec; IR (KBr) 2962, 1779, 1745, 1596, 1502, 1458, 1395, 1224, 1136, 1105, 1020, 866, 841, 764, 750, 684, 640, 597 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46 (s, 18 H), 6.84 (s, 2 H), 7.35–7.63 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 31.98 (q), 34.85 (s), 66.27 (d), 125.43 (d), 128.90 (d), 129.28 (d), 130.69 (s), 141.58 (s), 154.14 (s); MS (FAB) m/z 515 (M + 1). Anal. Calcd for $C_{28}H_{30}N_6O_4$: C, 65.36; H, 5.88; N, 16.33. Found: C, 65.40; H, 5.90; N, 16.23.

4,5-Di-*tert*-butylpyridazine (8). A solution of 630 mg (11.2 mmol) of KOH in 6 mL of MeOH was added dropwise to a stirring and ice-cooled suspension of 720 mg (1.4 mmol) of **7** in 20 mL of MeOH under nitrogen. The mixture was warmed slowly to room temperature and stirred for 3 h. The resulting clear yellow solution was evaporated under reduced pressure. Ether (200 mL) was added to the residue, and the mixture was stirred for 2 h, washed with water, dried, and evaporated. The crystalline residue was chromatographed on a column of silica gel (12 g). Elution with CH_2Cl_2 gave 164 mg of methyl phenylcarbamate and then 215 mg (80%) of **8**: colorless needles from hexane; mp 109 °C; IR (KBr) 3112, 3030, 2960, 1505, 1492, 1369, 1219, 709 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.58 (s, 18 H), 9.19 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 33.07 (q), 36.10 (s), 146.45 (s), 150.57 (d); MS m/z 192 (M). Anal. Calcd for $C_{12}H_{20}N_2$: C, 74.95; H, 10.48; N, 14.57. Found: C, 75.15; H, 10.22; N, 14.68.

***o*-Di-*tert*-butylbenzene (3).** A mixture of 229 mg (1 mmol) of **2** and 505 mg (3 mmol) of phenyl vinyl sulfone in 9 mL of *o*-chlorotoluene was heated at reflux for 14 h. The mixture was evaporated under reduced pressure, and the residue was chromatographed on a column of silica gel (30 g). Elution with pentane afforded 171 mg (89%) of **3** as a colorless liquid, whose spectroscopic data agreed with those of an authentic sample.[2] Further elution of the column with CH_2Cl_2 gave 275 mg of phenyl vinyl sulfone.

1,2-Di-*tert*-butyl-4-(phenylsulfonyl)benzene (10). A mixture of 115 mg (0.5 mmol) of **2** and 463 mg (1.5 mmol) of *cis*-1,2-bis(phenylsulfonyl)ethylene in 5 mL of *o*-dichlorobenzene was refluxed for 23 h. The mixture was purified by silica gel column chromatography with CH_2Cl_2/hexane (3:1) as eluent to give 87 mg (53%) of **10**: mp 150–151 °C (from hexane); IR (KBr) 2948, 1583, 1447, 1363, 1301, 1224, 1146,

(22) (a) Searles, S., Jr.; Tamres, M. In *The Chemistry of the Ether Linkage*; Patai, S., Ed.; John Wiley: New York, 1967; pp 243–308. (b) Hassel, O.; Romming, C. R. *Q. Rev., Chem. Soc.* **1962**, *16*, 1–18.

(23) Fieser, L. F.; Fieser, M. In *Reagents for Organic Synthesis*, John Wiley: New York, 1967; Vol. 1, pp 333, 334.

(24) Olah, G. A.; Prakash, G. K. S. *J. Org. Chem.* **1977**, *42*, 580–582.

1127, 1098, 1053, 817, 759, 714, 688, 613, 573, 548 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50 (s, 9 H), 1.53 (s, 9 H), 7.42–8.21 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 34.25 (q), 38.00 (s), 123.97 (d), 127.38 (d), 128.68 (d), 129.01 (d), 130.52 (d), 132.80 (d), 137.89 (s), 142.01 (s), 150.51 (s), 155.01 (s); MS m/z 330 (M). Anal. Calcd for $C_{20}H_{26}O_2S$: C, 72.69; H, 7.93. Found: C, 72.61; H, 8.14.

Reaction of 2 with Cyclopentene. A mixture of 228 mg (1 mmol) of **2**, 549 mg (8.7 mmol) of cyclopentene, and 4 mg of hydroquinone in 60 mL of benzene was heated at 210 °C for 10 h in a stainless steel autoclave. The mixture was evaporated, and the residue was passed through a short column of silica gel with benzene as eluent to give 89 mg of an oily mixture. Analysis of the mixture by NMR and GC/MS showed the presence of the monoadduct **11** as one of the major components.

Reduction of 4a to the Tetrol 12a. A solution of 3.62 g (10 mmol) of **4a** in 50 mL of anhydrous tetrahydrofuran (THF) was added to a stirring and ice-cooled suspension of 2.67 g (70 mmol) of $LiAlH_4$ in 50 mL of THF over a period of 45 min. The mixture was warmed slowly to room temperature and then refluxed for 7 h. The reaction was quenched by slow addition of 120 mL of wet THF (THF/H_2O, 14:1) to the ice-cooled mixture. The mixture was diluted with 100 mL of THF, stirred for 3 h, and filtered to remove inorganic precipitate. The precipitate was washed with THF, and the combined filtrate and washings were evaporated under reduced pressure. The resulting crystalline residue was recrystallized from EtOH/hexane to give 2.75 g (81%) of pure **12a**: white needles; mp 238–240 °C; IR (KBr) 3262, 2952, 2894, 1447, 1355, 1285, 1216, 1081, 1051, 1021, 983 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.25 (s, 18 H), 1.71–2.04 (m, 4 H), 2.88–3.54 (m, 10 H), 4.32–4.54 (m, 4 H, OH); ^{13}C NMR (DMSO-d_6) δ 33.25 (q), 34.93 (s), 39.27 (d), 44.47 (d), 61.53 (t), 142.96 (s); MS m/z 340 (M). Anal. Calcd for $C_{20}H_{36}O_4$: C, 70.55; H, 10.66. Found: C, 70.46; H, 10.64.

Reduction of 4b to the Tetrol 12b. A solution of 0.91 g (2.5 mmol) of **4b** in 10 mL of THF was added dropwise to a stirred and ice-cooled suspension of 0.71 g (18.7 mmol) of $LiAlH_4$ in 20 mL of THF during 0.5 h. The mixture was refluxed for 9 h and worked up as described previously to give 0.64 g (75%) of pure **12b**: mp 259–260 °C (from EtOH/hexane); IR (KBr) 3264, 2952, 2800, 1615, 1484, 1379, 1361, 1215, 1201, 1004, 984 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.23 (s, 18 H), 1.46–1.67 (m, 2 H), 1.80–2.03 (m, 2 H), 2.88 (m, 2 H), 2.96–3.85 (m, 8 H), 4.35–4.63 (m, 4 H, OH); ^{13}C NMR (DMSO-d_6) δ 32.98 (q), 35.37 (s), 36.67 (d), 38.78 (d), 41.27 (d), 60.67 (t), 62.51 (t), 144.42 (s); MS m/z 340 (M). Anal. Calcd for $C_{20}H_{36}O_4$: C, 70.55; H, 10.66. Found: C, 70.35; H, 10.70.

Reaction of 4a with Tosyl Chloride. (a) With 12 equiv of Tosyl Chloride. A solution of 238 mg (0.7 mmol) of **4a** in 10 mL of pyridine was added dropwise to a stirred and ice-cooled solution of 1.62 g (8.5 mmol) of tosyl chloride in 3 mL of pyridine over a period of 10 h. After the addition, the mixture was stirred for 2 h at 0 °C. The reaction was quenched by addition of 80 mL of ice–water. The resulting crystalline precipitate was collected by filtration, dissolved in 200 mL of CH_2Cl_2, washed with water, and dried. Evaporation of the solvent and then purification of the residue by silica gel column chromatography (20 g) with CH_2Cl_2 as eluent gave 270 mg (42%) of **13**, 171 mg (39%) of **14**, and 14 mg (7%) of **15a**.

(b) With 2 equiv of Tosyl Chloride. To a stirred and ice-cooled solution of 340 mg (1 mmol) of **12a** in 5 mL of pyridine was added 395 mg (2 mmol) of tosyl chloride. The mixture was warmed to room temperature, stirred for 15 h, and treated as described above to give **14** and **15a** in 8% and 69% yields, respectively.

13: mp 195–196 °C dec (from benzene); IR (KBr) 2954, 1597, 1357, 1173, 1094, 952, 840, 811, 779, 661, 552 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (s, 18 H), 1.86–2.10 (m, 4 H), 2.44 (s, 12 H), 3.01 (m, 2 H), 3.38–3.95 (m, 8 H), 7.35 (d, J = 8 Hz, 8 H), 7.74 (d, J = 8 Hz, 8 H); ^{13}C NMR ($CDCl_3$) δ 21.47 (q), 32.96 (q), 35.12 (s), 38.32 (d), 39.62 (d), 69.36 (t), 127.71 (d), 129.87 (d), 132.37 (s), 143.85 (s), 145.05 (s); MS m/z 784 (M – TsOH). Anal. Calcd for $C_{48}H_{60}O_{12}S_4$: C, 60.22; H, 6.32. Found: C, 60.15; H, 6.32.

14: mp 182–183 °C dec (from CCl_4); IR (KBr) 2948, 1597, 1456, 1356, 1172, 1092, 1030, 945, 816, 778, 659, 554 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (s, 18 H), 1.91–2.31 (m, 4 H), 2.45 (s, 6 H), 3.06 (m, 2 H), 3.15–4.02 (m, 8 H), 7.35 (d, J = 8 Hz, 4 H), 7.76 (d, J = 8 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.42 (q), 33.28 (q), 35.12 (s), 38.27 (d), 39.57 (d), 44.55 (d), 69.96 (t), 71.69 (t), 127.76 (d), 129.82 (d), 132.75 (s), 143.04 (s), 144.88 (s); MS m/z 630 (M). Anal. Calcd for $C_{34}H_{46}O_7S_2$: C, 64.73; H, 7.35. Found: C, 64.85; H, 7.44.

15a: mp 184–186 °C (purified by sublimation at 110 °C (0.9 mmHg)); IR (KBr) 2916, 1540, 1477, 1392, 1358, 1337, 1272, 1253, 1200, 1107, 1079, 1048, 1029, 958, 922, 683, 635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (s, 18 H), 2.18–2.39 (m, 4 H), 3.05 (m, 2 H), 3.23–3.45 (m, 4 H), 3.65–3.92 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 33.50 (q), 35.18 (s), 38.32 (d), 44.82 (d), 71.85 (t), 142.39 (s); MS m/z 304 (M). Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59. Found: C, 78.95; H, 10.65.

Conversion of 12a to 15a. (a) With CBr_4/PPh_3. A solution of 1.31 g of PPh_3 in 25 mL of CH_2Cl_2 (freed of MeOH) was added dropwise to a stirred solution of 0.34 g (1 mmol) of **12a** and 1.67 g (5 mmol) of CBr_4 in 20 mL of CH_2Cl_2 over a period of 40 min. The mixture was stirred for 17 h, diluted with 150 mL of CH_2Cl_2, washed with water, dried, and evaporated. Hexane (100 mL) was added to the residue, and the insoluble material was removed. The filtrate was evaporated and chromatographed on a column of silica gel (15 g). Elution with CH_2Cl_2 gave 243 mg (80%) of **15a**.

(b) With TsOH. A mixture of 170 mg (0.5 mmol) of **12a** and 100 mg of TsOH monohydrate in 7 mL of benzene was refluxed for 4 h. The mixture was diluted with 100 mL of ether, washed with water, dried, and evaporated. The residue was passed through a short column of silica gel with CH_2Cl_2 as eluent to give 132 mg (87%) of **15a**.

Conversion of 12b to 15b. A mixture of 170 mg (0.5 mmol) of **12b** and 50 mg of TsOH monohydrate in 7 mL of benzene was refluxed for 5 h. The mixture was treated in a manner similar to the case of **15a** to give 150 mg (99%) of **15b**: mp 96–97 °C (after purification by sublimation at 85 °C (0.9 mmHg)); IR (KBr) 2948, 2854, 1469, 1390, 1360, 1190, 1093, 1045, 952, 916, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (s, 18 H), 2.14–2.30 (m, 2 H), 2.44–2.68 (m, 2 H), 2.93 (m, 2 H), 3.18–3.64 (m, 4 H), 3.69–3.99 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 33.28 (q), 35.72 (s), 37.89 (d), 40.49 (d), 43.14 (d), 71.10 (t), 72.50 (t), 144.45 (s); MS m/z 304 (M). Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59. Found: C, 78.72; H, 10.73.

Reaction of 12a with Thionyl Chloride. To a stirred and ice-cooled solution of 340 mg (1 mmol) of **12a** and 356 mg (4.5 mmol) of pyridine in 5 mL of ether was added dropwise 250 mg (2.1 mmol) of thionyl chloride. The mixture was warmed slowly to room temperature and stirred for 8 h. The resulting mixture was diluted with 50 mL of CH_2Cl_2, washed with water, dried, and evaporated. The residue was chromatographed on a column of silica gel (20 g). Elution with benzene gave 72 mg (17%) of **16a**, 114 mg (27%) of **16b**, and 41 mg (9%) of **16c**.

16a: mp 248–249 °C (from CCl_4); IR $\nu_{S=O}$ 1190 cm^{-1} (CCl_4), 1186 cm^{-1} (CH_3CN); ^1H NMR ($CDCl_3$) δ 1.33 (s, 18 H, t-Bu), 2.35 (m, 4 H, exo-H), 2.93 (m, 2 H, bridgehead), 3.62 (dd, J = 11.8, 3.1 Hz, methylene), 4.62 (dd, J = 11.8, 8.0 Hz, methylene), (C_6D_6) δ 0.91 (s, 18 H), 1.71 (m, 4 H), 1.97 (m, 2 H), 3.11 (dd, 4 H), 4.53 (dd, 4 H); ^{13}C NMR ($CDCl_3$) δ 33.72 (q), 35.18 (s), 39.73 (d), 43.63 (d), 62.48 (t), 143.20 (s); MS m/z 432 (M); high-resolution MS, calcd for $C_{20}H_{32}O_6S_2$ 432.1641, found 432.1660.

16b: mp 224–226 °C dec (from CCl_4); IR $\nu_{S=O}$ 1190, 1223 cm^{-1} (CCl_4), 1186, 1209, 1225 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (s, 18 H), 2.24–2.47 (m, 4 H), 2.93 (m, 2 H), 3.51–4.05 (m, 4 H), 4.27–4.78 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 33.72 (q), 35.34 (s), 40.87 (d), 42.87 (d), 44.23 (d), 62.59 (t), 64.21 (t), 143.15 (s); MS m/z 432 (M); high-resolution MS found 432.1644.

16c: mp 241–242 °C dec (from CCl_4); IR (KBr) $\nu_{S=O}$ 1190 (w), 1223 cm^{-1} (s) (CCl_4), 1209 (w), 1225 cm^{-1} (s) (CH_3CN); ^1H NMR ($CDCl_3$) δ 1.34 (s, 18 H, t-Bu), 2.33 (m, 4 H, exo-H), 2.91 (m, 2 H, bridgehead), 3.89 (dd, J = 12.9, 7.6 Hz, 4 H, methylene), 4.37 (d, J = 12.9 Hz, 4 H, methylene), (C_6D_6) δ 1.03 (s, 18 H), 1.33–1.53 (m, 4 H), 1.97 (m, 2 H), 3.35 (dd, 4 H), 3.93 (d, 4 H); MS m/z 432 (M); high-resolution MS found 432.1643.

Attempted Hydroboration of 15a and 15b. To a stirred and ice-cooled solution of 152 mg (0.5 mmol) of **15a** or **15b** in 3 mL of THF was added 0.6 mL (0.6 mmol) of 1 M THF solution of borane–THF complex (Aldrich) under nitrogen. The mixture was stirred for 22 h at room temperature. Workup of the mixture followed by usual hydration procedure (oxidation with alkaline H_2O_2) afforded the starting material quantitatively.

Attempted Oxidation of 15a and 15b with Peracids. A mixture of 0.7 mmol of m-CPBA and 0.5 mmol of **15a** or **15b** in 5 mL of CH_2Cl_2 was stirred overnight and then refluxed for 10 h. Usual workup of the mixture afforded the starting material quantitatively. Treatment of **15a** with excess trifluoroperacetic acid in the presence of Na_2HPO_4 in refluxing CH_2Cl_2 for 6 h also afforded the starting material in 96% yield.

Attempted Reaction of 15a and 15b with Singlet Oxygen. A solution of 3 mg of methylene blue and 62 mg (0.2 mmol) of **15a** or **15b** in 10 mL of CH_2Cl_2 was irradiated for 6 h by two 500-W halogen lamps at 17 °C with bubbling oxygen. Workup of the mixture gave the starting material quantitatively. Under the same conditions, adamantylideneadamantane was completely consumed within 2 h to give the corresponding dioxetane.

Reaction of 15a with Br_2. A solution of 183 mg (1.1 mmol) of Br_2 in 4 mL of CCl_4 was added to a stirred and ice-cooled solution of 152 mg (0.5 mmol) of **15a** in 1 mL of CCl_4. The resulting yellow cloudy mixture was stirred for 24 h in the dark. The resulting yellow precipitate was collected by filtration and washed with a small amount of CCl_4 to give

141 mg of the adduct **18a**. The use of 1 equiv of Br_2 also afforded the same adduct. Anal. Calcd for $C_{20}H_{32}Br_2O_2$: C, 51.74; H, 6.95. Found: C, 53.64; H, 7.76. Keeping 27.0 mg (0.058 mmol) of the adduct under vacuum for 2 days affords 16.7 mg (0.055 mmol) of **15a**. A 0.1 M CCl_4 solution (0.5 mL) of tetramethylethylene and 23.9 mg of the adduct was mixed in an NMR tube. Analysis of the mixture by ^1H NMR showed the formation of a 1:1 mixture of **15a** and 2,3-dibromo-2,3-dimethylbutane. ^1H and ^{13}C NMR spectra of the adduct in $CDCl_3$ gave essentially the same spectra as those of **15a**. The mass spectrum also showed only peaks derived from **15a**. IR (KBr) 2912, 1472, 1389, 1359, 1268, 1194, 1104, 1012, 878, 706, 643, 597, 385 cm^{-1}.

Reaction of 15b with Br_2. A solution of 121 mg (0.76 mmol) of Br_2 in 2.4 mL of CCl_4 was added to a stirred and ice-cooled solution of 92 mg (0.3 mmol) of **15b** in 0.6 mL of CCl_4. The mixture was kept at room temperature in the dark without stirring, and the resulting yellow fine needles were collected by filtration and washed with a small amount of CCl_4 to give 82 mg of the adduct: mp 105-111 °C; IR (KBr) 2942, 2868, 1466, 1392, 1362, 1248, 1193, 1093, 1044, 953, 882, 721, 652, 585, 497, 419 cm^{-1}. Anal. Calcd for $C_{20}H_{32}Br_2O_2$: C, 51.74; H, 6.95. Found: C, 48.48; H, 7.00. Mixing a 0.1 M solution (0.5 mL) of tetramethylethylene in CCl_4 and 23.9 mg of the adduct in an NMR tube afforded a 1:1 mixture of **15b** and 2,3-dibromo-2,3-dimethylbutane. Keeping the adduct under vacuum at room temperature for several days afforded **15b** quantitatively.

Asymmetric Induction in the Ene Reactions of *N*-Sulfinylcarbamates

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Abstract: Ene reactions of *N*-sulfinylcarbamates derived from the chiral alcohols 8-phenylmenthol and *trans*-2-phenylcyclohexanol proceed with high levels (95+% de) of asymmetric induction. Where regioisomeric products are possible (with unsymmetrical alkenes), generally only that adduct with the more stable double bond is formed. In general, the reaction displays the characteristics of a concerted process with simultaneous carbon-sulfur bond formation and carbon-hydrogen bond cleavage at the transition state. The sulfinamide adducts can be transformed by 2,3 sigmatropic rearrangement of a derived sulfoxide into optically active allylic alcohols. Thus, the overall transformation effects allylic hydroxylation with high levels of regio- and absolute stereochemical control.

Since the late 1960s, there has been a serious effort by many research groups to develop synthetically viable transformations that proceed with absolute stereochemical control. Many of these efforts have been successful, resulting in practical methods for asymmetric induction, especially in carbon-carbon bond formation.[1] Special attention to this specific class of synthetic reactions is certainly justified by the central role that this bond plays in organic chemistry. In sharp contrast, there are relatively few techniques that result in absolute stereochemical control concomitant with the formation at a carbon-heteroatom linkage, with the contributions from Brown's laboratories in controlling hydroboration processes[2] and Sharpless epoxidation of allylic alcohols[3] representing notable exceptions. There are other techniques for absolute stereochemical control that result in heteroatom-substituted carbon stereocenters exemplified by Midland's reduction of alkinyl ketones,[4] but these processes do not result in an increase in molecular complexity from either the standpoint of the carbon framework or functional groups that are present.

A number of years ago we began a broad range of study of reactions that would transform simple alkenes into more complex arrays suitable for further synthetic manipulation.

Our first activities in this area involved ene reactions of alkenes with glyoxylate esters and were eminently successful, resulting in homoallylic alcohols through carbon-carbon bond formation with levels of stereochemical control in excess of 1000:1.[5] More recently, we have turned our attention to reactions that functionalize simple alkenes through the formation of new carbon-heteroatom bonds. We have already communicated initial findings relating to ene-like reactions of chiral *N*-sulfinylcarbamates with alkenes that result in allylic sulfinimides with high levels of stereochemical control at the carbon bearing the sulfur as well as the sulfur atom itself.[6] Further transformation of these adducts via 2,3 sigmatropic rearrangement of derived aryl sulfoxides afforded allylic alcohols. These ultimate products represent net allylic oxidation of the original alkene with retention of the position of the double bond and with high levels of regiocontrol at the two competing allylic sites as well as high levels of asymmetric induction. It is these studies that we describe here in some detail, providing significant new findings that relate to the mechanism for the ene reaction of *N*-sulfinylcarbamates in the presence of Lewis acids as well as to the synthetic scope of the overall process.

The thermal ene reactions of *N*-sulfinylsulfonamides have been study in great detail by Kresze.[7] Because we had previously observed a dramatic effect of Lewis acids on the level of absolute stereochemical control in the cycloaddition reactions of *N*-sulfinylcarbamates with dienes,[8] we restricted our study of the ene reactions of these species to similar conditions. Indeed, in the presence of an equivalent of $SnCl_4$, the reactions of alkenes with the *N*-sulfinylcarbamate **2** derived from our chiral auxiliary[9] *trans*-2-phenylcyclohexanol (**1**) provide adducts with excellent levels of stereochemical control (>95:5).

We have provided the stereo- and regiochemical outcomes from the reaction of the *N*-sulfinylcarbamate **2** with a number of simple, representative achiral alkenes in Table I and chiral alkenes in Table

(1) For reviews, see: Morrison, J. D., Ed. *Asymmetric Synthesis*; Wiley: New York, 1983-5; Vols. 1-5.
(2) For reviews, see: Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *Tetrahedron* **1981**, *37*, 3547.
(3) Pfenninger, A. *Synthesis* **1986**, 89.
(4) Midland, M. M. *Chem. Rev.* **1989**, *89*, 1553.
(5) Whitesell, J. K.; Bhattacharya, A.; Aguilar, D. A.; Henke, K. *J. Chem. Soc., Chem. Commun.* **1982**, 989.
(6) Whitesell, J. K.; Carpenter, J. *J. Am. Chem. Soc.* **1987**, *109*, 2839.
(7) For leading references, see: Muensterer, H.; Kresze, G.; Lamm, V.; Gieren, A. *J. Org. Chem.* **1983**, *48*, 2833. Schwobel, A.; Kresze, G. *Synthesis* **1984**, 945.
(8) Whitesell, J. K.; Carpenter, J. F. *J. Chem. Soc., Chem. Commun.* **1985**, 1449.
(9) Whitesell, J. K.; Chen, H.-H.; Lawrence, R. M. *J. Org. Chem.* **1986**, *51*, 551.

0002-7863/90/1512-7653$02.50/0