X-ray Analysis of 2a. Single crystals of **2a** were tetrahedral, space group $P4_3$ (for the configuration shown in Figure 1) or $P4_1$, with a = 12.896 (1) Å, c = 13.773 (3) Å, and d_{calcd} = 1.300 g cm^{-3} for Z = 4 ($C_{23}H_{28}O_9$, mol wt 448.47). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ-2θ scans, pulse-height discrimination). A crystal measuring approximately 0.30 × 0.6 × 0.6 mm was used for data collection. A total of 1616 reflections was measured for $\theta < 57°$, of which 1570 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple solution procedure[13] and was refined by full-matrix least-squares. In the final refinement anisotropic thermal parameters were used for the nonhydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indices are R = 0.043 and wR = 0.051 for the 1570 observed reflections. The final difference map has no peaks greater than ±0.2 e Å^{-3}.

(13) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *27*, 368.

Registry No. 2a, 76010-16-7; **2b**, 76010-17-8; **3a**, 76010-18-9; **3b**, 76010-19-0.

Supplementary Material Available: Tables III-VI listing final atomic and final anisotropic thermal parameters, bond lengths, and bond angles (5 pages). Ordering information is given on any current masthead page.

α-Nitro Sulfones. 2. Convenient New Synthesis and Selected Functional Group Transformations

Peter A. Wade,* Harry R. Hinney, Nayan V. Amin, Peter D. Vail, Scott D. Morrow, Steven A. Hardinger, and Mallory S. Saft

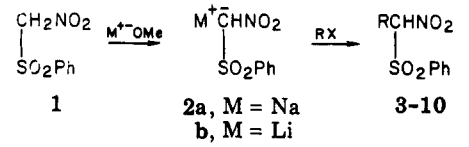
Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104

Received September 25, 1980

(Phenylsulfonyl)nitromethane (**1**) is preferentially C-alkylated by benzylic halides and primary alkyl iodides, affording secondary α-nitro sulfone products. α-Nitro sulfones are also obtained from the corresponding C-alkylation of allylic acetates in the presence of catalytic tetrakis(triphenylphosphine)palladium. The palladium(0)-catalyzed reaction is stereospecific for geranyl and neryl acetates and is also regioselective. Desulfonation of α-nitro sulfones is readily accomplished by light-induced reduction with 1-benzyl-1,4-dihydronicotinamide (BNAH). Reduction of secondary α-nitro sulfones with 20% aqueous titanium(III) chloride affords nitriles. Oxidation with alkaline permanganate affords carboxylic acids.

α-Nitro sulfones have been known since the early 1900's[1] but have only recently received much attention.[2] Our interest in these compounds stems from their potential as useful synthetic intermediates. In particular, a variety of chemospecific reactions at the carbon bearing both nitro and sulfone functionalities is envisioned. For example, secondary α-nitro sulfones bear one highly acidic ($pK_a \approx 6$)[2a] proton and are therefore known to undergo a limited number of carbanion processes such as Michael addition to 3-buten-2-one.[2b] Also of interest is the ease with which the sulfonyl group of tertiary α-nitro sulfones can be replaced in radical anion alkylations.[2c,d]

α-Nitro sulfones have previously been synthesized by three principal routes: sulfonylation of α-halo nitro compounds,[1,3] oxidation of α-nitro sulfides,[4] and alkaline nitration of sulfones.[2e] An alternate general route, useful for the preparation of secondary α-nitro sulfones, is presented here.[5] This new route involves alkylation of (phenylsulfonyl)nitromethane (**1**) (eq 1 and 2).



(1)

1 **2a**, M = Na; **b**, M = Li **3-10**

(Phenylsulfonyl)nitromethane was converted to its sodium (**2a**) or lithium salt (**2b**) by reaction with the appropriate alkali metal methoxide. The salts thus obtained are air insensitive and nonhygroscopic, so that they are easily handled without decomposition. The sodium salt **2a** gave predominant C-alkylation when treated with methyl iodide, primary alkyl iodides, and benzylic bromides or iodides, giving the alkylation products listed in Table I (eq 1). This is in sharp contrast to typical nitronates which give predominant O-alkylation under these conditions.[6] Yields of the C-alkylates were typically 50-75%, at least when polar aprotic solvent was employed. Conditions not permitting unencumbered nucleophile were deleterious to smooth reaction. For example, the lithium salt **2b** reacted only very slowly with benzyl iodide in re-

(1) Tröger, J.; Nolte, E. *J. Prakt. Chem.* **1920**, *101*, 136.

(2) (a) Zeilstra, J. J.; Engberts, J. B. F. N. *Synthesis* **1974**, 49. (b) Zeilstra, J. J.; Engberts, J. B. F. N. *J. Org. Chem.* **1974**, *39*, 3215. (c) Kornblum, N.; Boyd, S. D.; Ono, N. *J. Am. Chem. Soc.* **1974**, *96*, 2580. (d) Zeilstra, J. J.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 954. (e) Truce, W. E.; Klingler, T. C.; Paar, J. E.; Feuer, H.; Wu, D. K. *J. Org. Chem.* **1969**, *34*, 3104. (f) Zeilstra, J. J.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1975**, *97*, 7091.

(3) (a) Kornblum, N.; Kestner, M. M.; Boyd, S. D.; Cattran, L. C. *J. Am. Chem. Soc.* **1973**, *95*, 3356. (b) Arndt, F.; Rose, J. D. *J. Chem. Soc.* **1935**, 1. (c) Farrer, W. V. *Ibid.* **1964**, 904. (d) The reaction of arenesulfonyl bromides and iodides with nitronates apparently proceeds in a similar fashion: Zeilstra, J. J.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 11.

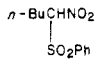
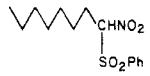
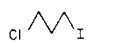
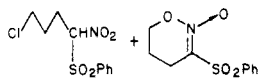
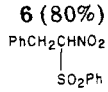
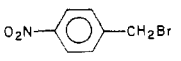
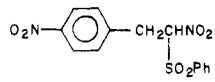
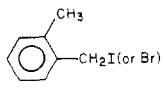
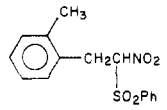
(4) (a) Kharasch, N.; Cameron, J. L. *J. Am. Chem. Soc.* **1953**, *75*, 1077. (b) Kharasch, N.; Cameron, J. L. *Ibid.* **1951**, *73*, 3864. (c) Hünig, S.; Boes, O. *Justus Liebigs Ann. Chem.* **1953**, *579*, 23.

(5) For a preliminary account, see: Wade, P. A.; Morrow, S. D.; Hardinger, S. A.; Saft, M. S.; Hinney, H. R. *J. Chem. Soc., Chem. Commun.* **1980**, 287.

(6) The difference is attributed to the electronic effect of the phenylsulfonyl substituent. For reviews concerning the chemistry of nitro compounds, particularly alkylation reactions, see: (a) Coombes, R. G. In "Comprehensive Organic Chemistry"; Sutherland, I. O., Ed.; Pergamon: New York, 1979; Vol. 2, p 305; (b) von Schickh, O.; Apel, G.; Padeken, H. G.; Schwartz, H. H.; Segnitz, A. In "Methoden der Organische Chemie (Houben-Weyl-Müller)"; Georg Thieme Verlag: Stuttgart, 1971; Vol. 10, p 1; (c) Ioffe, S. I.; Leont'eva, L. M.; Tartakovskii, V. A. *Russ. Chem. Rev. (Engl. Transl.)* **1977**, *46*, 872.

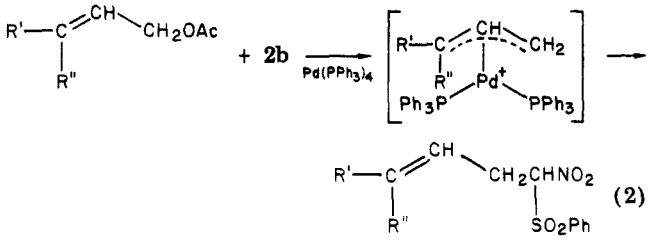
0022-3263/81/1946-0765$01.00/0

Table I. α-Nitro Sulfones Prepared by Alkylation of $Na^+ {}^-CH(SO_2Ph)NO_2$ (2a)

substrate	product	% yield
MeI		72
	3	
n-BuI		54
	4	
		59
	5	
		54
	6 (80%) 7 (20%)	
$PhCH_2I$ (or Br)		73 (68)
	8	
		75
	9	
		71 (64)
	10	

fluxing THF, and extensive side-product formation occurred. Dialkylation was never a serious problem, in part because excess nucleophile was routinely employed. However, in the case of *n*-butyl iodide when this precaution was not taken, no significant amount of dialkylate was obtained. One exception to the general trend was also noted: the cyclic C,O-dialkylate **7** was obtained in 11% yield from 1-chloro-3-iodopropane.

A second version of the alkylation process is centered on the use of allylic acetates (eq 2). These reacted with



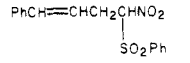
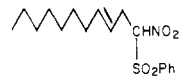
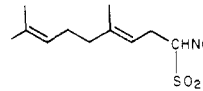
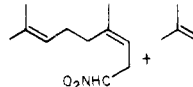
(2)

11-15

the lithium salt **2b** in the presence of 10–20 mol % of tetrakis(triphenylphosphine)palladium to produce routinely high yields of the α-nitro sulfones shown in Table II. Presumably an intermediate π-allylpalladium complex was the actual species attacked here by the nucleophile. This is consistent with similar alkylations of allylic acetates by other nucleophiles.[7]

The palladium(0)-catalyzed reaction was regiospecific in all cases examined except neryl acetate. Here an 88:12 ratio of two regioisomers was obtained, closely corresponding to the results reported by Trost[8] with methyl phenylsulfonylacetate as the nucleophile. It seems, then,

Table II. α-Nitro Sulfones Produced by Palladium-Catalyzed Alkylation of $Li^+ {}^-CH(SO_2Ph)NO_2$ (2b)

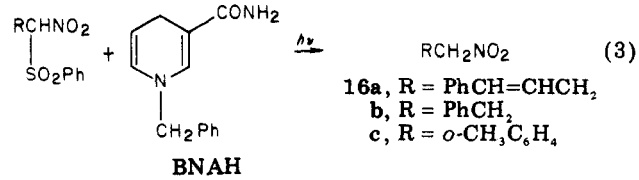
substrate	product	% yield
$PhCH{=}CHCH_2OAc$		90
	11	
		89
	12	
		83
	13	
		84
	14 (88%) 15 (12%)	

that the anion of **1** is fairly regioselective toward π-allyl palladium complexes in accordance with its bulky nature.

The alkylation reaction with neryl and geranyl acetates was also stereospecific, with at most 2% of crossover products. This is somewhat surprising since palladium complexes derived from an alkene geometric isomer pair are well-known to rapidly equilibrate.[7] Strong to moderate nucleophiles are capable of trapping π-allylpalladium complexes generated in situ before equilibration occurs. However, the anion of **1**, especially its lithium salt in THF solution, should be at best a weak nucleophile (pK_a of **1** = 5.7).[9] One possible explanation is that the anion and π-allylpalladium complex are well matched (both are "soft") for rapid reaction. It may also be that prior attachment of the anion to palladium occurs followed by a subsequent enhanced carbon–carbon bond formation. At any rate, the observed stereospecificity should be a boon to the synthesis of γ,δ-unsaturated α-nitro sulfones.

With several straightforward approaches available for the preparation of secondary α-nitro sulfones, we have commenced a detailed investigation of their chemical properties. The first matter investigated was the development of simple functional-group transformations. Except for two procedures[2a,f] allowing the conversion of nitro into oximino groups, such transformations were lacking.[10]

A reductive procedure which permits the desulfonation of α-nitro sulfones without concomitant attack on the nitro group is reported here (eq 3). This procedure, in con-



(3)

16a, R = $PhCH{=}CHCH_2$
b, R = $PhCH_2$
c, R = *o*-$CH_3C_6H_4$

BNAH

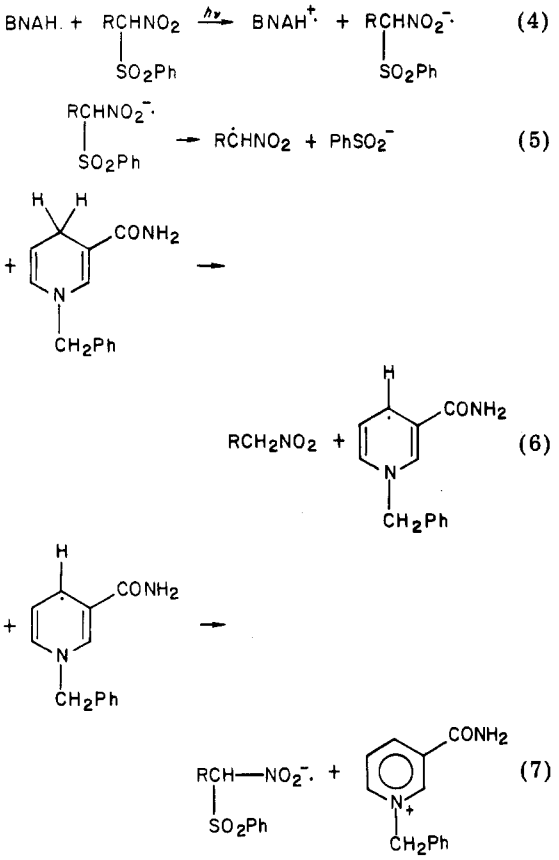
junction with the new preparation, allows introduction of a nitromethyl group in two steps. Thus, $CH(SO_2Ph)NO_2^-$

(7) The intermediacy of π-allyl palladium complexes in nucleophilic substitution reactions is well documented. (a) For a review, see: Trost, B. M. *Tetrahedron* **1977**, *33*, 2615. (b) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416.
(8) Trost, B. M.; Verhoeven, T. R. *J. Org. Chem.* **1976**, *41*, 3215.
(9) Bordwell, F. G.; Bartmess, J. E. *J. Org. Chem.* **1978**, *43*, 3101. For a discussion of the relation of pK_a and nucleophilicity pertaining to π-allyl palladium complexes, see: Trost, B. M.; Weber, L.; Strege, P.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3426 (1978). Of particular interest is the report that salts of Meldrum's acid, 2,2-dimethyl-1,3-dioxane-4,6-dione ($pK_a \approx 5$), do not even alkylate.
(10) Catalytic hydrogenolysis and reduction with $LiAlH_4$ have also been studied.[4a] These reactions appear to be of limited synthetic utility.

can serve as a $CH_2NO_2^-$ equivalent with the handy ability of preferential C-alkylation.[11]

Desulfonation is accomplished by sunlamp irradiation of solutions containing the α-nitro sulfone and 1-benzyl-1,4-dihydronicotinamide (BNAH). For example, irradiation of α-nitro sulfone 11 and BNAH afforded 3-nitro-1-phenyl-1-butene (**16a**) in 69% yield. Similarly, α-nitro sulfones 8 and 10 gave nitro compounds **16b** and **16c** in 62% and 61% yields, respectively.

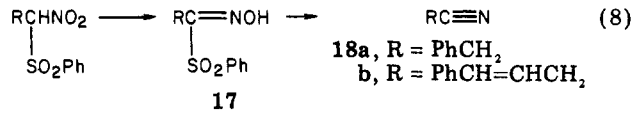
The BNAH desulfonation process resembles related debrominations of α-bromo nitro compounds[12] and denitrations of α-nitro esters, nitriles, and ketones.[13] A free radical–radical anion chain ($S_{RN}1$) mechanism has been postulated for the denitrations, and an analogous process would likely operate for desulfonation (eq 4–7). This hypothesis has been tested, especially since Katritzky[14] has recently reported a related radical anion nonchain ($S_{RN}2$) process.



The desulfonation of α-nitro sulfone 8 shows a pronounced light effect consistent with a free-radical (either chain or nonchain) process; at 50 °C in the dark, the reaction was just 3% complete after 14 h, in which time an irradiated control reaction was 60% complete. Addition of 10 mol % of *m*-dinitrobenzene[15] (*m*-DNB) to another irradiated reaction caused it to be only 20% complete at 14 h, a significant rate retardation indicating the radical–anion chain nature of the process.

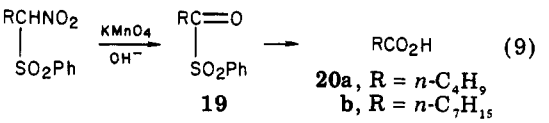
Perhaps the most common reagent for desulfonation is 6% sodium amalgam.[16] For α-nitro sulfones, however, this reagent is far too harsh. Reaction of α-nitro sulfone 8 with buffered 0.5% Na–Hg produced some 1-nitro-2-phenylethane along with considerable side-product formation. Thus, BNAH is the preferred reagent for desulfonation of α-nitro sulfones.

A typical reagent for the conversion of nitro compounds to carbonyl is 20% aqueous titanium(III) chloride.[17] It might be anticipated that acyl sulfones would be formed from α-nitro sulfones; these would then be expected to hydrolyze to carboxylic acids.[18] However, treatment of α-nitro sulfones with the titanium(III) reagent gives a totally different reaction (eq 8). The product, obtained



in 74% yield from α-nitro sulfone 8, was phenylacetonitrile (**18a**). Nitrile **18b** was similarly obtained in 74% yield from α-nitro sulfone 11. These reactions appear to involve an oxime intermediate, analogous to other titanium(III) reductions of nitro compounds.[17] In support of this view, treatment of oxime **17a** with 20% aqueous titanium(III) chloride afforded phenylacetonitrile. Apparently the reagent functions as a Lewis acid promoting abnormal Beckman rearrangement. A similar abnormal Beckman rearrangement has been reported.[2a]

The oxidation of secondary α-nitro sulfones has also been studied. Treatment of an alkaline solution of α-nitro sulfone 4 with excess aqueous potassium permanganate afforded valeric acid[19] (**20a**) in 89% yield (eq 9). Similarly,



α-nitro sulfone 5 gave octanoic acid (**20b**) in 82% yield. The anticipated intermediate in these reactions, acyl sulfone **19**, is apparently hydrolyzed to give the observed carboxylic acids. It is, unfortunately, not possible to obtain the same acids by simple hydrolysis[20] of the corresponding α-nitro sulfone salts; instead, unchanged α-nitro sulfone is recovered.

In summary, we have developed a new route for the preparation of secondary α-nitro sulfones and established simple procedures for their desulfonation, conversion to nitriles, and conversion to carboxylic acids. Also, when further transformations of nitro compounds, nitriles, and carboxylic acids are taken into account, it becomes apparent that α-nitro sulfones have considerable potential in organic synthesis.

Experimental Section

General Methods. Melting points (uncorrected) were recorded on a Thomas-Hoover Uni-melt apparatus. Infrared spectra were obtained on a Perkin-Elmer 457 spectrometer. ^1H NMR spectra were recorded on a Varian A-60A instrument unless otherwise noted; tetramethylsilane was employed as an internal standard.

(11) In contrast to the monoanion of nitromethane, the α,α-dianion gives predominant C-alkylation; the yield is, however, low: Seebach, D.; Henning, R.; Lehr, F.; Gonnerman, J. *Tetrahedron Lett.* **1977**, 1161.
(12) Kill, R. J.; Widdowson, D. A. *J. Chem. Soc., Chem. Commun.* **1976**, 755.
(13) Ono, N.; Tamura, R.; Kaji, A. *J. Am. Chem. Soc.* **1980**, *102*, 2581.
(14) Katritzky, A. R.; de Ville, G. Z.; Patel, R. C. *Tetrahedron Lett.* **1980**, 1723.
(15) *m*-Dinitrobenzene is a moderately effective one-electron acceptor and thus intercepts radical anions: Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *15*, 734.
(16) See, for example: (a) Posner, G. H.; Brunelle, D. J. *Tetrahedron Lett.* **1973**, 935; (b) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Ibid.* **1976**, 3477; (c) Chang, Y.-H., Pinnick; H. W. *J. Org. Chem.* **1978**, *43*, 373.
(17) For a review, see: McMurry, J. E. *Acc. Chem. Res.* **1974**, *7*, 281.
(18) Schank, K. *Tetrahedron Lett.* **1977**, 2567.
(19) Typical secondary nitro compounds afford ketones under these conditions: Shechter, H.; Williams, F. T. *J. Org. Chem.* **1962**, *27*, 3699 and references cited therein.
(20) For a review of nitronate hydrolysis (Nef reaction), see: Noland, W. E. *Chem. Rev.* **1955**, *55*, 137.

Gas chromatography was performed on a Varian 1420 instrument equipped with a $5 \times {}^1/_8$ 15% OV-101 (Chromosorb G-HP support) column. Thin-layer chromatography (TLC) was carried out on Analtech 0.25-mm, precoated, silica gel GF analytical plates with UV and I_2 development or on 0.50-mm, silica gel, preparative plates; methylene chloride was the eluting solvent.

Materials. THF was distilled under nitrogen from sodium–benzophenone ketyl. Me_2SO and HMPA were distilled from calcium hydride at reduced pressure. Benzyl iodide, α-iodo-o-xylene and 1-chloro-3-iodopropane were prepared from the corresponding bromides by reaction with sodium iodide in acetone. 2-Decen-1-yl acetate, geranyl acetate, and neryl acetate were prepared from the corresponding alcohols by reaction with excess acetic anhydride in pyridine. Tetrakis(triphenylphosphine)-palladium,[21] *N*-benzyl-1,4-dihydronicotinamide (BNAH),[22] 20% $TiCl_3$[17] and diazomethane[23] were prepared by standard procedures.

Preparation of (Phenylsulfonyl)nitromethane[24] (1) and Its Salts 2a,b. Sodium metal (18.43 g, 0.80 mol) was reacted with 240 mL of anhydrous methanol and the excess methanol evaporated. DMF (900 mL) was added and the solution cooled in an ice bath under nitrogen. Nitromethane (53.8 g, 0.88 mmol) was added, and, after 10 min, first sodium benzenesulfinate (74.1 g, 0.45 mol) and then iodine (102.5 g, 0.40 mol) were added to the well-stirred mixture. The cooling bath was removed and the initially bright orange solution stirred for 1 h. The darkened solution was then poured into 3 L of ice–water. Sodium sulfite was added and the solution acidified (pH 1–3) with 2.4 N HCl to deposit off-white solid. After overnight refrigeration, the precipitate was collected, recrystallized from 95% ethanol, sublimed (100–120 °C, 0.1 torr) and recrystallized to afford in typical runs 25–35 g[25] (31–44%) of compound 1, mp 78–79 °C (lit.[9] mp 78–78.5 °C).

Also isolable as the less soluble component from the initial alcohol recrystallization was 0–3.5 g (0–4%) of 1,3-bis(phenylsulfonyl)-1,3-dinitropropane: mp 165–66 °C; IR (KBr) 6.39 (NO_2), 7.51 (NO_2,SO_2), 8.67 μm (SO_2); ^{1}H NMR[26] ($CDCl_3$) [250 MHz] δ 7.65–8.14 (m, 10 H), 5.75–5.86 (m, 2 H, 2 $PhSO_2CHNO_2$), 3.29–3.60 (m, 2 H).

Anal. Calcd for $C_{15}H_{14}N_2S_2O_8$: C, 43.48; H, 3.41; N, 6.76. Found: C, 43.51; H, 3.43; N, 6.66.

Sodium (0.97 g, 42.2 mmol) was reacted with 20 mL of anhydrous methanol, and a solution of 1 (8.53 g, 42.4 mmol) in 25 mL of methylene chloride was added. After overnight refrigeration, the resulting precipitate was collected, washed with methylene chloride, and dried for 8 h in vacuo to afford 8.99 g (96%) of sodium salt **2a**. After 2 weeks, an aliquot of **2a**, when hydrolyzed with 0.6 N HCl, gave pure compound **1**.

Lithium (188 mg, 26.9 mmol) was reacted with 15 mL of anhydrous methanol, and a solution of 1 (5.43 g, 27.0 mmol) in 15 mL of methylene chloride was added. The resulting solution was *partially* evaporated at reduced pressure (**Caution**: *avoid strong heat; salt* **2b** *vigorously decomposes above 150 °C*). Addition of five 15-mL portions of cyclohexane alternated by continued concentration afforded a precipitate. It was collected, washed with methylene chloride, and dried in vacuo to provide 5.15 g (93%) of lithium salt **2b**.

Preparation of 4-Chloro-1-nitro-1-(phenylsulfonyl)butane (6) and 3-(Phenylsulfonyl)-5,6-dihydro-4*H*-1,2-oxazine *N*-Oxide (7). A mixture of sodium salt **2a** (1.46 g, 6.57 mmol), 1-chloro-3-iodopropane (0.40 g, 1.98 mmol), and 3 mL of HMPA was stirred for 6 h under nitrogen. The resulting solution was added to ice–water. Acidification (pH 1) with 2.4 N HCl, extraction with 50:50 benzene–ether, and thorough washing with five portions of water to which a few drops of dilute acid had been added afforded a solution containing **1**, **6**, and **7**. Compounds **1** and **6** were removed from **7** by extraction with three portions of 5% NaOH (10-min contact time for each extraction, vigorous stirring). Preparative TLC on the residue derived from the benzene–ether layer afforded 55 mg (11%) of the cyclic nitronic ester **7** as an oil: IR (neat) 6.34 (C=N), 7.63 (SO_2), 8.67 μm (SO_2) [additional absorptions at 3.0–3.3 (NOH) and 5.67 μm (CHO) rapidly developed, indicating decomposition typical of nitronic esters]; NMR ($CDCl_3$) δ 7.5–8.2 (m, 5 H), 4.42 (t, J = 5 Hz, 2 H), 3.00 (t, J = 7 Hz, 2 H), 1.9–2.3 (m, 2 H). Solutions of **7** were reasonably stable at 0 °C for several days.

The basic aqueous fractions containing **6** and **1** were combined, acidified (pH 1), and extracted with methylene chloride. The organic layer was rapidly extracted (30-s contact time, two inversions of the separatory funnel) with 5% NaOH. The resulting methylene chloride layer contained mostly **6** with just a trace of **1** (TLC). The aqueous layer, when acidified and extracted with methylene chloride, afforded a solution containing both **6** and **1**. Five repetitions of the rapid extraction procedure removed **6** from the bulk of **1**. For removal of **1** which carried over, it was necessary to twice repeat the entire sequence on combined fractions containing **6**. The resulting solution contained only **6** and base-line material when examined by TLC. Column chromatography (silica gel, methylene chloride elution) afforded 0.24 g (43%) of pure **6** as an oil. The analytical sample was crystallized from absolute ethanol: mp 73.5–74.5 °C; IR (melt) 6.41 (NO_2), 7.49 (NO_2, SO_2), 8.67 μm (SO_2); NMR ($CDCl_3$) δ 7.5–8.1 (m, 5 H), 5.57 (dd, J = 5, 9 Hz, 1 H), 3.55 (t, J = 6 Hz, 2 H), 2.2–2.7 (m, 2 H), 1.7–2.2 (m, 2 H).

Anal. Calcd for $C_{10}H_{12}ClNO_4S$: C, 43.22; H, 4.36; N, 5.04; Cl, 12.77. Found: C, 43.06; H, 4.36; N, 5.23; Cl, 12.80.

Preparation of 1-Nitro-1-(phenylsulfonyl)ethane (3). Procedure A. A mixture of sodium salt **2a** (2.25 g, 10.1 mmol) and 10 mL of HMPA was cooled in an ice bath, and methyl iodide (0.70 g, 4.94 mmol) was added. The cooling bath was removed, and after 4 h of being stirred, the reaction solution was added to ice–water. The workup and purification were as described for α-nitro sulfone **6**. Separation of **3** and **1** was, however, more tedious; it was necessary to carry out three repetitions of eight rapid extractions each to remove starting material **1**. This reaction afforded 0.77 g (63%) of α-nitro sulfone **3**. The analytical sample was distilled [Kugelrohr, bp 130–140 °C (0.1 torr)] whereupon it crystallized: mp 48–49 °C; IR (melt) 6.41 (NO_2), 7.51 (NO_2, SO_2), 8.70 μm (SO_2); NMR ($CDCl_3$) δ 7.4–8.0 (m, 5 H), 5.68 (q, J = 7 Hz, 1 H), 1.85 (d, J = 7 Hz, 3 H).

Anal. Calcd for $C_8H_9NO_4S$: C, 44.64; H, 4.22; N, 6.51. Found: C, 45.01; H, 4.06; N, 6.53.

Procedure B. A solution of **2a** (1.67 g, 7.51 mmol), 3.0 mL of methyl iodide, and 12 mL of methanol was refluxed for 7 h, 2 mL more of methyl iodide being added at the halfway point. Workup and purification as in procedure A afforded 1.10 g (68%) of pure **3**. Starting material **1** (80 mg, 5%) was recovered by preparative TLC. This procedure was ineffective for all other α-nitro sulfones.

Preparation of 1-Nitro-1-(phenylsulfonyl)pentane (4). Procedure A. A mixture containing sodium salt **2a** (0.91 g, 4.10 mmol), *n*-butyl iodide (0.17 g, 0.95 mmol), and 2 mL of HMPA was stirred under nitrogen for 4 h. Workup and purification as described for α-nitro sulfone **6** afforded 0.13 g (54%) of pure **4** as an oil. The analytical sample was crystallized from 95% ethanol: mp 30.5–31.5 °C; IR (melt) 6.46 (NO_2), 7.50 (NO_2, SO_2), 8.67 μm (SO_2); NMR ($CDCl_3$) δ 7.5–8.0 (m, 5 H), 5.52 (t, J = 7 Hz, 1 H), 2.27 (m, 2 H), 1.15–1.6 (m, 4 H), 0.8–1.1 (skewed t, 3 H).

Anal. Calcd for $C_{11}H_{15}NO_4S$: C, 51.35; H, 5.88; N, 5.44. Found: C, 51.26; H, 5.82; N, 5.40.

Procedure B. A mixture containing **2a** (4.56 g, 20.4 mmol), *n*-butyl iodide (7.49 g, 40.7 mmol), and 10 mL of HMPA was stirred for 14 h. Workup and purification as for α-nitro sulfone **6** aforded 2.10 g (40%) of pure **4** as an oil. The neutral fraction was column chromotographed (silica gel, methylene chloride elution), affording 10 mg (<1%) of an oil which, on the basis of its spectra, was 5-nitro-5-(phenylsulfonyl)nonane: IR (neat), 6.46 (NO_2), 7.52 (NO_2, SO_2), 8.69 μm (SO_2); NMR[26] ($CDCl_3$, 250 MHz) δ 7.5–7.9 (m, 5 H), 2.33 (dtd, 4 H), 1.2–1.6 (m, 8 H), 0.94 (t, J = 7 Hz, 6 H).

Procedure C. A solution containing lithium salt **2b** (0.21 g, 1.01 mmol) and *n*-butyl iodide (0.38 g, 2.10 mmol) in 3 mL of THF

(21) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.
(22) Dittmer, D. C.; Fouty, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 91 and references cited therein.
(23) Moore, J. A.; Reed, D. E. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. 5, p 351.
(24) A modification of the general procedure of ref 3d.
(25) In one case, 42.6 g (53%) was obtained, but this result is not routinely reproducible.
(26) We thank Mr. Robert Zipkin (Department of Chemistry, University of Pennsylvania) for obtaining these spectra.

was refluxed under nitrogen for 2 days. NMR and TLC analysis of the crude products obtained after a routine workup indicated a large amount of starting material 1, some 4, and other unidentified materials.

Preparation of 1-Nitro-1-(phenylsulfonyl)octane (5). A mixture of sodium salt **2a** (2.70 g, 12.1 mmol), *n*-heptyl iodide (0.67 g, 2.96 mmol) and 6 mL of HMPA was stirred for 14 h under nitrogen. Workup and purification as described for α-nitro sulfone **6** afforded 0.52 g (59%) of pure **5** as an oil. The analytical sample was crystallized from absolute ethanol: mp 53.5–54.5 °C; IR (melt) 6.40 (NO_2), 7.49 (NO_2, SO_2), 8.67 μm (SO_2); NMR ($CDCl_3$) δ 7.5–8.1 (m, 5 H), 5.58 (t, J = 7 Hz, 1 H), 2.0–2.5 (m, 2 H), 1.1–1.6 (m, 10 H), 0.87 (skewed t, 3 H).

Anal. Calcd for $C_{14}H_{21}NO_4S$: C, 56.17; H, 7.07; N, 4.68. Found: C, 56.07; H, 7.18; N, 4.74.

Preparation of [2-Nitro-2-(phenylsulfulfonyl)ethyl]benzene (8). Procedure A. A mixture of the sodium salt **2a** (11.03 g, 49.5 mmol), benzyl bromide (3.17 g, 18.52 mmol), and 25 mL of Me_2SO was stirred under nitrogen for 24 h and then added to ice–water. After acidification (pH 1), the organic products were extracted into methylene chloride, and the extract was washed with water to which a few drops of dilute acid had been added. This solution was then rapidly extracted (30-s contact time, thorough mixing) with 5% NaOH. The separated methylene chloride layer contained mostly product **8** while the aqueous layer contained a mixture of **1** and **8**. The aqueous layer was acidified to pH 1 and extracted with more methylene chloride. Four repetitions of the rapid extraction procedure on this extract allowed the removal of **8** from the bulk of **1**. For removal of **1** which carried over into fractions of **8**, these were combined, and the entire procedure was twice repeated. TLC showed **8** thus obtained to be free of all impurities except base-line material. Column chromatography (silica gel, methylene chloride elution) followed by recrystallization from 95% ethanol afforded 3.66 g (68%) of pure **8**: mp 86.5–87.5 °C; IR (KBr), 6.43 (NO_2), 7.40, 7.46 (NO_2, SO_2), 8.76 μm (SO_2); NMR ($CDCl_3$) δ 7.5–8.0 (m, 5 H), 7.22 (s, 5 H), 5.78 (dd, J = 5, 10 Hz, 1 H) and 3.2–3.8 (m, 2 H) (on addition of D_2O–Na_2CO_3, the δ 5.78 signal slowly disappeared, and the δ 3.2–3.8 signal collapsed to an AB quartet).

Anal. Calcd for $C_{14}H_{13}NO_4S$: C, 57.73; H, 4.47; N, 4.81. Found: C, 57.91; H, 4.49; N, 4.63.

Recrystallization from 95% ethanol of the residue from combined fractions containing starting material afforded 3.06 g (28%) of **1**, mp 79–80 °C.

Procedure B. A repetition of procedure A using benzyl iodide instead of benzyl bromide afforded α-nitro sulfone **8** in 73% yield.

Preparation of 4-Nitro-1-[2-nitro-2-(phenylsulfonyl)ethyl]benzene (9). A solution containing **2a** (1.32 g, 5.92 mmol) and *p*-nitrobenzyl bromide (0.43 g, 2.02 mmol) dissolved in 4 mL of Me_2SO was stirred under nitrogen for 24 h. Workup and purification as described for compound **8** gave 0.51 g (75%) of pure **9**: mp 105–106 °C; IR (KBr) 6.34 (NO_2), 6.55 (aryl NO_2), 7.36, 7.48 (2 NO_2, SO_2), 8.65 μm (SO_2); NMR ($CDCl_3$) δ 7.2–8.2 (m, 9 H), 5.80 (dd, J = 5, 10 Hz, 1 H), 3.2–3.9 (m, 2 H).

Anal. Calcd for $C_{14}H_{12}N_2O_6S$: C, 50.00; H, 3.60; N, 8.33. Found: C, 49.95; H, 3.53; N, 8.35.

Preparation of 1-Methyl-2-[2-nitro-2-(phenylsulfonyl)ethyl]benzene (10). Procedure A. A solution containing **2a** (0.67 g, 3.00 mmol) and α-bromo-*o*-xylene (0.19 g, 1.03 mmol) in 2 mL of Me_2SO was stirred under nitrogen for 24 h. Workup and purification as described for α-nitro sulfone **8** afforded 0.20 g (62%) of pure **10**: mp 139.5–140 °C; IR (KBr) 6.30 (NO_2), 7.46, 7.53 (NO_2, SO_2), 7.69 μm (SO_2); NMR ($CDCl_3$) δ 7.5–8.1 (m, 5 H), 7.0–7.3 (m, 4 H), 5.72 (dd, J = 5, 10 Hz, 1 H), 3.2–3.9 (m, 2 H), 2.30 (s, 3 H).

Anal. Calcd for $C_{15}H_{15}NO_4S$: C, 59.02; H, 4.92; N, 4.59. Found: C, 59.21; H, 5.11; N, 4.37.

Procedure B. A repetition of procedure A employing α-iodo-*o*-xylene rather than the bromide afforded **10** in 71% yield.

Preparation of 4-Nitro-1-phenyl-4-(phenylsulfonyl)-1-butene (11). A solution of lithium salt **2b** (4.67 g, 22.56 mmol), cinnamyl acetate (0.99 g, 5.61 mmol), $Pd(PPh_3)_4$ (0.63 g, 0.54 mmol), and triphenylphosphine (1.62 g, 6.18 mmol) in 50 mL of THF was refluxed for 3 h under nitrogen. The solution was concentrated and acidified with 0.6 N HCl. The mixture was extracted with methylene chloride and the organic layer further worked up as described for α-nitro sulfone **6**, affording 1.60 g (90%) of pure **11**: mp 70.5–71 °C; IR (melt) 6.40 (NO_2), 7.47 (NO_2, SO_2), 8.65 μm (SO_2); NMR ($CDCl_3$) δ 7.5–8.0 (m, 5 H), 7.23 (s, 5 H), 6.53 (d, J = 16 Hz, 1 H), 5.92 (dt, J = 7, 16 Hz, 1 H), 5.62 (dd, J = 6, 8 Hz, 1 H), 3.0–3.3 (m, 2 H).

Anal. Calcd for $C_{16}H_{15}NO_4S$: C, 60.55; H, 4.76; N, 4.41. Found: C, 60.43; H, 4.70; N, 4.35.

Preparation of (*E*)-2,6-Dimethyl-9-nitro-9-(phenylsulfonyl)-2,6-nonadiene (13). A solution containing lithium salt **2b** (1.41 g, 6.80 mmol), geranyl acetate (0.41 g, 2.09 mmol), $Pd(PPh_3)_4$ (0.49 g, 0.42 mmol), and triphenylphosphine (0.67 g, 2.56 mmol) in 8 mL of THF was refluxed for 5 h under nitrogen. The reaction solution was concentrated and the residue treated with dilute acid (pH 1). The resulting mixture was extracted with methylene chloride, and the organic layer was rapidly extracted with 5% NaOH. The basic aqueous extract was acidified (pH 1) and extracted with more methylene chloride to afford a solution containing **1** and a trace of **13**. This solution was rapidly extracted with more 5% NaOH, and the organic layer was combined with the main fraction of **13**. Concentration and column chromatography (silica gel, 50:50 CCl_4–CH_2Cl_2) afforded 0.61 g (86%) of α-nitro sulfone **13** as an oil: VPC (220 °C) t_R = 7.2 min (>98%), 5.2 (<1%), 6.4 (<1%); IR (neat) 6.40 (NO_2), 7.42 (NO_2, SO_2), 8.59 μm (SO_2); ^1H NMR ($CDCl_3$) δ 7.5–8.1 (m, 5 H), 5.50 (dd, J = 7, 7.5 Hz, 1 H), 4.8–5.2 (m, 2 H), 2.99 (br t, J = 7 Hz, 2 H) 1.9–2.1 (m, 4 H), 1.5–1.7 (m, 9 H) (at 360 MHz[27] the δ 1.5–1.7 multiplet appeared as three singlets: δ 1.65, 1.60, and 1.56); ^{13}C NMR[28] ($CDCl_3$, fully decoupled) δ 16.20, 17.66, 25.61 (assigned to methyl C), and 26.14, 27.01, 39.54 (assigned to methylene C).

Anal. Calcd for $C_{17}H_{23}NO_4S$: C, 60.52; H, 6.87; N, 4.15. Found: C, 60.43; H, 6.63; N, 4.32.

Preparation of (*Z*)-2,6-Dimethyl-9-nitro-9-(phenylsulfonyl)-2,6-nonadiene (14) and 3,7-Dimethyl-3-[1-nitro-1-(phenylsulfonyl)methyl]-1,6-octadiene (15). A solution containing lithium salt **2b** (2.86 g, 13.82 mmol), neryl acetate (98% pure by VPC, contaminated with 2% geranyl acetate; 0.83 g, 4.18 mmol), $Pd(PPh_3)_4$ (0.98 g, 0.85 mmol), and triphenylphosphine (1.31 g, 5.00 mmol) in 15 mL of THF was refluxed for 5 h under nitrogen. Workup and purification as described for α-nitro sulfone **13** afforded 1.20 g (84%) of a mixture, as determined by VPC at 220 °C, of the three α-nitro sulfones **14** (t_R = 6.4 min, 85%), **15** (t_R = 5.2 min, 12%), **13** (t_R = 7.2 min, 3%). Attempts to crystallize the products or separate them by distillation and TLC were unsuccessful; preparative VPC afforded a decomposed sample. Structures of **14** and **15** were assigned for the mixture: IR (neat) 6.40 (NO_2), 7.45 (NO_2, SO_2), 8.67 μm (SO_2); ^1H NMR ($CDCl_3$) δ 7.5–8.0 (m, 5 H), 5.40 (t, J = 7 Hz, 1 H) superimposed on 4.8–5.5 (m, 2 H), 2.92 (br t, J = 7 Hz, 2 H), 1.9–2.1 (m, 4 H), 1.5–1.7 (m, 9 H of **14** and 6 H of **1**), 1.33 (s, 3 H of **15** assuming **14**/**15** ratio is 10:1) [360-MHz[27] NMR resolved the δ 1.5–1.7 multiplet into two main singlets at δ 1.69 (6 H) and 1.59 (3 H)]; ^{13}C NMR[28] ($CDCl_3$, fully decoupled) δ 17.72, 23.45, 25.78 (assigned to methyl C of **14**) and 26.15, 26.81, 31.98 (assigned to methylene C of **14**).

Anal. Calcd for $C_{17}H_{23}NO_4S$: C, 60.52; H, 6.87; N, 4.15. Found: C, 60.23; H, 6.97; N, 4.49.

Preparation of 1-Nitro-1-(phenylsulfonyl)-2-undecene (12). A solution containing **2b** (2.49 g, 12.03 mmol), 2-decen-1-yl acetate (0.93 g of 91% pure material,[29] 4.28 mmol), $Pd(PPh_3)_4$ (0.49 g, 0.43 mmol), and triphenylphosphine (1.06 g, 4.05 mmol) in 40 mL of THF was refluxed for 3 h under nitrogen. The reaction was worked up and the product purified as described for α-nitro sulfone **13**, affording 1.28 g (88%) of α-nitro sulfone **12** as an oil: IR (neat) 6.40 (NO_2), 7.45 (NO_2, SO_2), 8.66 μm (SO_2); NMR ($CDCl_3$) δ 7.5–8.1 (m, 5 H), 5.0–5.9 (m, 3 H), 2.8–3.1 (m, 2 H), 1.7–2.1 (m, 2 H), 1.1–1.4 (m, 10 H), 0.87 (skewed t, 3 H).

Anal. Calcd for $C_{17}H_{25}NO_4S$: C, 60.16; H, 7.42; N, 4.13. Found: C, 60.38; H, 7.24; N, 4.21.

(27) Spectra taken at the Mid-Atlantic Regional NMR Facility, University of Pennsylvania.

(28) We thank Mrs. M. G. K. Hutchins (Laboratory for Magnetic Resonance, Temple University; NSF Grant CHE 76-05757 and ACS Grant IN-88J) for obtaining these spectra.

(29) The 2-decen-1-ol (Bedoukian) used for the preparation of 2-decen-1-yl acetate contained 9% of a nonallylic alcohol impurity which could not be separated by distillation. This impurity, as its acetate, did not interfere with the alkylation reaction.

Desulfonation of [2-Nitro-2-(phenylsulfonyl)ethyl]-benzene (8). Procedure A. A stream of nitrogen was passed for 1 h through a solution of 8 (0.32 g, 1.08 mmol) and BNAH[21] (0.74 g, 3.44 mmol) in 100 mL of benzene. The solution was irradiated for 42 h, an additional portion of BNAH (0.70 g) being added at the halfway point. The benzene solution was diluted with ether, washed with 0.6 N HCl and then water, dried over anhydrous sodium sulfate, and concentrated. The residue was column chromatographed (silica gel, methylene chloride elution) and distilled [Kugelrohr, bp 70–80 °C (0.1 torr)] to afford 0.10 g (62%) of 1-nitro-2-phenylethane (**16b**): NMR ($CDCl_3$) δ 7.25 (s, 5 H), 4.58 (t, J = 7 Hz, 2 H), 3.28 (t, J = 7 Hz, 2 H).

Procedure B. α-Nitro sulfone 8 was reduced under nitrogen with excess 0.5% Na–Hg in NaH_2PO_4–Na_2HPO_4-buffered methanol. Nitro compound **16b** (25%) and recovered 8 (13%) as well as unidentified products were obtained.

Desulfonation of 4-Nitro-1-phenyl-4-(phenylsulfonyl)-1-butene (11). The procedure as described for α-nitro sulfone 8 afforded 0.12 g (69%) of 4-nitro-1-phenyl-1-butene (**16a**) as an oil: bp (Kugelrohr) 80–90 °C (0.1 torr); IR (neat) 6.45 and 7.25 μm (NO_2); NMR ($CDCl_3$) δ 7.28 (s, 5 H), 6.55 (d, J = 15 Hz, 1 H), 6.05 (dt, J = 7, 15 Hz, 1 H) 4.48 (t, J = 7 Hz, 2 H), 2.88 (q, J = 7 Hz, 2 H).

Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.79; H, 7.91; N, 6.22. Found: C, 67.77; H, 8.15; N, 6.43.

Desulfonation of 1-Methyl-2-(2-Nitro-2-(phenylsulfonyl)ethyl)benzene (10). The procedure as described for α-nitro sulfone 8 afforded 0.11 g (61%) of 1-methyl-2-(2-nitroethyl)benzene (**16c**): bp (Kugelrohr) 80–90 °C (0.2 torr); IR (neat) 6.47 (NO_2), 7.27 μm (NO_2); NMR ($CDCl_3$) δ 7.20 (s, 4 H), 4.52 (t, J = 7 Hz, 2 H), 3.27 (t, J = 7 Hz, 2 H), 2.32 (s, 3 H).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.66; H, 7.01; N, 8.60.

Desulfonation. Mechanistic Studies. A stream of nitrogen was passed for 45 min through three solutions each containing α-nitro sulfone 8 (0.10 g, 0.34 mmol) and BNAH (0.24 g, 1.12 mmol) in 30 mL of benzene. The first of these solutions also contained m-DNB (6.1 mg, 0.036 mmol); it was irradiated for 14 h. The second solution was kept in the dark at 45–50 °C for 14 h. The third solution, the control, was irradiated for 14 h, at which time its temperature was 46 °C. Each solution was then worked up as previously described. NMR analysis indicated each reaction to contain two main materials: 8 and **16b**. The material balance was above 80% in all cases.

Preparation of α-(Phenylsulfonyl)benzaldoxime (17a). The general procedure of Zeilstra and Engberts[22] for the conversion of α-nitro sulfones to oximes was employed. The crude product was purified by acid–base extraction followed by recrystallization from carbon tetrachloride to afford pure (TLC) **17a**, mp 112–113.5 °C. An additional recrystallization provided the analytical sample: mp 115.5–16.5 °C; IR (KBr) 3.02 (br, OH), 6.10 (vw, C=N), 7.64 (SO_2), 8.67 μm (SO_2); NMR ($CDCl_3$) δ 7.2–7.8 (m, 5 H), 7.13 (s, 5 H), 4.03 (s, 2 H).

Anal. Calcd for $C_{14}H_{13}NO_3S$: C, 61.07; H, 4.76; N, 5.09. Found: C, 61.31; H, 4.84; N, 5.26.

$TiCl_3$ Reduction of [2-Nitro-2-(phenylsulfonyl)ethyl]-benzene (8). A solution containing α-nitro sulfone 8 (0.20 g, 0.69 mmol) in 5 mL of THF was treated under nitrogen with 5 mL of 20% aqueous $TiCl_3$. After 4 h, more water was added and the mixture extracted with methylene chloride. The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated to 0.12 g of an oil. TLC indicated one major and several minor products. Column chromatography (silica gel, methylene chloride elution) followed by distillation [Kugelrohr; bp 50–60 °C (0.15 torr)] afforded 60 mg (74%) of VPC-pure phenylacetonitrile (**18a**), identified by its spectra and comparison to an authentic sample.

$TiCl_3$ Reduction of α-(Phenylsulfonyl)benzaldoxime (17a). The procedure employed for α-nitro sulfone 8 was repeated on oxime **17a** (92 mg, 0.34 mmol), affording 34 mg (85%) of VPC-pure phenylacetonitrile.

$TiCl_3$ Reduction of 4-Nitro-1-phenyl-4-(phenylsulfonyl)-1-butene (11). The procedure employed for 8 was repeated on α-nitro sulfone 11 (0.21 g, 0.66 mmol). The crude product was column chromatographed (silica gel, methylene chloride elution) and recrystallized from hexane to afford 64 mg (74%) of 4-phenyl-3-butenenitrile (**18b**), mp 57.5–58.5 °C (lit.[30] mp 59–60 °C).

Oxidation of 1-Nitro-1-(phenylsulfonyl)pentane (4). Compound 4 (0.28 g, 1.11 mmol) was dissolved in 30 mL of 5% NaOH. A second solution containing potassium permanganate (3.61 g, 22.84 mmol) in 175 mL of water was added dropwise over 30 min. The resulting mixture was stirred 30 min, and sodium bisulfite (7.1 g) was added followed by 20 mL of 2.4 N HCl. The resulting clear solution was treated with salt (90 g) and extracted with four portions of methylene chloride. The combined organic layers were washed with brine, dried (anhydrous Na_2SO_4), and concentrated. The oily residue was distilled (Kugelrohr, bp 35–45 °C (0.9 torr)] to afford 101 mg (89%) of VPC-pure valeric acid, identified by its spectra.

Oxidation of 1-Nitro-1-(phenylsulfonyl)octane (5). The procedure employed for the oxidation of 4 was repeated on α-nitro sulfone 5 (0.31 g, 1.04 mmol), affording 0.12 g (82%) of VPC-pure octanoic acid, bp (Kugelrohr) 70–80 °C (0.15 torr).

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. 1, 21272-85-5; **2a**, 74737-89-6; **2b**, 74738-03-7; **3**, 74737-90-9; **4**, 74737-91-0; **5**, 74737-92-1; **6**, 74737-93-2; **7**, 74738-02-6; **8**, 74737-94-3; **9**, 74737-95-4; **10**, 74737-96-5; **11**, 74737-97-6; **12**, 76024-90-3; **13**, 74737-99-8; **14**, 74738-00-4; **15**, 74738-01-5; **16a**, 76024-91-4; **16b**, 6125-24-2; **16c**, 76024-92-5; **17a**, 76024-93-6; **18a**, 140-29-4; **18b**, 16170-45-9; **20a**, 109-52-4; **20b**, 124-07-2; 1,3-bis(phenylsulfonyl)-1,3-dinitropropane, 76024-94-7; 1-chloro-3-iodopropane, 6940-76-7; methyl iodide, 74-88-4; n-butyl iodide, 542-69-8; 5-nitro-5-(phenylsulfonyl)nonane, 76024-95-8; n-heptyl iodide, 4282-40-0; benzyl bromide, 100-39-0; p-nitrobenzyl bromide, 100-11-8; α-bromo-o-xylene, 89-92-9; α-iodo-o-xylene, 35509-93-4; cinnamyl acetate, 10521-96-7; geranyl acetate, 74408-53-0; neryl acetate, 74408-52-9; 2-decen-1-yl acetate, 40813-86-3.

(30) Oda, R.; Tanimoto, S. *Tetrahedron Lett.* **1964**, 1653.