1.78 (d, J = 7.5 Hz, 2 H of the E isomer), 1.64 (d, J = 7.4 Hz, 2 H of the Z isomer), 0.1 (s, 9 H); mass spectrum, m/z 222 (parent), 73 (base).

General Procedure for the Conversion of 1-Alkynyl Sulfones into 1-Alkenyl Sulfones. To a stirred solution of copper(I) compound **1a** (15.0 mmol) in THF (50 mL) was added, at -60 °C, the 1-alkynyl sulfone **22** or **24** (15.0 mmol). The mixture was stirred for 2 h at -30 °C in the case of **22** and for 1.5 h at 25 °C in the case of **24**. The 1-alkenyl sulfones **23a**, **23b**, and **25a** were obtained by pouring the respective reaction mixtures into an aqueous NH_4Cl solution (150 mL) containing NaCN (ca. 1 g). The products were isolated by extraction with methylene chloride (3 × 50 mL), washing the combined extracts with water (3 × 50 mL) and drying with $MgSO_4$. The solvent was evaporated in vacuo at 25 °C. Sulfone **23a** was obtained as a pure, white crystalline compoune (purity >95% by ^1H NMR); sulfones **23b** and **25a** were oils and could be distilled under high vacuum (purity of **23b** >95% by GLC and ^1H NMR; purity of **25a** ca. 90% by ^1H NMR). The allylated compound **25b** was prepared by adding allyl bromide (38 mmol) to the intermediary vinylcopper(I) compound **25** (E = Cu) and stirring the mixture for 1 h at 25 °C. Its isolation was performed as described for the other sulfones. The allylated adduct was a white solid and contained ca. 10% of an unknown impurity (by ^1H NMR).

(*E*)-1-(Methylsulfonyl)-3-(trimethylsilyl)-2-phenyl-1-propene (23a): mp 129.7 °C; IR (KBr) 1605, 1592, 1280, 1245, 1132, 1120 cm^{-1}; ^1H NMR ($CDCl_3$) 7.34 (s, 5 H), 6.18 (s, 1 H), 2.47 (s, 3 H), 2.00 (s, 2 H), -0.14 (s, 9 H); mass spectrum, m/z 268 (parent), 73 (base). Anal. Calcd for $C_{13}H_{20}O_2SSi$: C, 58.16; H, 7.51; S, 11.95; Si, 10.46. Found: C, 58.14; H, 7.42; S, 11.95; Si, 10.27.

(*E*)-1-(Methylsulfonyl)-2-[(trimethylsilyl)methyl]-1-hexene (23b): bp 115-120 °C (0.05 mmHg); $[n]^{20}_D$ 1.4817; IR (neat) 1603, 1300, 1248, 1123 cm^{-1}; ^1H NMR (CCl_4) 5.62 (s, 1 H), 2.60 (s, 3 H), 2.22 (br t, J = 7.5 Hz, 2 H), 1.49 (s, 2 H), 0.90-1.40 (m, 4 H), 0.68 (t, J = 6.5 Hz, 3 H), -0.15 (s, 9 H).

(*E*)-1-(Phenylsulfonyl)-3-(trimethylsilyl)-2-phenyl-1-propene (25a): bp 140-150 °C (0.2 mmHg); $[n]^{20}_D$ 1.5687; IR (neat) 3050, 1585, 1248 cm^{-1}; ^1H NMR (CCl_4) 7.0-8.0 (m, 10 H), 6.38 (s, 1 H), 2.05 (s, 2 H), -0.01 (s, 9 H); mass spectrum, m/z 330 (parent), 192 (base).

(*E*)-4-(Phenylsulfonyl)-6-(trimethylsilyl)-5-phenyl-1,4-hexadiene (25b): mp 43.2 °C; IR (neat) 3060, 1635, 1607, 1590, 1250 cm^{-1}; ^1H NMR (CCl_4) 6.8-8.1 (m, 10 H), 5.7-6.2 (m, J = 6.2, 10.8, 17.1 Hz, 1 H), 5.18 (br d, J = 17.1 Hz, 1 H), 5.15 (br d, J = 10.8 Hz, 1 H), 3.38 (d, J = 6.2 Hz, 2 H), 1.96 (s, 2 H), -0.13 (s, 9 H).

Preparation of (*Z*)-1,6-Bis(trimethylsilyl)-2,5-diphenyl-2,3,4-hexatriene (29). Excess of methyl iodide (70 mmol) was added at -30 °C to the mixed homocuprate **19** (E = $CuCH_2Me_3SiMgCl$; 15.0 mmol; 65 mL of THF). The mixture was stirred for 1 h at 25 °C and then poured into an aqueous NH_4Cl solution (200 mL) containing NaCN (ca. 1 g). The product was isolated as described for **15a,b** and purified by crystallization from methanol (purity >95% by ^1H NMR): mp 119.5 °C; Raman 2043, 1592, 1490, 1320, 1303, 1280, 1184, 1103, 1001 cm^{-1}; ^1H NMR (CCl_4) 7.50 (br d, J = 6.9 Hz, 4 H), 7.0-7.4 (m, 6 H), 2.12 (s, 4 H), -0.08 (s, 18 H); mass spectrum, m/z 376 (parent), 73 (base).

Preparation of 3-(Trimethylsilyl)-2-phenyl-1-propene (30). Aluminum amalgam (0.16 mol of Al in 2% aqueous $HgCl_2$)[48] was added to a stirred solution of 1-alkenyl sulfone **25a** (5.0 mmol) in a mixture of THF (190 mL) and water (10 mL). The mixture was refluxed for 2 h. After the reaction mixture was poured into an aqueous NH_4Cl solution (400 mL), the product was extracted with pentane (3 × 50 mL). The combined extracts were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was evaporated and the residue distilled at reduced pressure to give **30** in 70% yield and with a purity of at least 95% (by GLC and ^1H NMR): bp 100-102 °C (15 mmHg); $[n]^{20}_D$ 1.5109; IR (neat) 3080, 1615, 1250 cm^{-1}; ^1H NMR (CCl_4) 7.1-7.5 (m, 5 H), 5.09 (br s, 1 H), 4.79 (br s, 1 H), 1.97 (s, 2 H), -0.11 (s, 9 H).

(48) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1345.

Synthesis of α-Arylsulfonoxy Ketones from Ketone Derivatives

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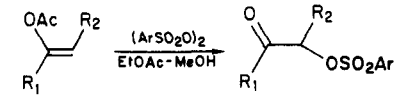
Silyl enol ethers, enamines, and enols can all be efficiently converted to α-arylsulfonoxy ketones by reaction with arylsulfonyl peroxides.

There has been increasing interest in the chemistry of α-sulfonoxy ketones. They have been used as precursors for α-keto carbocations,[1] as Favorski ring contraction substrates,[2] and as thiol-specific electrophiles.[3] In addition, Creary has described some interesting base-catalyzed reactions of these compounds.[1] The most common preparation of these materials begins with an α-hydroxy ketone that is condensed with a sulfonyl chloride in the presence of base.[4] This method is quite erratic,[5] and often it is necessary to first prepare the corresponding sulfinate ester, which is then oxidized to the sulfonate ester.[6] A recent paper by Koser describes the preparation of α-tosyloxy ketones by the reaction of ketones with [hydroxy(tosyloxy)iodo]benzene. This method is not regiospecific for unsymmetric ketones, although good yields are obtained.[7]

Work in these laboratories has shown that arylsulfonyl peroxides react with enol acetates in the presence of methanol to give α-arylsulfonoxy ketones in high yields (eq 1).[8] Many preparations for enol acetates have been



(1)

reported.[9] Enol acetates are most commonly prepared from ketones by one of several methods.[10] They can also

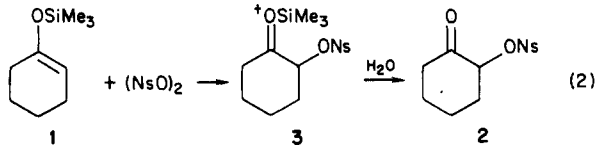
(1) Creary, X. *Acc. Chem. Res.* **1985**, *18*, 3. This is an excellent summary of the solvolytic work done with these compounds.
(2) Conia, J. M.; Salaun, J. R. *Acc. Chem. Res.* **1972**, *5*, 33.
(3) Simons, S. S., Jr.; Pons, M.; Johnson, D. F. *J. Org. Chem.* **1980**, *45*, 3084 and references therein.
(4) (a) Tipson, R. S. *J. Org. Chem.* **1944**, *9*, 235. (b) Crossland, R. K.; Servis, K. L. *Ibid.* **1970**, *35*, 3195.
(5) See for example: (a) Creary, X.; Geiger, C. C. *J. Am. Chem. Soc.* **1982**, *104*, 4151. (b) Creary, X.; Geiger, C. C. *Ibid.* **1983**, *105*, 7123.
(6) Coates, R. M.; Chen, J. E. *Tetrahedron Lett.* **1969**, 2705.
(7) Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1982**, *47*, 2487.
(8) Hoffman, R. V. *Synthesis*, in press.
(9) An excellent compilation of methods: Larock, R. C.; Oertle, K.; Beatty, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 1966.

0022-3263/85/1950-5148$01.50/0

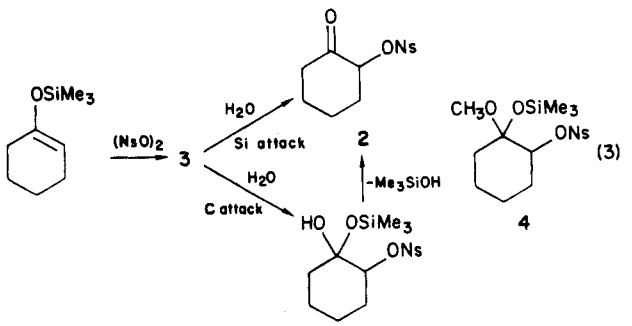
be prepared efficiently from vinyl mercurials.[9] However, in many cases access to enol esters remains problematic. We therefore examined other readily available ketone derivatives to determine whether they might also serve as precursors to α-arylsulfonoxy ketones by reaction with sulfonyl peroxides. The compounds chosen were enamines and silyl enol ethers since (a) they are easily available from the ketone, (b) they have an electron-rich double bond that should react with the electrophilic peroxides, and (c) they may be prepared regiospecifically from unsymmetric ketones. We report that both of these ketone derivatives are converted efficiently to α-arylsulfonoxy ketones under appropriate conditions.

Results and Discussion

Our experience with the reactions of sulfonyl peroxides and enol ethers[11] and enol esters[8] suggested that silyl enol ethers[12] should react readily with sulfonyl peroxides. When an ethyl acetate solution of 1-(trimethylsiloxy)cyclohexene was treated with bis[(*p*-nitrophenyl)sulfonyl] peroxide (*p*-NPSP), iodometric monitoring showed a smooth loss of active oxygen; however, TLC analysis of the reaction mixture showed several components in addition to the desired α-(*p*-nitrophenyl)sulfonoxy ketone. These byproducts were thought to originate from the *O*-(trimethylsilyl)oxonium ion, **3**, produced from electrophilic addition (eq 2).

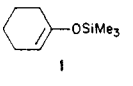
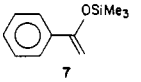
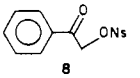
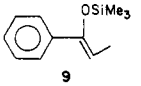
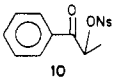
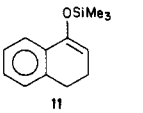
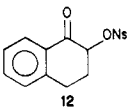
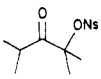
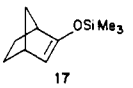


Nucleophiles were therefore added to the reaction mixture in order to trap ion **3** by transfer of the trimethylsilyl group and thereby deliver the α-substituted product. The use of methanol for the same purpose had proven efficacious in the reactions of enol acetates. When the reaction was carried out in the presence of methanol, only two components were evident. Examination of the crude products by ^{1}H NMR revealed that the α-nosyl ketone was accompanied by a compound that was postulated to be the mixed ketal **4** on the basis of methoxy, trimethylsiloxy, and aromatic absorptions in the ^{1}H NMR spectrum. It was thus evident that methanol attacked oxonium ion **3** at both silicon and carbon. These two modes of attack could be made equivalent if water were the attacking nucleophile (eq 3).



Indeed, if water was added to the reaction mixture, addition proceeded smoothly to give the α-nosyl ketone in good yield and purity. A series of silyl enol ethers were prepared and reacted with *p*-NPSP in ethyl acetate containing 2% water. The results are summarized in Table I.

Table I. Preparation of α-Nosyl Ketones from the Reaction of Silyl Enol Ethers with (*p*-Nitrophenyl)sulfonyl Peroxide in Ethyl Acetate/2% Water at 25 °C

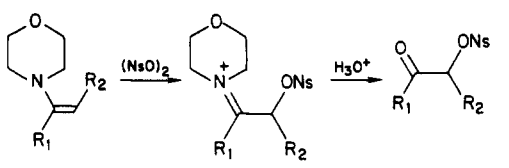
entry	silyl ether	α-nosyl ketone	time, h	yield,[a] %
1	 1	 2	5	77
2	 5	 6	10	69
3	 7	 8	33	76
4	 9	 10	24	>95
5	 11	 12	20	>95
6	 13	 14	29	30
7	 15	 16	20	71[b]
8	 17	 18	24	>95[b]

[a] Isolated yield of pure product. Results averaged from several runs. [b] Reaction run in pure ethyl acetate.

The presence of water in the reaction mixture proved to be a mixed blessing, since some hydrolysis of the silyl enol ether was noted. Generally an excess of the enol ether component (10%) was used to compensate for hydrolysis. In two cases, entries 7 and 8, best results were obtained in the absence of water. These two examples, which are the most sterically congested, suggest that other crowded precursors would similarly work well without added water.

In order to minimize the problem of competetive hydrolysis, several (2,4,6-tri-*tert*-butylphenoxy)dimethylsilyl enol ethers were prepared.[13] These derivatives are quite resistant to hydrolysis; however, reaction with *p*-NPSP gave very complex product mixtures.

Enamines are also very common and useful carbonyl derivatives[14] that could yield α-arylsulfonoxy ketones by reaction with sulfonyl peroxides. It was initially felt that electrophilic addition might yield an iminium ion sufficiently stable to preclude the need for added nucleophiles (eq 4). In the event, reaction of *N*-(1-cyclohexenyl)-



(10) (a) House, H. O. *Rec. Chem. Prog.* **1967**, *28*, 99. (b) House, H. O.; Trost, B. M. *J. Org. Chem.* **1965**, *30*, 1341. (c) House, H. O.; Kramar, V. *Ibid.* **1963**, *28*, 3362.

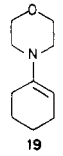
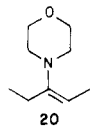
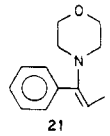
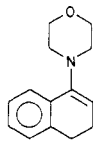
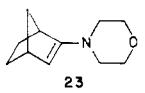
(11) Hoffman, R. V.; Buntain, G. A. *J. Org. Chem.* **1983**, *48*, 3308.

(12) For excellent reviews see: (a) Brownbridge, P. *Synthesis* **1983**, 1, 85. (b) Rasmussen, J. K. *Ibid.* **1977**, 91.

(13) Manis, P. A.; Rathke, M. W. *J. Org. Chem.* **1981**, *46*, 5348.

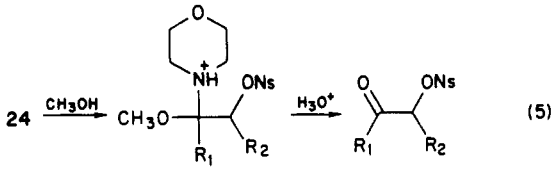
(14) Hickmott, P. W. *Tetrahedron* **1982**, *38*, 1975, 3363. Cook, A. G. "Enamines"; Marcel Dekker: New York, 1969.

Table II. Preparation of α-Nosyl Ketones from Enamines and p-NPSP in Ethyl Acetate/2% Methanol at −78 °C

entry	enamine	product	time, h	yield,[a] %
1	 19	2	4	82
2	 20	6	4	81
3	 21	10	7	88
4	 22	12	4	60
5	 23	18	8	52[b]

[a] Isolated yield of pure product. Results averaged from several runs. [b] Reaction run in pure ethyl acetate.

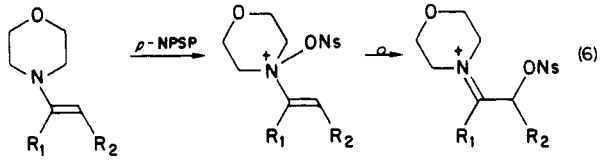
morpholine (19) with p-NPSP in ethyl acetate at −78 °C gave α-nosylcyclohexanone (2) in good yield. Examination of the crude products by TLC revealed that there were one or more minor byproducts. By analogy to the halogenation of enamines,[15] these products may arise from side reactions of the iminium ion, 24. When a small amount of methanol was added to the reaction solvent, high yields of the α-nosyl ketone were obtained, and there were no other components present in the crude product as determined by TLC analysis. Presumably, nucleophilic trapping of the iminium ion by methanol gives a more stable tetrahedral intermediate that delivers the ketone upon aqueous workup (eq 5).



(5)

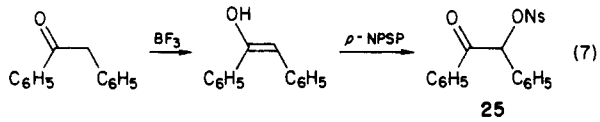
A series of enamines were prepared and reacted with p-NPSP in ethyl acetate containing 2% methanol at −78 °C. The results, presented in Table II, show that enamines are very satisfactory substrates for conversion to α-nosyl ketones. Best results were obtained with freshly prepared enamines. Yields tend to decrease, and the products are less pure if the enamines are stored for several weeks.

Noteworthy is the reactivity of enamines toward p-NPSP relative to the enol derivatives utilized. The latter require temperatures of 0 °C or above, whereas enamines react smoothly at −78 °C. It is likely that the difference in reactivity lies in the site of electrophilic attack. Enol derivatives probably react at the electron-rich carbon–carbon π bond and thus exhibit reactivities comparable to other reactive olefins.[16] On the other hand, enamines probably react at nitrogen, giving an N-arylsulfonoxy adduct that undergoes a 1,3-rearrangement to the α-arylsulfonoxy iminium product (eq 6). The reactivity exhibited by enamines is similar to that found for the oxidation of the amino nitrogen of amines by p-NPSP.[17] Furthermore, 1,3-rearrangements of both acyloxy and arylsulfonoxy groups from nitrogen to carbon are well-known to be facile.[18] Good precedent for this route is also found in the chlorination of indoles, which have been found to proceed by 1,3-rearrangement of initial chloramines.[19]



(6)

The most straightforward ketone derivative to react with p-NPSP would be enols themselves. Indeed, when deoxybenzoin is treated with p-NPSP and boron trifluoride etherate (1 equiv), smooth conversion to the α-nosyl ketone 25 is observed (eq 7). However, other simple ketones like cyclohexanone and acetophenone failed to give α-substitution under these conditions. Apparently the concentration of enol is too low to sustain the bimolecular addition reaction. The method might be valuable, however, in cases where conjugation favors enol formation and where regiospecificity is not a concern.



(7)
25

While only the (p-nitrophenyl)sulfonoxy group has been utilized in this work through the agency of p-NPSP, similar results have been obtained with [m-(trifluoromethyl)-phenyl]sulfonyl peroxide. The products are spectrally identical with the nosylate products, except for the aromatic contributions; however, they are oils.

In summary it is seen that α-arylsulfonoxy ketones are easily accessible from enamines, silyl enol ethers, and enol acetates.[8] These methods are complementary in that at least one of these derivatives can usually be prepared from the ketone in good yield.

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer as potassium bromide disks; ^{1}H NMR spectra were taken on a Jeol PS-100 instrument. Thin-layer chromatography was performed with Eastman TLC sheets of silica gel that were developed with chloroform.

p-NPSP[20] and [m-(trifluoromethyl)phenyl]sulfonyl peroxide[21] were prepared by literature methods. Commercially available ketones (Aldrich) were converted to silyl enol ethers by reaction with trimethylsilyl triflate.[22] Enamines were prepared from the

(15) De Kimpe, N.; Schamp, N. *Org. Prep. Proc. Int.* **1981**, *13*, 241.

(16) (a) Hoffman, R. V.; Bishop, R. D. *Tetrahedron Lett.* **1976**, 33. (b) Hoffman, R. V.; Cadena, R., unpublished data.

(17) (a) Hoffman, R. V.; Kumar, A. *J. Org. Chem.* **1984**, *49*, 4011. (b) Hoffman, R. V.; Belfoure, E. L. *Synthesis* **1983**, 34. (c) Hoffman, R. V.; Belfoure, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 2183.

(18) (a) Oae, S.; Sakurai, T. *Tetrahedron* **1976**, *32*, 2289. (b) Krower, J. S.; Richmond, J. P. *J. Org. Chem.* **1978**, *43*, 2464. (c) Tisue, G. T.; Grassman, M.; Lwowski, W. *Tetrahedron* **1968**, *24*, 999.

(19) DeRosa, M.; Carbognani, L.; Febres, A. *J. Org. Chem.* **1981**, *46*, 2054 and references therein.

(20) Dannley, R. L.; Gagen, J. E.; Stewart, O. J. *J. Org. Chem.* **1970**, *35*, 3076.

(21) Dannley, R. L.; Tornstrom, P. K. *Ibid.* **1975**, *40*, 2278. The sulfonyl peroxides used in this work can decompose exothermically, but not violently, in the presence of strong electron donors (neat). In solution the reactions proceed smoothly.

ketones by a standard procedure.[23]

General Procedure for the Reaction of Silyl Enol Ethers with *p*-NPSP. The silyl enol ether (1.65 mmol) was dissolved in a mixture of ethyl acetate (30 mL) and water (0.6 ml), and *p*-NPSP (0.60 g, 1.5 mmol) was added as a solid. The mixture was stirred vigorously at room temperature. The peroxide dissolved, the reaction took on a yellow color, and the active oxygen was monitored by quenching a small amount in 10% potassium iodide/acetic acid (1:1). After all the peroxide was consumed, the reaction was extracted with 2.5 M hydrochloric acid (2 × 20 mL) and water (2 × 20 mL), dried ($MgSO_4$), and evaporated to give a pale oil that solidified. Products **2**, **6**, **8**, **10**, **12**, and **14** were prepared by this method. The crude products generally showed no detectable impurities in the ^1H NMR spectra, and TLC analyses likewise showed only the α-nosyl ketone. Occasionally trace amounts of the parent ketone were detected in the product. Crystallization from ethyl acetate/hexane gave analytically pure materials. These products were identified by comparison to authentic samples.[8]

2,4-Dimethyl-2-[(*p*-nitrophenyl)sulfonoxy]-3-pentanone (16). To a solution of 2,4-dimethyl-3-(trimethylsiloxy)-2-pentene (**15**; 0.28 g, 1.5 mmol) in ethyl acetate (30 ml) was added *p*-NPSP (0.60 g, 1.5 mmol). The pale yellow mixture was stirred at room temperature for 20 h, at which time iodometry showed that all the peroxide was consumed. Workup as above yielded 0.36 g (77%) of a clear oil that showed only one component by TLC. Recrystallization from ethyl acetate/hexane gave **16** as a white solid: mp 84.5–85.5 °C; IR ν 3120 (aromatic CH), 2980–2880 (aliphatic CH), 1725 (C=O), 1610 (aromatic C=C), 1540 (NO_2), 1360, 1190 (SO_3) cm^{-1}; ^1H NMR δ 1.15 (d, J = 7 Hz, 6 H, CH-(CH_3)$_2$, 1.72 (s, 6 H, CH_3), 3.2 (h, J = 7 Hz, 1 H, CH), 8.25 (AA′BB′, 4 H, aromatic H). Anal. Calcd for $C_{13}H_{17}NO_4S$: C, 49.67; H, 5.43; N, 4.46; S, 10.20. Found: C, 49.57; H, 5.53; N, 4.26; S, 10.01.

3-[(*p*-Nitrophenyl)sulfonoxy]norbornanone (18). To a solution of 2-(trimethylsiloxy)norbornene (**17**; 0.60 g, 3.3 mmol) in ethyl acetate (60 ml) was added *p*-NPSP (1.2 g, 3 mmol). The mixture was stirred at room temperature 24 h and worked up as above to give 0.87 g (95%) of a tan solid that had only one component by TLC. Recrystallization from ethyl acetate/hexane gave pure **18** as pale yellow crystals: mp 137.5–139 °C; IR ν 3105 (aromatic CH), 2950–2880 (aliphatic CH), 1760 (C=O), 1605 (aromatic C=C), 1532 (NO_2), 1360, 1185 (SO_3) cm^{-1}; ^1H NMR δ 1.4–2.6 (m, 6 H), 2.6 (br s, 1 H), 2.82 (br s, 1 H), 4.18 (d, J = 3 Hz, 1 H, C*H*ONs), 8.25 (AA′BB′, aromatic H). Anal. Calcd for $C_{13}H_{13}NO_6S$: C, 50.15; H, 4.21; N, 4.50. Found: C, 50.20; H, 4.09; N, 4.33.

The stereochemistry of **18** is probably exo as evidenced by the coupling constant J = 3 Hz of the methine proton at δ 4.18. The analogous exo triflate has J = 2.8 Hz whereas the endo isomer has J = 5 Hz.[24]

General Procedure for the Reaction of Enamines with *p*-NPSP. A solution of the enamine (1.1–1.2 equiv) in ethyl acetate (50 mL) was cooled in dry ice. Methanol (1 mL) and then *p*-NPSP (0.6 g, 1.5 mmol) were added. The mixture was stirred vigorously, it became homogeneous, and then some precipitate formed. The reaction was monitored for active oxygen with potassium iodide/acetic acid. When the active oxygen was gone, the reaction was extracted with 2.5 M hydrochloric acid (2 × 20 mL) and water (2 × 20 mL), dried ($MgSO_4$), and evaporated to yield the solid α-nosyl ketone. Usually no byproducts were observed by ^1H NMR or TLC. Occasionally, traces of the parent ketone could be detected; however, the crude product is sufficiently pure for most purposes.

Preparation of 25. To a solution of boron trifluoride etherate (0.213 g, 1.5 mmol) and deoxybenzoin (0.294 g, 1.5 mmol) in dichloromethane was added *p*-NPSP (0.60 g, 1.5 mmol). The peroxide was not completely soluble at first; however, the mixture was stirred at room temperature for 3 h to give a homogeneous solution that was devoid of active oxygen. After storage at −20 °C overnight, the reaction was extracted with water (2 × 50 mL), saturated sodium chloride (50 mL), and water (50 mL). The organic layer was dried ($MgSO_4$) and evaporated to give a pale yellow oil (0.53 g, 89%) that had one principal component and a small amount of deoxybenzoin by TLC. Recrystallization from ethyl acetate/hexane gave pure **25**: mp 99–101 °C; IR ν 3077 (aromatic CH), 1668 (C=O), 1604 (aromatic C=C), 1530 (NO_2), 1360, 1190 (SO_3) cm^{-1}; ^1H NMR δ 6.84 (s, 1 H, methine CH), 7.3 (br m, 8 H, aromatic H), 7.85 (d, 2 H, aromatic H σ to C=O), 8.12 (AA′BB′, nosyl H). Anal. Calcd for $C_{20}H_{15}NO_6S$: C, 60.45; H, 3.77; N, 3.52. Found: C, 60.22; H, 3.70; N, 3.61.

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Registry No. **1**, 6651-36-1; **2**, 98990-62-6; **5**, 17510-47-3; **6**, 98990-63-7; **7**, 13735-81-4; **8**, 98990-64-8; **9**, 37471-46-8; **10**, 98990-64-8; **11**, 38858-72-9; **12**, 98990-65-9; **13**, 1833-53-0; **14**, 98990-66-0; **15**, 55339-64-5; **16**, 98990-67-1; **17**, 57722-40-4; **18**, 98990-68-2; **19**, 670-80-4; **20**, 13654-48-3; **21**, 39655-41-9; **22**, 31401-28-2; **23**, 5024-92-0; **25**, 87119-38-8; $PhCOCH_2Ph$, 451-40-1; bis[(*p*-nitrophenyl)sulfonyl] peroxide, 6209-72-9; bis[(*m*-trifluoromethyl)phenylsulfonyl] peroxide, 35673-10-0; boron trifluoride etherate, 109-63-7.

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Unsaturated Crown Ethers. 3.[1] Syntheses of Stilbeno Crown Ethers[2]

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A series of 6-, 9-, and 15-membered monostilbeno crown ethers (**3**) and 18-, 24-, and 30-membered distilbeno crown ethers (**4**), some of which are new compounds, were synthesized in the base-induced reactions of benzoin (**1**) with oligoethylene glycol ditosylates (**2a–d**) in homogeneous and heterogeneous solutions. The template effect is shown to be effective in controlling product yields and **4**/**3** ratios.

Except for the areno crown ethers with benzo and naphtho substituents, unsaturated crown ethers possessing C–C double, or triple, bond(s) on the crown ring have not been synthesized extensively.[3-7] Merz[4a] first prepared the

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