Notes

Allylic Deuteration and Tritiation of Olefins with *N*-Sulfinylsulfonamides

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Received June 22, 1977

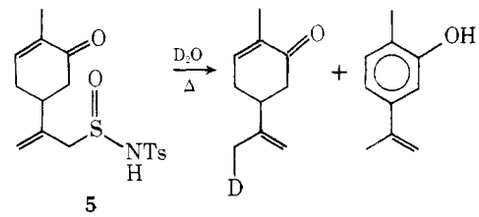
Recently, we have explored the synthetic applications of the reactions of both bis(*N*-*p*-toluenesulfonyl)selenodiimide[1-3] and bis(*N*-*p*-toluenesulfonyl)sulfodiimide.[4,5] These aza analogues of SeO_2 and SO_2 are powerful enophiles in their reactions with olefins and eventually result in the formation of allylic sulfonamides. Kresze and Schönberger independently discovered that the sulfur diimide species effect allylic amination of olefins.[6] We now report that the ene reaction[7] of the related monooxo compounds, the *N*-sulfinylsulfonamides,[8] is reversible under mild conditions and that this reversibility can be exploited to specifically introduce deuterium (or tritium) into the allylic position of an alkene.

When 1.1 equiv of **1** was stirred with β-pinene in benzene for 3 h at 25 °C, a 1:1 adduct, the *N*-tosylsulfinamide **3**, was isolated in 89% yield (Scheme I). However, upon standing in moist air at room temperature for a few days or upon strong heating (>150 °C), **3** was found to decompose with the liberation of β-pinene. When **3** was refluxed in benzene, no change occurred until an excess of H_2O was added which resulted in the formation of β-pinene and *p*-toluenesulfonamide. The observed behavior is consistent with a reversible ene reaction. However, initial hydrolysis of the allylic sulfinamide adduct to an allylic sulfinic acid, which then undergoes retroene reaction, is another possibility.

When the H_2O was replaced by D_2O, exchange of the acidic N–H proton followed by retroene reaction led to the incorporation of a deuterium in the allylic position. In the case of β-pinene (Scheme II), the recovered material was 86% d_1 and 14% d_0 with the deuterium being introduced trans (>97%) to the dimethyl bridge as shown by ^2H NMR[9,10] and confirmed by the loss of the deuterium upon oxidation with SeO_2 to *trans*-pinocarveol.[11] These results are similar to the stereospecific retroene reaction of the deuterated adduct of β-pinene and methyl phenyl glyoxylate[10] with the exception that in the present case much lower temperatures are needed.

Table I shows the results for the allylic deuteration of a variety of olefins. Generally, the olefins were recovered in yields greater than 50% and greater than 75% monodeuterated. It was not necessary to isolate the initial ene adduct. It should be pointed out that the reaction is not general since some cyclic olefins as well as electron-poor or hindered olefins are poor substrates for this system. Among the compounds which failed to form an isolable ene adduct were cyclohexene, 4-*tert*-butylcyclohexene, Δ^2-cholestene, cholesterol, and α-pinene. Under forcing conditions, 4-*tert*-butylcyclohexene gave *tert*-butylbenzene in good yield.[12]

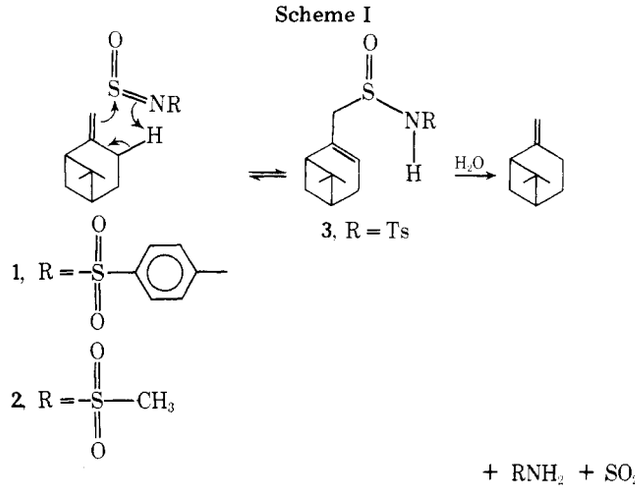
l-Carvone is the only example in Table I of an olefin with exchangeable protons. Exchange of the crude deuterated product with ethanolic NaOH at 60 °C for 3 h gave *l*-carvone that was >75% d_1. NMR integration indicated that the deuterium was located in the vinyl methyl group (although Büchi and Wüest[13] have shown that the major product of SeO_2 oxidation of *l*-carvone is the racemic tertiary allylic alcohol). In support of the proposed location of the deuterium, the initial 1:1 adduct was found to have the structure **5**.[15] In addition,



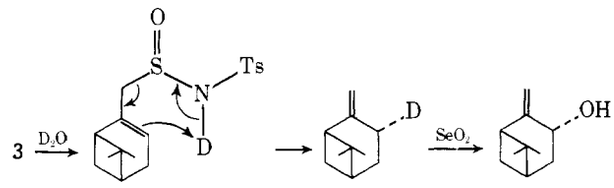
there was no loss in the optical activity of the recovered deuterated *l*-carvone. During the reaction, some aromatization[12] of the *l*-carvone to dehydrocarvacrol (2-methyl-5-isopropenylphenol) occurred.

Of course, alkenes can be tritiated in the same manner using T_2O in place of D_2O. As shown in Scheme III, α-methylstyrene with a specific radioactivity of 0.8 mCi/mmol was isolated when 2 mmol of its crystalline adduct **5** was refluxed for 20 h in 5 mL of benzene containing 0.1 mL of T_2O (1 Ci/mL). Correcting for the 2 mmol of protons introduced with the adduct **5**, the specific activity of the medium was 7.7 mCi/mmol of H^+. Therefore tritium was incorporated into the olefin at a specific radioactivity 10% that of the reaction medium. This calculation is based on the notion that only one allylic hydrogen is available for exchange. This would be true if the *N*-sulfinylsulfonamide (TsN=S=O) hydrolyzed as it

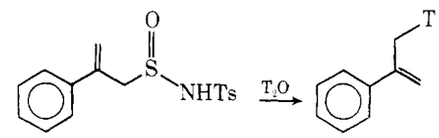
Scheme I



Scheme II



Scheme III



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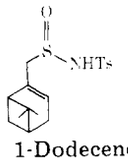
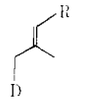
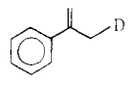
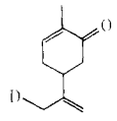
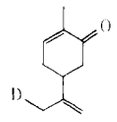
0022-3263/78/1943-1456$01.00/0

Table I. Allylic Deuteration of Alkenes

Case	Olefin	Registry no.	Reagent[b]	Product[a]	Registry no.	Deuterium incorporation[a]	Recovery[c]
1	β-Pinene	127-91-3	1.2 TsNSO[e]		65025-52-7	14% d_0 86% d_1	59%
2	β-Pinene		2 MsNSO[f]			3% d_0 94% d_1 4% d_2	51%
3		64976-20-1				4% d_0 95% d_1 3% d_2	78%
4	1-Dodecene	112-41-4	3 TsNSO		64976-21-2	4% d_0 93% d_1 2% d_2	46%
5	Citronellol methyl ether	55915-70-3	2 TsNSO		64976-22-3	11% d_0 87% d_1 2% d_2	68%
6	α-Methyl-styrene	98-83-9	1.2 TsNSO		64976-23-4	15% d_0 84% d_1 1% d_2	79%
7	*l*-Carvone	6485-40-1	2 TsNSO		64976-24-5	(Crude)(Exchanged) 13% d_0 16% d_0 46% d_1 82% d_1 35% d_2 2% d_2 6% d_3	39% (After exchange)
8	*l*-Carvone		2 MsNSO			(Crude)(Exchanged) 16% d_0 16% d_0 20% d_1 37% d_2 75% d_1 25% d_3 2% d_4 9% d_2	39% (After exchange)

[a] See the Experimental Section for all details. The location of the deuterium was determined by NMR. [b] TsNSO = *N*-sulfinyl-*p*-toluenesulfonamide. MsNSO = *N*-sulfinylmethanesulfonamide. The numbers refer to the number of equivalents used. [c] Based on starting olefin. [d] Adduct heated in benzene/D_2O at 140 °C for 10 h (sealed tube). [e] Registry no.: 4104-47-6. [f] Registry no.: 40866-96-4.

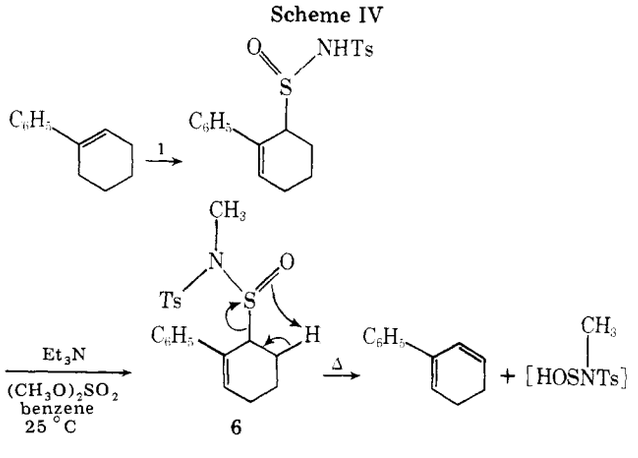
was produced in the retroene process. However, the validity of this assumption was challenged by the following experiment: under the same conditions described above, the T_2O was replaced with 0.1 mL of D_2O and this gave α-methylstyrene which was 25% d_0, 40% d_1, 22% d_2, and 10% d_3. Apparently, under these conditions (much less water than is usually employed), the ene and retroene reactions are occurring several times over before the *N*-sulfinylsulfonamide (TsN=S=O) is hydrolyzed.

Although this single example of allylic tritiation was performed using an isolated sulfinamide adduct, the in situ method (in which the adduct is formed in benzene and then D_2O or T_2O is added directly to the solution of the crude adduct in benzene) is much simpler and should be preferable in most cases where allylic tritiation is desired. We have found that the sulfinamide adducts are often too unstable to isolate. Moreover, if one wished to allylically tritiate a few micrograms of olefin, isolation of the adduct would not be feasible.

One consequence of the ene/retroene mechanism is the loss of stereochemistry in the case of di- and trisubstituted olefins. For example, reaction of either *cis*- or *trans*-5-decene with 1 followed by hydrolysis afforded the same mixture of 23% *cis*- and 77% *trans*-5-decene. Similar results were found for (*Z*)- and (*E*)-3-methyl-2-hexene (the recovered olefin in both cases was 33% (*Z*) and 67% (*E*)). Control experiments showed the olefins were stable (no cis–trans isomerization) to the conditions of the retroene–hydrolysis procedure.

If a suitable β-hydrogen is available, a side reaction involving syn elimination of the allylic sulfinamide group to a diene sometimes competes with the retroene reaction. The yield of diene was generally less than 15%. However, diene formation can be made the exclusive event by obstruction of the retroene pathway through alkylation of the nitrogen of the intermediate allylic sulfinamides. As a particular example (Scheme IV), pyrolysis (by GLPC injection) of the *N*-methylsulfinamide derivative **6** (obtained in only 26% yield) from 1-phenylcyclohexene gave a 90% yield of 2-phenyl-1,3-cyclohexadiene and none of the isomeric diene.[14] Similarly, cyclooctene and (*E*)-5-decene were transformed to 1,3-cyclooctadiene and 4,6-decadiene, respectively.[15a] This sequence

Scheme IV



effects symmetrical (i.e., Δ^2-olefin → $\Delta^{1,3}$-diene) dehydrogenation of an olefin to a conjugated diene, but this new diene synthesis is limited by the fact that the *N*-methylsulfinamide adducts are generally formed in poor overall yield.[15b] In contrast to allylic sulfoxides,[16] these derivatives have given no indication of undergoing 2,3-sigmatropic rearrangement.[17]

In summary, the reversible ene reaction of *N*-sulfinylsulfonamides represents a convenient procedure for the allylic deuteration and tritiation of certain alkenes.

Experimental Section

All mass spectra were collected using a Hitachi Perkin-Elmer RMU-6E mass spectrometer and the percentage of deuterium incorporation was calculated using standard techniques[18] including corrections for natural abundance. Kugelrohr distillation refers to bulb-to-bulb distillation using a Büchi kugelrohr apparatus. The temperatures reported are the air bath temperatures at which the material distilled and are not the true boiling points.

***N*-Sulfinyl-*p*-toluenesulfonamide (1). A.** This procedure is a slightly modified version of Kresze's.[8,20] In a 2.0-L round-bottomed flask fitted with a reflux condenser and a $CaCl_2$ drying tube, a mixture of 250 g of *p*-toluenesulfonamide (1.46 mol, Eastman Organic Chemicals) and 200 g of thionyl chloride (1.68 mol) in 1.0 L of dry benzene was heated for 5 days at reflux. After cooling to room temperature the solvent and excess $SOCl_2$ were evaporated, first at aspirator pressure, then under high vacuum, to leave approximately 300 g of dark orange oil. Kugelrohr distillation in three 100-g portions gave a total of 196 g of **1** (130–140 °C, 0.06 Torr, 62%) which crystallized upon standing to a bright yellow solid, mp 47–51 °C (lit.[8] mp 53 °C).

B. Addition of 1% *N,N*-dichloro-*p*-toluenesulfonamide[21] decreased the time needed for completion. For example, the reaction of 125 g of $TsNH_2$ (0.73 mol) and 173 g of thionyl chloride (1.46 mol) in 100 mL of benzene at reflux (using a $CaCl_2$ drying tube as above) was complete in only 16 h. Evaporation followed by kugelrohr distillation as above gave **1** in 69% yield. *This modified procedure (B) represents a great saving in time (only 16 h instead of 5 days) with no decrease in yield.* Note also that procedure B employs different proportions of reactants and solvent than procedure A.

***N*-Sulfinylmethanesulfonamide (2).**[19] Following procedure A above, **2** was prepared using 15.5 g of methanesulfonamide (16 mmol) and 14 mL of $SOCl_2$ (19 mmol) in 30 mL of benzene. Kugelrohr distillation (165 °C, 0.02 Torr; lit.[8] bp 80 °C, 10^{-4} Torr) gave 13.9 g (62%) of bright yellow oil.

Reaction of 1 with β-Pinene. To a 100-mL round-bottomed flask under anhydrous conditions containing a solution of 5.4 g of TsNSO (24.9 mmol) in 50 mL of benzene (THF or CH_3CN gave equivalent results) was added, with stirring and cooling (ice bath), 3.6 mL of β-pinene (22.7 mmol). After stirring overnight at room temperature, the solution was concentrated to about one-half of its volume and cooled. The resulting white precipitate was collected and washed with a small amount of hexanes. After drying in vacuo, 7.13 g of 6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl-*N*-(*p*-toluenesulfonyl)methylsulfinamide (**3**) was obtained (89%), mp 137–139 °C: IR (KBr) 3050 (NH), 2920 (CH), 1595, 1375 (SO_2), 1320, 1185, 1165 (SO_2), 1080, 1065, 860, and 815 cm^{-1}; NMR ($CDCl_3$) δ 9.0 (1 H, broad s, exchangeable with D_2O, NH), 7.9–7.2 (4 H, q, aromatic), 5.60 (1 H, broad s, olefinic), 3.55 (2 H, broad s, $-CH_2S$), 2.4 (3 H, s, aromatic $-CH_3$), 2.2 (5 H, m, ring –H), 1.2 (3 H, s, $-CH_3$), 1.0 (1 H, m, bridgehead) and 0.7 (3 H, d, $-CH_3$). Upon standing at room temperature in the solid state, **14** slowly decomposed to β-pinene and a solid residue consisting mostly of $TsNH_2$.

Anal. Calcd for $C_{17}H_{23}NO_3S_2$: C, 57.76; H, 6.56; N, 3.96. Found: C, 57.00; H, 6.90; N, 3.80.

Allylic Deuteration of β-Pinene with TsNSO (1). A solution of 520 mg of TsNSO (2.4 mmol) in 20 mL of benzene was prepared in a 50-mL round-bottomed flask under anhydrous condition. β-Pinene (0.32 mL 2 mmol) was added with stirring. The reaction could be conveniently monitored by GLPC for the disappearance of olefin (after the removal of the adduct by passing an aliquot through a plug of neutral alumina with hexanes). When the reaction was complete (6 h), 2 mL of D_2O (>99.7% isotopic purity, obtained from Merck Sharp & Dohme, Ltd.) was added to the flask. After stirring at room temperature for 15 min while fitting the flask with a reflux condenser, the mixture was heated (oil bath at 90 °C) for 12 h (after which time no adduct remained by TLC). The benzene layer was separated and passed through a short column of silica gel (30 g) with hexanes (50 mL). The resulting solution was concentrated to leave 190 mg of crude product which was kugelrohr distilled (90–100 °C, water aspirator pressure) to give 162 mg of *trans*-3-deuterio-β-pinene (59%): NMR ($CDCl_3$) δ 4.5 (2 H, m, $=CH_2$), 2.35 (3 H, m, ring H), 1.9 (3 H, m, ring H), 1.4 (1 H, d, bridgehead H), 1.25 (3 H, s, $-CH_3$) and 0.7 (3 H, s, $-CH_3$). Mass spectral analysis showed the deuterated β-pinene to be 14% d_0 and 86% d_1.

Allylic Deuteration of *l*-Carvone Using TsNSO. A mixture of 1.0 g of *l*-carvone (Aldrich, 6.66 mmol, $[\alpha]^{25}_D$ −55.6° (*c* 8.65, EtOH)) and 2.89 g of TsNSO (13.3 mmol) was stirred in 20 mL of benzene in a 50-mL round-bottomed flask (anhydrous conditions) for 24 h. GLPC showed no olefin remaining, so 12 mL of D_2O (>99.7% *d*) was added and the mixture refluxed for 7.5 h. The reaction was cooled, taken up in ether which was washed once with H_2O and once with brine, and dried. Filtration and evaporation left 700 mg of crude oil which was kugelrohr distilled (50–70 °C, 0.5 Torr) to give 450 mg of deuterated *l*-carvone contaminated with approximately 5% dehydrocarvacrol. Pure *l*-carvone, isolated by preparative GLPC (8 ft × ¼ in. 20% SE-30 on 45/60 mesh Chromsorb W, 150 °C) was 13% d_0, 46% d_1, 35% d_2 and 6% d_3, and showed little change in optical rotation ($[\alpha]^{25}_D$ −54.7° (*c* 8.45, EtOH)).

The excess deuterium was exchanged by heating the crude deuterated *l*-carvone (250 mg) in 5 mL of 60% EtOH containing 3 drops of 50% NaOH solution at 50–60 °C for 3 h in a 25-mL round-bottomed flask under N_2. Extraction with hexane (washed once with H_2O and once with brine, and dried) followed by evaporation gave 240 mg of yellowish oil which was kugelrohr distilled to give 230 mg of 10-deuterio-*l*-carvone (90%, 39% overall): NMR ($CDCl_3$) δ 6.75 (1 H, m, olefinic), 4.7 (2 H, broad s, $=CH_2$), 2.5 (5 H, m, ring H) and 1.75 (5 H, two overlapping s, $-CH_3$ and $-CH_2D$). A pure sample of 10-deuterio-l-carvone was collected by preparative GLPC: 16% d_0, 82% d_1, and 2% d_2, $[\alpha]^{25}_D$ −55.0° (*c* 9.45, EtOH).

Allylic Tritiation of α-Methylstyrene. In a dry 25-mL round-bottomed flask fitted with a reflux condenser and $CaCl_2$ trap, a mixture of 670 mg of *N*-(*p*-toluenesulfonyl)-2-phenyl-2-propenylsulfinamide[6] (2 mmol, recrystallized from $CHCl_3$ and dried in vacuo) and 0.1 mL of 1 Ci/mL T_2O (100 mCi) in 5 mL of benzene was refluxed for 14 h. After cooling, 5 mL of pentane was added and the organic phase eluted through a 7.0 × 0.5 cm silica gel column with an additional 5 mL of pentane (this removes the T_2O and the *p*-toluenesulfonamide). The resulting solution was concentrated to afford 120 mg of an oil which was kugelrohr distilled (80–90 °C, water aspirator pressure) to give 110 mg (49%) of tritiated α-methylstyrene: specific radioactivity = 1.78×10^6 dpm/μmol or 0.8 μCi/μmol; GLPC analysis (6 ft × 0.125 in. OV-17 on 80/100 mesh Gas Chrom Q, 70 °C) showed only one peak which coinjected with an authentic sample. Redistillation of the product caused no change in the specific activity. The original 100 μL of T_2O contained about 11 mmol of protons and another 2 mmol of protons were introduced with the sulfinamide adduct. Thus the 100 mCi of activity was distributed over 13 mmol of protons resulting in a specific activity for the reaction medium of 7.7 mCi/mmol of H^+. The activity of the α-methylstyrene was 0.8 Ci/mmol, which represents incorporation of tritium into the sample at a specific radioactivity 10% that of the reaction medium (based on replacement of one allylic hydrogen). Replacement of T_2O by 0.1 mL of D_2O under identical conditions and workup gave α-methylstyrene which was 25% d_0, 40% d_1, 22% d_2, and 10% d_3.

2-Phenylcyclohex-2-enyl-*N*-methyl-*N*-(*p*-toluenesulfonyl)sulfinamide. In a 50-mL round-bottomed flask with a magnetic stirrer, under anhydrous conditions, 3.25 g of TsNSO (15 mmol) was added to a solution of 1.0 g of 1-phenyl-1-cyclohexene (6.3 mmol, Aldrich Chemical Co.) in 20 mL of benzene. After 36 h, the reaction mixture was cooled in a refrigerator for approximately 1 h. The resulting precipitate was collected by suction filtration (washed with 25 mL of dry pentane) and dried (1.90 g, 80% yield of 2-phenylcyclohex-2-enyl-*N*-(*p*-toluenesulfonyl)sulfinamide). This solid (5 mmol) was suspended in 40 mL of benzene and 0.80 mL of Et_3N (5.7 mmol) was added followed by 0.6 mL of dimethyl sulfate (96.3 mmol). After 2 h at room temperature, the reaction was taken up in ether which was washed twice with H_2O, once with brine, and dried. Filtration and evaporation left 0.96 g of a white solid which was purified by column chromatography (25 g of silica gel, packed with hexane and eluted with 100 mL: hexanes, 5%; EtOAc/hexanes, 10%, 15%; 10-mL fractions). Concentration of the appropriate fractions gave 0.52 g (26%) of the *N*-methyl adduct (recrystallized from EtOAc/hexanes), mp 160–161 °C (decomposition with evolution of gas), R_f = 0.47 (35% EtOAc/hexanes), not very soluble in ether, benzene, or EtOAc: IR ($CHCl_3$) 2940, 1595, 1490, 1445, 1360 (SO_2), 1305, 1165 (SO_2), 1090, 900, and 890 cm^{-1}; NMR ($CDCl_3$) δ 7.2–7.9 (4 H), 4.15 (1 H, broad s, R_2CHS), 2.4 (6 H, s, aromatic $-CH_3$ and NCH_3, addition of shift reagent causes splitting into 2 singlets in ratio of 1:1) and 2.4–1.8 (6 H, m, ring H).

Anal. Calcd for $C_{20}H_{23}NO_3S_2$: C, 61.67; H, 5.95; N, 3.60. Found: C, 61.56; H, 5.98; N, 3.64.

Pyrolysis of 2-Phenylcyclohex-2-enyl-*N*-methyl-*N*-(*p*-toluenesulfonyl)sulfinamide. Injection of a 25% solution of the N-methyl adduct in CH_3OH directly into the gas chromatograph (injection port temperature 250 °C) gave (by area %) 6.4% 1-phenylcyclohexene, 3.6% biphenyl, and 90% diene.

The diene was isolated by preparative GLPC (20 ft × 3/8 in. stainless steel, 20% Carbowax 20M on 45/60 mesh Chromsorb W at 200 °C, t_r = 22 min (t_r(biphenyl) = 26.5 min, t_r (1-phenylcyclohexene) = 19 min, collected at liquid N_2 temperatures). The resulting oil was weighed and dissolved in cyclohexane: UV_{max} 279 nm (ε 7500).

Some biphenyl (230 nm) was present. Both 2-phenyl-1,3-cyclohexadiene (276 nm (ε 8140)) and 1-phenyl-1,3-cyclohexadiene (303 nm (ε 13 800)) are known.[14] Not more than 14% of the 1-phenyl isomer can be present in the isolated samples.

Both 1-phenylcyclohexene and biphenyl were identified by coinjection which authentic samples. Biphenyl was isolated and found to be identical (TLC, melting point, and mixture melting point) with an authentic sample.

Acknowledgments. We are grateful to our colleagues, Yak Cheung and Christopher T. Walsh, for assistance with the tritium incorporation experiments. We thank the National Science Foundation (CHE 74-21260) and the National Institutes of Health (GM 21686) for financial support.

Registry No.—*p*-Toluenesulfonamide, 70-55-3; thionyl chloride, 7719-09-7; *N,N*-dichloro-*p*-toluenesulfonamide, 473-34-7; methanesulfonamide, 3144-09-0; *N*-(*p*-toluenesulfonyl)-2-phenyl-2-propenylsulfinamide, 64976-25-6; α-methyl-β-tritriostyrene, 64976-26-7; 1-phenyl-1-cyclohexene, 771-98-2; 2-phenylcyclohex-2-enyl-*N*-(*p*-toluenesulfonyl)sulfinamide, 64976-27-8; 2-phenylcyclohex-2-enyl-*N*-methyl-*N*-(*p*-toluenesulfonyl)sulfinamide, 64976-28-9; biphenyl, 92-52-4; 2-phenyl-1,3-cyclohexadiene, 15619-34-8; 1-phenyl-1,3-cyclohexadiene, 15619-32-6.

References and Notes

(1) K. B. Sharpless, T. Hori, L. K. Truesdale, and C. O. Dietrich, *J. Am. Chem. Soc.*, **98**, 269 (1976).
(2) K. B. Sharpless, K. M. Gordon, R. F. Lauer, D. W. Patrick, S. P. Singer, and M. W. Young, *Chem. Scr.*, **8A**, 9 (1975).
(3) K. B. Sharpless and S. P. Singer, *J. Org. Chem.*, **41**, 2504 (1976).
(4) K. B. Sharpless and T. Hori, *J. Org. Chem.*, **41**, 176 (1976).
(5) S. Singer and K. B. Sharpless, preceding paper in this issue.
(6) N. Schönberger and G. Kresze, *Justus Liebigs. Ann. Chem.*, 1725 (1975).
(7) For a general review, see H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969). The first example of an ene reaction of an O=S=N— moiety was in 1966 [E. Kataev and V. Plemenkov, *J. Org. Chem. USSR*, **2**, 1119 (1966)]. The ene reaction of *N*-sulfinylsulfonamides was also discovered by Kresze (ref 6).
(8) G. Kresze and W. Wucherpfennig, *Angew. Chem., Int. Ed. Engl.*, **6**, 149 (1967).
(9) R. K. Hill, J. W. Morgan, R. V. Shetty, and M. E. Synerholm, *J. Am. Chem. Soc.*, **96**, 4201 (1974).
(10) V. Garsky, D. Koster, and R. T. Arnold, *J. Am. Chem. Soc.*, **96**, 4207 (1974).
(11) M. A. Umbreit and K. B. Sharpless, *J. Am. Chem. Soc.*, **99**, 5526 (1977).
(12) Kresze has also noticed aromatization in the reaction of sulfur diimides with certain olefins [G. Kresze and N. Schönberger, *Justus Liebigs Ann. Chem.*, 847 (1974)].
(13) G. Büchi and H. Wüest, *J. Org. Chem.*, **34**, 857 (1969).
(14) P. J. Grinsdale, *J. Org. Chem.*, **33**, 1116 (1968).
(15) (a) S. P. Singer, Ph.D. Thesis, Massachusetts Institute of Technology, Jan 1977. Cyclooctene afforded the *N*-methyl adduct (mp 109–111 °C) in 34% yield, and destructive kugelrohr distillation of the adduct at 150–175 °C gave 1,3-cyclooctadiene in 75% yield. (*E*)-5-Decene gave the *N*-methyl adduct in 46% yield and destructive kugelrohr distillation (150–175 °C) produced 4,6-decadiene (as a mixture of *E* and *Z* isomers) in 72% yield. (b) The methylation of the initial ene adducts appears to be the source of the trouble, but in spite of considerable effort (ref 15a), we were not able to obtain high yields in this step. In the case of cyclooctene and (*E*)-5-decene the ene adducts with TsN=S=O were dissolved in DMF and treated with aqueous Me_4NOH followed by CH_3I to afford the *N*-methyl adducts mentioned above.
(16) D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 147 (1974).
(17) In an attempt to force **3** or its *N*-methyl derivative to undergo 2,3 rearrangement to either an allylic alcohol or allylic sulfonamide, it was treated with various thiophiles (Et_2NH, Et_2NH–HCl, Ac_2O, trivalent phosphorus compounds, thiols, thioacetic acid, and $HgCl_2$). Only β-pinene could be recovered in all cases.
(18) K. Biemann, "Mass Spectrometry, Organic Chemical Applications", McGraw-Hill, New York, N.Y., 1962.
(19) This experiment was performed by John-Stephen Taylor and we are grateful for his assistance.
(20) TsNSO is also obtainable (80% yield) by reaction of $TsNCl_2$ with $SOCl_2$: W. A. Zunnebeld, Ph.D. Thesis, University of Amsterdam, 1969. We are grateful to Professor W. N. Speckamp of the University of Amsterdam for informing us of this novel and effective route to TsNSO.
(21) (a) For preparation of $TsNCl_2$, see F. Muth, in Houben-Weyl, "Methoden der Organishen Chemie", 4th ed, Georg Thieme Verlag, Stuttgart, Vol. 9, 1955, p 642. (b) $TsNCl_2$ is also available from Pfaltz and Bauer, Inc. and MC & B Manufacturing Chemists.

Aliphatic Azoxy Compounds. 7. Unsymmetrical (Dialkoxymethyl)phenyldiazenes: Deoxygenation of an Azoxy Function[1]

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Received September 2, 1977

In an investigation of the reactivity of the biologically important distal carbon atom of a model azoxyalkane, we observed that **1a** was converted, in good yield, to phenyldimethoxymethyldiazene (**2a**).[2] We wanted to know if the reaction conditions permitted the incorporation of two different alkoxyl group nucleophiles into **2** or if alkoxyl group interchange (e.g., via addition to tautomer **3**[3]) would prevent this. In so doing we wanted to learn more about the scope of this reaction for the synthesis of compounds **2**, an unusual, and new, class of azo compound. Herein we report on the preparation, stability, and spectral properties of **2b–d**, results which apply in a practical way to the questions raised above.

The starting azoxy compound **1c** was prepared by the procedure used previously for **1a,b,d**.[2] Compounds **1b–d** were smoothly converted to liquids **2b–d** by treatment with triethylamine in methanol at 25 °C in the presence of a drying agent (see Scheme I). Conversion of **1** to **2** was 95–98% complete as determined by VPC; isolated yields of 49–58% of 98% pure **2** were obtained after silica gel chromatography. Diazene **2c** was prepared in comparable yield by alternate routes starting with **1a** in 1-propanol and using triethylamine or potassium hydroxide as bases. Diazene **2c** was stable for more than 1 day in refluxing 0.05 N aqueous methanolic potassium hydroxide solution, conditions expected to hydrolyze hydrazone **3** should it be formed in situ. In contrast, **2c** was quickly destroyed in 0.03 N hydrochloric acid at room temperature.

Scheme I