(6) A. R. Osborn, K. Schofield, and L. N. Short, *J. Chem. Soc.*, 4191 (1956).
(7) In initial reactions the solution of the trans amine in glacial acetic acid was added to the sodium nitrite solution according to the method described by Mathison and Gueldner.[1a] However, reversal of the addition reduced the amount of olefins produced from 25 to 4.5% as evidenced by vpc.
(8) (a) S. Durand-Henchoz and R. C. Moreau, *Bull. Soc. Chim. Fr.*, 3428 (1966); (b) W. Huckel and Y. Raid, *Justus Liebigs Ann. Chem.*, **637**, 33 (1960).
(9) (a) Y. M. H. Haddad, H. B. Henbest, J. Husbands, and T. R. B. Mitchell, *Proc. Chem. Soc.*, 361 (1964); (b) M. Feiser and L. R. Feiser, "Reagents for Organic Synthesis," Vol. 2, Wiley-Interscience, New York, N. Y., 1969, p 228.
(10) (a) S. Durand-Henchoz and R. C. Moreau, *Bull. Soc. Chim. Fr.*, 3422 (1966); (b) D. N. Kirk and A. Mudd, *J. Chem. Soc. C*, 968 (1969).

Chemistry of α-Nitro Sulfones. IV.[1] Functionalization at the Activated Carbon

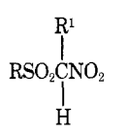
Job J. Zeilstra and Jan B. F. N. Engberts*

Department of Organic Chemistry, The University, Zernikelaan, Groningen, The Netherlands

Received April 8, 1974

Condensation reactions of nitromethyl *p*-tolyl sulfone (1) with formaldehyde and benzenesulfinic acid are described. A proposed rationalization of the reaction involves the intermediacy of the vinyl sulfone **6**. Some other aldehydes than formaldehyde may be used as well. The product derived from acetaldehyde can be reduced by sodium borohydride to 1-nitro-1-tosylpropane (11). Primary and secondary α-nitro sulfones undergo Michael-type addition reactions to certain activated carbon–carbon double bonds.

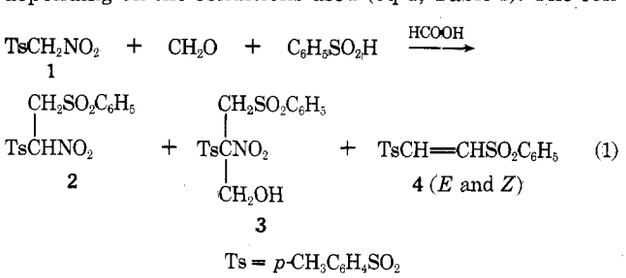
Electron-withdrawing substituents usually activate a neighboring C–H bond toward alkylation and condensation reactions.[2] However, several studies have demonstrated that the twofold activated C–H group in primary and secondary α-nitro sulfones (pK_a's of about 6 in 50% ethanol–water[3]) often is only reluctantly—or indeed not at all—functionalized by means of these types of reaction.[4,5] This is noteworthy since rather similar systems like α-nitro esters,[6] nitroacetonitrile,[7] bis(phenylsulfonyl)methane,[8] and bis(alkylsulfonyl)methanes[9] easily react with aldehydes to give alcohols, alkenes, or bisadducts; moreover, nitroalkanes can also condense with, for instance, *C*-nitroso compounds[10] and benzofuroxan.[11] With these results in mind and in continuation of our studies on α-nitro sulfones,[1,3,12] we have probed further into the propensity of α-nitro sulfones for functionalization at the activated carbon atom.



R^1 = H, alkyl, aryl

Results and Discussion

Under a variety of conditions and in the presence of either basic or acidic catalysts, nitromethyl *p*-tolyl sulfone (1) did not react with a series of aliphatic or aromatic aldehydes,[13] or with nitrosobenzene, *p*-dimethylaminonitrosobenzene, and benzofuroxan. However, when 1 was allowed to react with formaldehyde and benzenesulfinic acid in refluxing 90% aqueous formic acid, three types of condensation products (**2**, **3**, and **4**) could be isolated in yields depending on the conditions used (eq 1, Table I). The conversion of **1** into **2** is reminiscent of the condensation of carbon acids like indole or β-naphthol with formaldehyde and sulfinic acids.[14] Neither **2** nor **3** could be converted into **4** by refluxing in formic acid. Instead, starting material and partially esterified **3** were the only materials isolated. Surprisingly, an excess of benzenesulfinic acid effected the transformation of **3** into **4** in a yield of 31%. Since sulfinic acids are fairly strong reducing agents,[15] we presume that a reduction process induced by the sulfinic acid is part of the reaction.



Ts = *p*-$CH_3C_6H_4SO_2$

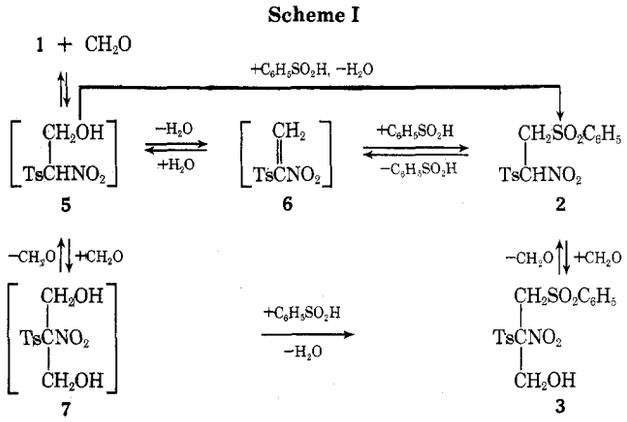
Table I
Condensation Products from 1 (Equation 1)

Formaldehyde, equiv[a]	Benzenesulfinic acid, equiv[a]	Reaction temp, °C	Reaction time, min	Yield, % product
1	1	100	13	31 (**2**), 6 (**3**)[b]
3	2	100	13	8 (**2**), 28 (**3**)
1	1	70	90	20 (**2**)[c]
3	2	50	180	93 (**3**)
3	1	50	180	89 (**3**)
3	2	100	180	42 (**4**)

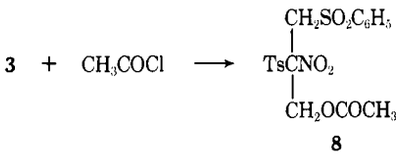
[a] Relative to 1 equiv of **1**. [b] 44% recovery of **1**. [c] 60% recovery of **1**.

At the moment no clear-cut choice can be made between the several reaction pathways conceivable for the production of **2** and **3** from **1** (Scheme I). The intermediacy of hy-

Scheme I



droxymethyl phenyl sulfone, the adduct of benzenesulfinic acid to formaldehyde, is highly unlikely in view of the steric and field effects of the sulfonyl moiety which will prevent SN2 displacement of the hydroxyl substituent.[16] In addition, entry to **3** *via* **7** is implausible for steric reasons (*vide infra*). In regard to the formation of **2** from **5**, we favor an elimination–addition mechanism over nucleophilic substitution of the OH group in **5** by sulfinate anion. The resistance of **3** to further coupling with benzenesulfinic acid may be understood on this basis, because no vinyl sulfone can be generated from **3**. However, steric hindrance may also be invoked to explain the absence of further conversion. The importance of this factor may be judged from the observation that refluxing of **3** for 2 hr with pure thionyl chloride did not effect substitution of the hydroxyl moiety. Acylation of **3** could only be achieved by refluxing with acetyl chloride for 3 hr. The products formed upon treatment



8

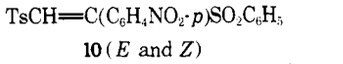
of **3** with base suggest that the reactions proposed in Scheme I are reversible processes. Thus, **2** was obtained from **3** by using 5% aqueous sodium hydroxide.[17] When **2** was subjected to further reaction with base, **1** was formed in high yield. This reaction most likely involves the vinyl sulfone **6** as an intermediate; this idea receives support from the well-known sulfinate elimination from β-nitroethyl sulfones in dilute alkali.[18] Addition of water to **6**, which is highly susceptible to nucleophilic addition,[19] will afford **5**. Subsequent β-elimination of formaldehyde from the labile **5**, also induced by base, then leads to the conjugated base of **1**. The great ease of this reaction may well explain our inability to isolate addition products from the reaction of primary and secondary α-nitro sulfones with aldehydes.[13]

The condensation according to eq 1 is not restricted to formaldehyde. With several aliphatic and aromatic aldehydes the corresponding condensation products could also be obtained (eq 2, Table II). However, the success of

(2)

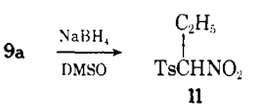
9a-f

the reaction clearly depends on the nature of the carbonyl component, since the starting materials were recovered almost quantitatively when butyraldehyde, isobutyraldehyde, *p*-methoxybenzaldehyde, or ketones were used. In the case of *p*-nitrobenzaldehyde and using prolonged reaction times, the disulfonylalkene **10** was formed as the major



10 (*E* and *Z*)

product. The condensation given in eq 2 may be of considerable synthetic utility, since we found that **9a** may be reduced to **11** by treatment with sodium borohydride in DMSO. This reaction constitutes a useful and facile alter-



11

native synthesis of secondary α-nitro sulfones starting from the readily available **1**. Most probably the reduction proceeds *via* a vinyl sulfone intermediate by analogy with similar reductions of β-substituted nitroalkanes in which nitroalkenes are initially formed.[20]

Table II
Condensation Products from 1 (Equation 2)

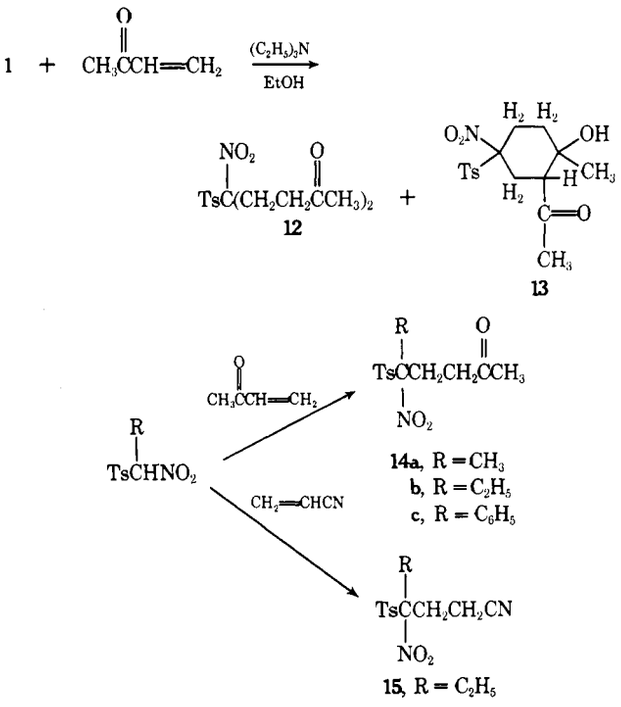
Compd	R	Reaction time, hr	Reaction temp, °C	Yield, %
9a	CH_3	3	50	85
9b	C_2H_5	3	50	39
9c	p-$CH_3C_6H_4$	15	70	11[a]
9d	C_6H_5	15	70	85
9e	p-ClC_6H_4	15	70	53
9f	p-$NO_2C_6H_4$	1	70	24
10	p-$NO_2C_6H_4$	15	70	66

[a] 53% recovery of **1**.

Attempts to condense secondary α-nitro sulfones like **11** with formaldehyde and benzenesulfinic acid were unsuccessful, lending support to the idea that an unsaturated sulfone, formed *via* initial addition of **11** to the aldehyde, is a key intermediate in the condensation reaction. The more severe steric requirements, as compared with the corresponding reaction with **1**, may also contribute to inertness of **11**.

We have so far also not been able to isolate Mannich bases from the reaction of α-nitro sulfones with formaldehyde and amines, using either basic or acidic conditions (normally in acetic acid rather than formic acid to avoid the Leuckart reaction).[21] In one case we have isolated **7** (*cf.* Scheme I) from the reaction of **1** with formaldehyde and diethylamine in an acidic medium after chromatography of the complex reaction mixture. Since **7** was absent in the crude products (nmr analysis) and **7** cannot be prepared from **1** and formaldehyde, the possibility remains that **7** originates from decomposition of a labile Mannich base derived from **1** during purification.

Finally we report that both primary and secondary α-nitro sulfones can undergo Michael-type addition reactions, using a catalytic amount of triethylamine. With **1** and an excess of methyl vinyl ketone, the bisadduct **12** is obtained besides the intramolecular aldol condensation product **13**. Conditions may be varied so that **13** becomes the sole product of the reaction. As anticipated, secondary



14a, R = CH_3
b, R = C_2H_5
c, R = C_6H_5

15, R = C_2H_5

α-nitro sulfones afforded monoaddition products. Under comparable conditions, **1** does not add to methyl cinnamate and **11** fails to react with benzalacetone. These observations contrast sharply with the known smooth addition of ethyl nitroacetate to the above carbonyl compounds.[22] More severe steric demands in the reactions of **1** and **11** may well contribute to this striking difference in reactivity.

Experimental Section

Elemental analyses were carried out in the Analytical Department of this laboratory under the supervision of Mr. W. M. Hazenberg and Mr. A. F. Hamminga. Melting points were determined using a Mettler FP1 melting point apparatus with a Mettler FP52 microscope attachment. Nmr spectra were recorded on a Varian A-60 spectrometer, using TMS (δ 0) as an internal standard. Ir spectra were measured with a Perkin-Elmer instrument, Model 257. Mass spectra were taken on a AEI MS-9 double-focusing mass spectrometer.

The α-nitro sulfones were prepared according to our previously described method[1] or according to the method of Truce, *et al.*[23] The other chemicals were commercial products and were adequately purified before use.

Attempted Condensations with 1. These include the following: (1) with formaldehyde: in EtOH–NH_3, 3 hr at 50°; in refluxing HCOOH, 10–30 min; in HCOOH, 3 hr at 50°; (2) with benzaldehyde: in EtOH with a catalytic amount of $MeNH_2$ or K_2CO_3, reflux, 10 min; without solvent, catalytic amount of $MeNH_2$, reflux, 2 hr; in benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid, azeotropic distillation over anhydrous Cu(II)SO_4, 15 hr; (3) with nitrosobenzene: in HCOOH–H_2O (2:1), 1 hr at 50°; in HCOOH, 1 hr at 50°; (4) with *p*-dimethylaminonitrosobenzene: in EtOH–H_2O in the presence of K_2CO_3, reflux, 30 min; in MeOH–K_2CO_3, 10 min at 25°; (5) with benzofuroxan: in EtOH in the presence of NH_3, 20 min at 0° or reflux for 1 hr; in HCOOH, 3 hr at 50°. In all cases **1** was recovered unchanged, usually in high yield. No evidence could be obtained for the formation of the desired condensation products.

1-Nitro-1-(*p*-tolylsulfonyl)-2-(phenylsulfonyl)ethane (2). A solution of **1** (2.15 g, 10 mmol), sodium benzenesulfinate (1.64 g, 10 mmol), and 1 ml of 36% aqueous formaldehyde in 28 ml of 90% formic acid was refluxed for 13 min. After dilution with water, the mixture was extracted with CH_2Cl_2 (200 ml). The CH_2Cl_2 extract was washed with water and dried over Na_2SO_4. Removal of the solvent *in vacuo* gave an oil which crystallized after adding some ethanol. Recrystallization from ethanol furnished 1.15 g (31%) of **2**: mp 143.6–144.7°; nmr ($CDCl_3$) δ 2.50 (s, 3 H, aryl CH_3), 4.0–4.3 (m, 2 H, CH_2SO_2), 5.35 and 5.49 (2 d, 1 H, J = 3 Hz, $CHNO_2$), 7.3–8.1 ppm (m, 9 H, aryl protons); ir (KBr) 1570, 1300–1350, 1150 cm^{-1}.

Anal. Calcd for $C_{15}H_{15}NO_6S_2$: C, 48.77; H, 4.10; N, 3.80; S, 17.36. Found: C, 48.88; H, 4.14; N, 3.86; S, 17.24.

The filtrate was concentrated and allowed to stand at 0° in a refrigerator. The solid that separated was recrystallized from ethanol to give 0.94 g of **1** (44%), mp 115.0–116.0°. After standing for 3 days an additional solid precipitated. Recrystallization from benzene–*n*-hexane yielded 0.51 g of **3** (6%), mp 167.9–169.3° (*vide infra*).

2-Nitro-2-(*p*-tolylsulfonyl)-3-(phenylsulfonyl)propanol-1 (3). A solution of **1** (2.15 g, 10 mmol), sodium benzenesulfinate (3.28 g, 20 mmol), and 3 ml of 36% aqueous formaldehyde in 28 ml of 90% formic acid was stirred for 3 hr at 50°. After standing at 0° for 15 hr, the separated solid was filtered off, dried *in vacuo*, and recrystallized from benzene–*n*-hexane to give 3.48 g of **3**. A second portion of **3** (0.25 g) was obtained after dilution of the mother liquor with water and subsequent cooling at 0°, total yield 3.73 g (93%) of **3**: mp 168.4–169.5; nmr ($CDCl_3$) δ 2.49 (s, 3 H, aryl CH_3), 2.89 (br s, 1 H, OH), 4.40 (d, 2 H, J = 4 Hz, SO_2CH_2), 4.63 (s, 2 H, CH_2OH), 7.2–8.1 ppm (m, 9 H, aryl protons); ir (KBr) 3540, 1550, 1280–1340, 1150 cm^{-1}.

Anal. Calcd for $C_{16}H_{17}NO_7S_2$: C, 48.11; H, 4.29; N, 3.51; S, 16.05. Found: C, 48.04; H, 4.32; N, 3.47; S, 16.03.

Reaction of 3 with NaOH. Sulfone **3** (2.00 g, 5 mmol) was dissolved in 30 ml of 5% aqueous NaOH kept under an atmosphere of nitrogen. After stirring for 5 min at room temperature, the solution was filtered, cooled to 5°, acidified with acetic acid, and extracted with 150 ml of CH_2Cl_2. The extract was washed with water and dried over Na_2SO_4. Recrystallization of the solid, obtained after removal of the solvent *in vacuo*, yielded 0.92 g (50%) of **2**, mp 140.3–142.3°.

Reaction of 2 with NaOH. A solution of 0.74 g (2 mmol) of **2** in 10 ml of 10% aqueous NaOH was refluxed under nitrogen for 15 hr. After cooling to 5° and acidification with acetic acid, solid material was obtained that was recrystallized from ethanol to afford 0.35 g (81%) of **1**, mp 114.9–115.8°.

1-(*p*-Tolylsulfonyl)-2-(phenylsulfonyl)ethene (4). A solution of **1** (2.15 g, 10 mmol), sodium benzenesulfinate (3.28 g, 20 mmol), and 3 ml of 36% aqueous formaldehyde in 28 ml of 90% aqueous formic acid was refluxed for 3 hr. Work-up was carried out as described for **2**. Crude **4** was recrystallized from ethanol, yield 1.34 g (42%): mp 182.0–196.5° (*E* and *Z* isomers); nmr ($CDCl_3$) δ 2.50 (s, 3 H, aryl CH_3), 7.3–8.1 ppm (unresolved multiplet, 11 H, aryl and vinyl protons); ir (KBr) 1320, 1150 cm^{-1}.

Anal. Calcd for $C_{15}H_{14}O_4S_2$: C, 55.88; H, 4.38; S, 19.89. Found: C, 55.80, H, 4.42; S, 19.83.

2-Nitro-2-(*p*-tolylsulfonyl)propane-1,3-diol (7). A solution of **1** (2.15 g, 10 mmol), diethylamine (1.60 g, 22 mmol), and 3 ml of 36% aqueous formaldehyde in 20 ml of formic acid was stirred for 2 hr at 50°. The solution was diluted with water and extracted with 200 ml of CH_2Cl_2. The CH_2Cl_2 extract was washed with water, dried over Na_2SO_4, and evaporated to dryness. The residue was purified by chromatography on silica gel, using a mixture of CH_2Cl_2 and EtOAc with increasing concentrations of EtOAc as the eluent. Recrystallization from benzene afforded 0.55 g of pure **7** (20%): mp 100.0–105.5°; nmr ($CDCl_3$) δ 2.50 (s, 3 H, aryl CH_3), 3.20 (t, 2 H, J = 7 Hz, OH), 4.3–4.7 (m, 4 H, CH_2O), 7.3–7.9 ppm (m, 4 H, aryl protons); ir (KBr) 3480, 1550, 1350–1300, 1150 cm^{-1}; mol wt (osmotically) 287 ± 10; mass spectrum *m/e* 275 (M^+).

Anal. Calcd for $C_{10}H_{13}NO_6S$: C, 43.64; H, 4.76; N, 5.09; S, 11.65. Found: C, 43.67; H, 4.71; N, 4.90; S, 11.64.

2-Nitro-2-(*p*-tolylsulfonyl)-3-(phenylsulfonyl)propyl Acetate (8). A solution of **3** (1.50 g, 3.75 mmol) in 15 ml of acetyl chloride was refluxed for 3 hr. Evaporation to dryness and crystallization from EtOH gave 1.61 g of **8** (97%): mp 135.2–135.5°; nmr ($CDCl_3$) δ 2.00 (s, 3 H, $CH_3C{=}O$), 2.50 (s, 3 H, aryl CH_3), 4.30 and 4.60 (2 d, 2 H, J = 15 Hz, SO_2CH_2), 4.92 and 5.12 (2 d, 2 H, J = 13 Hz, CH_2O), 7.3–8.1 ppm (m, 9 H, aryl protons); ir (KBr) 1740, 1560, 1340–1180, 1210, 1150 cm^{-1}.

Anal. Calcd for $C_{18}H_{19}NO_8S_2$: C, 48.95; H, 4.35; N, 3.18; S, 14.57. Found: C, 49.00; H, 4.30; N, 3.02; S, 14.42.

1-Nitro-1-(*p*-tolylsulfonyl)-2-(phenylsulfonyl)propane (9a). A solution of **1** (2.15 g, 10 mmol), acetaldehyde (0.97 g, 22 mmol), and sodium benzenesulfinate (1.80 g, 11 mmol) in 28 ml of 90% aqueous formic acid was stirred under nitrogen for 3 hr at 50°. After crystallization in a refrigerator and subsequent filtration, the crystals were dried *in vacuo* and recrystallized from EtOH–H_2O, yielding 3.26 g of **9a** (85%): mp 159.2–161.2°; nmr ($CDCl_3$) δ 1.75 (d, 3 H, J = 7 Hz, CH_3CH), 2.50 (s, 3 H, aryl CH_3), 4.2–4.6 (m, 1 H, CH_3CH), 5.80 (d, 1 H, J = 10 Hz, O_2NCH), 7.3–8.1 ppm (m, 9 H, aryl protons). Refluxing of a solution of **9a** in EtOH caused epimerization, mp 122–156°. The 1:1 mixture of epimers gave additional absorptions in the nmr spectrum: δ 1.69 (d, 1 H, J = 7 Hz, CH_3CH), 6.20 ppm (d, 1 H, J = 1.5 Hz, O_2NCH).

Anal. Calcd for $C_{16}H_{17}NO_6S_2$: C, 50.12; H, 4.47; N, 3.66; S, 16.72. Found: C, 50.23; H, 4.43; N, 3.55; S, 16.76.

1-Nitro-1-(*p*-tolylsulfonyl)-2-(phenylsulfonyl)butane (9b) was prepared as described for **9a** starting from 1.28 g (22 mmol) of propionaldehyde. The reaction mixture was allowed to stand in a refrigerator for several days and was subsequently filtered to remove the crystals. These crystals were dried *in vacuo* and recrystallized from EtOH to give 1.54 g of **9b** (39%): mp 136–153°; nmr ($CDCl_3$) δ 1.20 (t, 3 H, J = 7 Hz, CH_3CH_2), 2.2–2.6 (m, 2 H, CH_3CH_2), 2.50 (s, 3 H, aryl CH_3), 4.1–4.5 (m, 1 H, CH_2CH), 6.03 (d, 1 H, J = 10 Hz, O_2NCH), 7.3–8.0 ppm (m, 9 H, aryl protons); ir (KBr) 1560, 1330, 1150 cm^{-1}.

Anal. Calcd for $C_{17}H_{19}NO_6S_2$: C, 51.37; H, 4.82; N, 3.53; S, 16.13. Found: C, 51.14; H, 4.72; N, 3.49; S, 16.15.

1-Nitro-1-(*p*-tolylsulfonyl)-2-(phenylsulfonyl)-2-(*p*-tolyl)ethane (9c). A solution of **1** (2.15 g, 10 mmol), *p*-methylbenzaldehyde (2.64 g, 22 mmol), and sodium benzenesulfinate (1.80 g, 11 mmol) in 28 ml of 90% aqueous formic acid was stirred under nitrogen for 15 hr at 70°. The reaction mixture was allowed to stand in a refrigerator for several days. Crystals separated, which were removed by filtration and dried *in vacuo*. Recrystallization from EtOH gave 0.50 g of pure **9c** (11%): mp 166.9–178.2° dec; nmr ($CDCl_3$) δ 2.31 (s, 3 H, aryl CH_3), 2.44 (s, 3 H, aryl CH_3 of Ts), 5.18 (d, 1 H, J = 12 Hz, SO_2CH), 6.48 (d, 1 H, J = 12 Hz, O_2NCH), 6.9–7.6 ppm (m, 13 H, aryl protons); ir (KBr) 1570, 1350–1290, 1150 cm^{-1}.

Anal. Calcd for $C_{22}H_{21}NO_6S_2$: C, 57.50; H, 4.61; N, 3.05; S, 13.94. Found: C, 57.34; H, 4.64; N, 2.97; S 13.97.

The mother liquor was diluted with water and extracted with CH_2Cl_2. The extract was washed with water, dried over Na_2SO_4, and evaporated to dryness. Crystallization of the residue from EtOH gave 1.13 g of 1 (53%), mp 115.5–116.1°.

1-Nitro-1-(*p*-tolylsulfonyl)-2-(phenylsulfonyl)-2-phenylethane (9d) was prepared from 2.32 g (22 mmol) of benzaldehyde following the procedure given for **9c.** Recrystallization from (EtOAc–DMSO)–*n*-hexane gave 4.08 g of pure **9d** (85%): mp 208.8° dec; nmr (DMSO-d_6) δ 2.40 (s, 3 H, aryl CH_3), 5.59 (d, 1 H, J = 12 Hz, SO_2CH), 7.0–8.0 ppm (m, 14 H, 13 aryl protons + O_2NCH); ir (KBr) 1560, 1350–1290, 1150 cm^{-1}.

Anal. Calcd for $C_{21}H_{19}NO_6S_2$: C, 56.62; H, 4.30; N, 3.15; S, 14.41. Found: C, 56.34; H, 4.62; N, 3.00; S, 14.50.

1-Nitro-1-(*p*-tolylsulfonyl)-2-(phenylsulfonyl)-2-(*p*-chlorophenyl)ethane (9e) was prepared from *p*-chlorobenzaldehyde (2.87 g, 22 mmol) according to the procedure given for **9c.** Recrystallization from acetone–DMSO–water gave 2.55 g of pure **9e** (53%): mp 192.1–193.5° dec; nmr (acetone-d_6) δ 2.47 (s, 3 H, aryl CH_3), 5.48 (d, 1 H, J = 13 Hz, SO_2CH), 7.0–7.7 ppm (m, 14 H, 13 aryl protons + O_2NCH); ir (KBr) 1560, 1350–1280, 1150 cm^{-1}.

Anal. Calcd for $C_{21}H_{18}ClNO_6S_2$: C, 52.55; H, 3.78; Cl, 7.39; N, 2.92; S, 13.36. Found: C, 52.78; H, 3.80; Cl, 7.40; N, 2.88; S, 13.40.

1-Nitro-1-(*p*-tolylsulfonyl)-2-(phenylsulfonyl)-2-(*p*-nitrophenyl)ethane (9f). A solution of 1 (2.15 g, 10 mmol), *p*-nitrobenzaldehyde (3.32 g, 22 mmol), and sodium benzenesulfinate (1.80 g, 11 mmol) in 28 ml of 90% aqueous formic acid was stirred under nitrogen for 1 hr at 70°. After cooling to 35° the separated solid was filtered off. Drying of this material *in vacuo* and recrystallization from acetone–water gave 1.16 g of pure **9f** (24%): mp 193.4–196.7° dec; nmr (acetone-d_6) δ 2.45 (s, 3 H, aryl CH_3), 5.70 (d, 1 H, J = 12 Hz, SO_2CH), 7.2–8.1 ppm (m, 14 H, 13 aryl protons + O_2NCH); ir (KBr) 1560, 1520, 1350–1310, 1150 cm^{-1}.

Anal. Calcd for $C_{21}H_{18}N_2O_8S_2$: C, 51.42; H, 3.70; N, 5.72; S, 13.09. Found: C, 51.44; H, 3.71; N, 5.55; S, 12.77.

1-(Phenylsulfonyl)-1-(*p*-nitrophenyl)-2-(*p*-tolylsulfonyl)ethene (10). The same solution of starting materials as used for the preparation of **9f** was stirred under nitrogen for 15 hr at 70°. Cooling to room temperature and filtration of the solid gave a powder. Drying of this powder *in vacuo* and recrystallization from acetone–water gave 1.85 g of pure **10** as light-yellow needles. The mother liquor was diluted with water and extracted with CH_2Cl_2 (200 ml). The CH_2Cl_2 extract was washed with water, dried over Na_2SO_4, and evaporated to dryness. Crystallization of the residue from acetone–water gave another 1.06 g of **10,** total yield 2.92 g (66%): mp 224.3–230.4°; nmr (DMSO-d_6) δ 2.45 (s, 3 H, aryl CH_3), 7.0–8.3 ppm (m, 14 H, 13 aryl protons + 1 vinyl proton); ir (KBr) 1520, 1350–1280, 1150 cm^{-1}.

Anal. Calcd for $C_{21}H_{17}NO_6S_2$: C, 56.88; H, 3.86; N, 3.16; S, 14.45. Found: C, 56.94; H, 3.75; N, 13.12; S, 14.37.

Reduction of 9a with $NaBH_4$. To a stirred solution of **9a** (1.91 g, 5 mmol) in 25 ml of anhydrous DMSO (under nitrogen) was slowly added $NaBH_4$ (0.80 g, 20 mmol) at room temperature. After 3 hr the solution was acidified with acetic acid and diluted with water. The resulting solution was extracted with 150 ml of CH_2Cl_2, and the CH_2Cl_2 extract washed with water, dried over Na_2SO_4 and evaporated to dryness. The residue was diluted with EtOH and allowed to stand in the refrigerator, after which the solid was filtered and recrystallized from EtOH, yield 0.91 g of **11** (75%), mp 66.0–67.2° (lit.[1] mp 67.0–67.5°).

5-Nitro-5-(*p*-tolylsulfonyl)-2,8-nonanedione (12). A solution of 1 (2.15 g, 10 mmol), methyl vinyl ketone (1.54 g, 22 mmol), and 0.2 ml of triethylamine in a mixture of 10 ml of EtOH and 10 ml of CH_2Cl_2 was stirred for 1 hr at room temperature. After acidification with acetic acid, followed by evaporation *in vacuo* of the CH_2Cl_2 and part of the EtOH, the solution was allowed to stand in the refrigerator. Crystals separated which were filtered off. Recrystallization from EtOH gave 0.64 g of pure **12** (18%): mp 122.7–123.4°; nmr ($CDCl_3$) δ 2.17 (s, 6 H, $CH_3C{=}O$), 2.50 (s, 3 H, aryl CH_3), 2.4–3.0 (m, 8 H, CH_2), 7.3–7.9 ppm (m, 4 H, aryl protons); ir (KBr) 1710, 1550, 1350–1270, 1150 cm^{-1}.

Anal. Calcd for $C_{16}H_{21}NO_6S$: C, 54.07; H, 5.96; N, 3.94; S, 9.02. Found: C, 53.90; H, 6.01; N, 3.86; S, 8.93.

1-Methyl-2-acetyl-4-nitro-4-(*p*-tolylsulfonyl)-1-cyclohexanol (13). A solution of 1 (2.15 g, 10 mmol), methyl vinyl ketone (1.54 g, 22 mmol), and 0.2 ml of triethylamine in 15 ml of EtOH was refluxed for 5 hr. After acidification with acetic acid the solution was allowed to stand in the refrigerator. The separated crystals were filtered off. Recrystallization from acetone–water gave 2.89 g of pure **13** (81%): mp 188.4–188.5°; nmr ($CDCl_3$) δ 1.17 (s, 3 H, CH_3), 2.30 (s, 3 H, $CH_3C{=}O$), 1.3–3.0 (m, 7 H, ring H), 3.83 (d, 1 H, J = 2 Hz, OH), 7.3–7.8 ppm (m, 4 H, aryl protons); ir (KBr) 3420, 1690, 1550, 1370–1260, 1150 cm^{-1}; mol wt (osmotically) 354 ± 11; mass spectrum *m/e* 340 ($M^+ - CH_3$), 312 (M^+ – acetyl), 249 (M^+ – tolyl), 200 (M^+ – Ts).

Anal. Calcd for $C_{16}H_{21}NO_6S$: C, 54.07; H, 5.96; N, 3.94; S, 9.02. Found: C, 54.19; H, 5.97; N, 3.77; S, 8.84.

5-Nitro-5-(*p*-tolylsulfonyl)-2-hexanone (14a). According to the procedure followed for the preparation of **13,** 1-nitro-1-(*p*-tolylsulfonyl)ethane (2.29 g, 10 mmol) was treated with methyl vinyl ketone (0.77 g, 11 mmol) for 30 min, yield 2.80 g (94%) of **14a:** mp 119.0–119.1° (from EtOH); nmr ($CDCl_3$) δ 1.90 (s, 3 H, CH_3), 2.18 (s, 3 H, $CH_3C{=}O$), 2.50 (s, 3 H, aryl CH_3), 2.59 (s, 2 H, $CH_2C{=}O$), 7.3–7.9 ppm (m, 4 H, aryl protons); ir (KBr) 1710, 1550, 1350–1290, 1150 cm^{-1}.

Anal. Calcd for $C_{13}H_{17}NO_5S$: C, 52.16; H, 5.72; N, 4.68; S, 10.71. Found: C, 52.10; H, 5.78; N, 4.61; S, 10.64.

5-Nitro-5-(*p*-tolylsulfonyl)-2-heptanone (14b). According to the procedure given for the preparation of **13,** 1-nitro-1-(*p*-tolylsulfonyl)propane (2.43 g, 10 mmol) was treated with methyl vinyl ketone (0.77 g, 11 mmol) for 30 min, yield 3.06 g (98%) of **14b:** mp 84.2–84.4° (from EtOH); nmr ($CDCl_3$) δ 0.98 (t, 3 H, J = 8 Hz, CH_3CH_2), 2.20 (s, 3 H, $CH_3C{=}O$), 2.50 (s, 3 H, aryl CH_3), 2.0–3.0 (m, 6 H, CH_2), 7.2–7.9 ppm (m, 4 H, aryl protons); ir (KBr) 1720, 1550, 1350–1280, 1150 cm^{-1}.

Anal. Calcd for $C_{14}H_{19}NO_5S$: C, 53.66; H, 6.11; N, 4.47; S, 10.23. Found: C, 53.78; H, 6.08; N, 4.28; S, 10.25.

5-Nitro-5-(*p*-tolylsulfonyl)-5-phenyl-2-pentanone (14c). According to the procedure given for the preparation of **13,** α-nitrobenzyl *p*-tolyl sulfone (2.91 g, 10 mmol) was treated with methyl vinyl ketone (0.77 g, 11 mmol) for 2 hr, yield 3.41 g (94%) of **14c:** mp 105.4–106.1° (from EtOH); nmr ($CDCl_3$) δ 2.10 (s, 3 H, $CH_3C{=}O$), 2.33 (s, 3 H, aryl CH_3), 2.3–3.4 (m, 4 H, CH_2), 7.0–7.6 ppm (m, 9 H, aryl protons); ir (KBr) 1720, 1550, 1350–1280, 1150 cm^{-1}.

Anal. Calcd for $C_{18}H_{19}NO_5S$: C, 59.82; H, 5.30; N, 3.88; S, 8.87. Found: C, 59.44; H, 5.36; N, 3.80; S, 8.72.

1-Cyano-3-nitro-3-(*p*-tolylsulfonyl)pentane (15). According to the procedure given for the preparation of **13,** 1-nitro-1-(*p*-tolylsulfonyl)propane (2.43 g, 10 mmol) was treated with acrylonitrile (0.58 g, 11 mmol) for 1 hr, yield 1.85 g (62%) of **15:** mp 83.8–85.5° (from EtOH); nmr ($CDCl_3$) δ 0.97 (t, 3 H, J = 7 Hz, CH_3CH_2), 2.26 (q, 2 H, J = 7 Hz, CH_3CH_2), 2.50 (s, 3 H, aryl CH_3), 2.6–3.0 (m, 4 H, CH_2), 7.2–7.9 ppm (m, 4 H, aryl protons); ir (KBr) 2260, 1550, 1350–1280, 1150 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}N_2O_4S$: C, 52.69; H, 5.44; N, 9.45; S, 10.82. Found: C, 52.58; H, 5.49; N, 9.35; S, 10.73.

Registry No.—**1,** 51351-89-4; **2,** 52260-52-3; **3,** 52358-28-8; (*E*)-**4,** 52260-53-4; (*Z*)-**4,** 52260-54-5; **7,** 52341-43-2; **8,** 52341-44-3; **9a** epimer A, 52260-55-6; **9a** epimer B, 52260-56-7; **9b,** 52260-57-8; **9c,** 52260-58-9; **9d,** 52260-59-0; **9e,** 52260-60-3; **9f,** 52260-61-4; (*E*)-**10,** 52260-62-5; (*Z*)-**10,** 52260-63-6; **12,** 52260-64-7; **13,** 52260-65-8; **14a,** 52260-66-9; **14b,** 52260-67-0; **14c,** 52260-68-1; **15,** 52341-45-4; formaldehyde, 50-00-0; sodium benzenesulfinate, 873-55-2; benzaldehyde, 100-52-7; nitrosobenzene, 586-96-9; *p*-dimethylaminonitrosobenzene, 138-89-6; benzofuroxan, 480-96-6; acetyl chloride, 75-36-5; acetaldehyde, 75-07-0; propionaldehyde, 123-38-6; *p*-methylbenzaldehyde, 104-87-0; *p*-chlorobenzaldehyde, 104-88-1; *p*-nitrobenzaldehyde, 555-16-8; methyl vinyl ketone, 78-94-4; 1-nitro-1-(*p*-tolylsulfonyl)ethane, 51351-86-1; 1-nitro-1-(*p*-tolylsulfonyl)propane, 42759-54-6; α-nitrobenzyl *p*-tolyl sulfone, 21272-79-7; acrylonitrile, 107-13-1.

References and Notes

(1) Part III: J. J. Zeilstra and J. B. F. N. Engberts, *Recl. Trav. Chim. Pays-Bas,* **93,** 11 (1974).
(2) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, pp 595, 629.
(3) J. J. Zeilstra and J. B. F. N. Engberts, *Synthesis,* 49 (1974). Although these data should be considered as approximate because of the possibility of some side reaction during the measurements, they nevertheless demonstrate the pronounced acidity of these types of α-nitro sulfones.
(4) S. Hünig and O. Boes, *Justus Liebigs Ann. Chem.,* **579,** 28 (1953).
(5) R. L. Shriner and S. O. Greenlee, *J. Org. Chem.,* **4,** 242 (1939).
(6) (a) A. Dornow and G. Wiehler, *Justus Liebigs Ann. Chem.,* **578,** 113 (1952); (b) A. Dornow and A. Frese, *ibid.,* **581,** 211 (1953).
(7) W. Ried and E. Köhler, *Justus Liebigs Ann. Chem.,* **598,** 145 (1956).
(8) L. A. Carpino, *J. Org. Chem.,* **38,** 2600 (1973).
(9) A. R. Friedman and D. R. Graber, *J. Org. Chem.,* **37,** 1902 (1972).
(10) F. Kröhnke and H. H. Steuernagel, *Chem. Ber.,* **96,** 494 (1963).
(11) D. W. S. Latham, O. Meth-Cohn, and H. Suschitzky, *J. Chem. Soc., Chem. Commun.,* 1040 (1972).

(12) J. J. Zeilstra and J. B. F. N. Engberts, *Recl. Trav. Chim. Pays-Bas*, **92**, 954 (1973).
(13) Compare ref 5.
(14) H. Hellmann and K. Müller, *Chem. Ber.*, **98**, 638 (1965).
(15) C. J. M. Stirling, *Int. J. Sulfur Chem., Part B*, **6**, 277 (1971).
(16) F. G. Bordwell and W. T. Brannen, *J. Amer. Chem. Soc.*, **86**, 4645 (1964).
(17) Compare the decompositon of β-dinitro alcohols under the influence of base: G. A. Shvekhgeimer, N. F. Pyatakov, and S. S. Novikov, *Usp. Khim.*, **28**, 484 (1959); *Chem. Abstr.*, **53**, 16951*d* (1959).
(18) L. F. Cason and C. C. Wanser, *J. Amer. Chem. Soc.*, **73**, 142 (1951).
(19) A. T. Kader and C. J. M. Stirling, *J. Chem. Soc.*, 3686 (1962).
(20) (a) J. M. Larkin and K. L. Kreuz, *J. Org. Chem.*, **36**, 2574 (1971); (b) G. B. Bachman and R. J. Maleski, *ibid.*, **37**, 2810 (1972).
(21) Simple nitroalkanes react easily in the Mannich reaction: H. Hellmann and G. Opitz, "α-Aminoalkylierung," Verlag Chemie, Weinheim/Bergstr., Germany, 1960, p 156; M. Tramontini, *Synthesis*, 703 (1973).
(22) A. Dornow and A. Frese, *Justus Liebigs Ann. Chem.*, **578**, 122 (1952).
(23) W. E. Truce, T. C. Kingler, J. E. Paar, H. Feuer, and D. K. Wu, *J. Org. Chem.*, **34**, 3104 (1969).

Free-Radical Chain Isomerization of *N*-Vinylsulfonamides

W. R. Hertler

Contribution No. 2144 from the Central Research Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware 19898

Received May 7, 1974

Several new *N*-vinylsulfonamides were synthesized and photochemically or thermally caused to isomerize to β-sulfonylvinylamines. The chain length for the isomerization of *N*-methyl-*N*-(α-styryl)-*p*-toluenesulfonamide photoinitiated by benzoin methyl ether is estimated to be 1430.

The irradiation of certain *N*-vinylsulfonamides with high energy electrons was reported to induce a free-radical chain reaction leading to the formation of β-sulfonylvinylamines.[1] The same transformation was found to occur upon photolysis or thermolysis of an azonitrile initiator in the presence of an *N*-vinylsulfonamide.[2] This paper details our study of the generality of the photo- and thermal rearrangement of *N*-vinylsulfonamides and describes the synthesis of several new *N*-vinylsulfonamides.

Stacey, Sauer, and McKusick[1] proposed the mechanism shown in Scheme I for the radiation-induced rearrangement of *N*-methyl-*N*-vinylbenzenesulfonamide to *N*-methyl-2-benzenesulfonylvinylamine. Certain *N*-vinylsulfonamides were found to undergo electron-induced topotactic rearrangement in the crystalline state.

Scheme I

Initiation

$$C_6H_5SO_2N(CH_3)CH{=}CH_2 \longrightarrow R\cdot$$
(1)

$$R\cdot + 1 \longrightarrow C_6H_5SO_2N(CH_3)\dot{C}HCH_2R \downarrow$$

$$C_6H_5SO_2\cdot + CH_3N{=}CHCH_2R$$

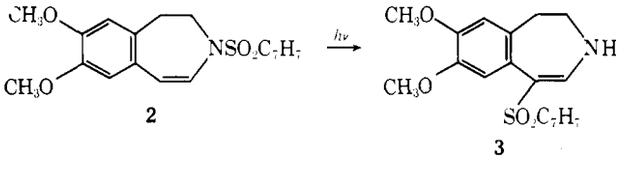
Propagation

$$C_6H_5SO_2\cdot + 1 \longrightarrow C_6H_5SO_2N(CH_3)\dot{C}HCH_2SO_2C_6H_5 \downarrow$$

$$C_6H_5SO_2\cdot + CH_3N{=}CHCH_2SO_2C_6H_5 \downarrow$$

$$CH_3NHCH{=}CHSO_2C_6H_5$$

More recently, Graftieaux and Gardent[3] reported the light-induced rearrangement of 3-*p*-toluenesulfonyl-7,8-dimethoxy-4,5-dihydro-3*H*-benzazepine-3 (**2**) to the sulfone, **3**. A mechanism involving homolytic S–N scission with recombination of the radicals in a solvent cage was suggested; however, no evidence was presented to rule out a Stacey–Sauer–McKusick chain mechanism.



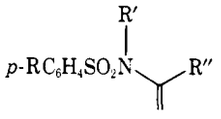
2 3

Table I
***N*-Vinylsulfonamides, *p*-$RC_6H_4SO_2NR'C(R'')=CH_2$**

Compd	R	R′	R″
5[1]	CH_3	CH_3	H
6	CH_3O	CH_3	H
7[4]	CH_3	CH_3	C_6H_5
8	CH_3	*p*-$CH_3OC_6H_4$	C_6H_5
9	CH_3	CH_3	*p*-$CH_3OC_6H_4$
10	Br	CH_3	C_6H_5
11	CH_3	CH_3	*p*-BrC_6H_4
12	CH_3O	CH_3	C_6H_5
13	CH_3	*p*-$(CH_3)_2NC_6H_4$	C_6H_5
14	CH_3	C_2H_5	CH_3
15	H	C_2H_5	CH_3

Results

Synthesis. Three general methods were used for the preparation of the *N*-vinylsulfonamides of general formula **4**. The literature[4] reaction of acetylene with an *N*-alkylar-



4

enesulfonamide was used for the preparation of **4** where R″ = H. For the preparation of *N*-(α-styryl)sulfonamides (**4**, R″ = aryl), the procedure[1] outlined in eq 1 was used, and the procedure of eq 2 was used to prepare *N*-2-(alkenyl)sulfonamides (**4**, R″ = alky). The *N*-vinylsulfonamides prepared by these procedures are listed in Table I. The properties of the new *N*-vinylsulfonamides are summarized in Table II, and the properties of some of the intermediates are summarized in Table III.

The reaction sequence of eq 1 does not appear to be entirely general for the preparation of *N*-(α-styryl)sulfonamides as evidenced by an interesting anomalous reaction which was found to occur in attempting to carry out the first step (eq 1) when R = CH_3, R′ = isopropyl, and R″ =