Base-Induced α Nitration of Sulfones

W. E. Truce, T. C. Klingler, J. E. Paar, H. Feuer, and D. K. Wu

Department of Chemistry, Purdue University, Lafayette, Indiana 47907

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Sulfones are converted into their α-nitro derivatives *via* displacement by sulfone-stabilized carbanions on alkyl nitrates. The α-nitro sulfones are readily converted into the corresponding α-nitro-α-halo sulfones by sequential treatment with base and halogen or by treatment with N-halosuccinimides. Conversion of α-nitro-α-bromobutyl butyl sulfone with potassium amide in liquid ammonia into an octenesulfonamide constitutes a novel extension of the Ramberg–Bäcklund reaction.

In an extension of our studies of the chemistry and synthetic utility of sulfur-stabilized carbanions[1] and of the alkyl nitrate nitration of active methylene compounds,[2] we have found base-induced nitrations with alkyl nitrates to be a useful method for the preparation of α-nitro sulfones.

Base-catalyzed nitration of active methylene groups with alkyl nitrates has previously afforded a synthetic route to simple α-nitronitriles, ketones, and amides.[2,3] Recently, this method has been utilized for the preparation of α-nitrosulfonamides.[1d,4]

The first direct synthesis of an α-nitro sulfone involved the displacement by sodium benzenesulfinate on chloronitromethane to yield nitromethyl phenyl sulfone.[5] Nitration of trissulfonylmethanes was effected by Backer[6] with the use of concentrated nitric and sulfuric acids. A third synthetic approach to α-nitro sulfones involving decarboxylative nitration of β-keto sulfides with alkyl nitrates, followed by oxidation of the crude α-nitro sulfide with acidic hydrogen peroxide, has been reported.[7]

The nitration of sulfone-stabilized carbanions (eq 1)

$$RCH_2SO_2R' \xrightarrow[2.\ R''ONO_2]{1.\ base} [RC(NO_2)SO_2R']^- \tag{1}$$

was found to be influenced by (a) the strength of the base used for carbanion formation, (b) the relative molar ratios of reactants, and (c) the nitration time. Benzylic sulfones were found to undergo nitration in good to excellent yield using the potassium *t*-butoxide–tetrahydrofuran (THF) base–solvent system (see Table I). Reaction periods as noted in the Experimental Section have been optimized. Shorter reaction times resulted in reduced yields. In all cases, material balances were excellent (90–99%). Use of stronger base–solvent systems, *i.e.*, *n*-butyllithium–THF, for the anion formation with benzylic sulfones greatly diminished the yield of product (Table I).[8] Tetramethylethylenediamine (TMEDA) in conjunction with *n*-butyllithium reduced yields even more drastically.

Table I

Nitrations of Sulfones with Alkyl Nitrates

Starting material	Product	Yield, %
$C_6H_5CH_2SO_2C_6H_5$[a]	$C_6H_5CH(NO_2)SO_2C_6H_5$ (**1**)	81
$C_6H_5CH_2SO_2C_6H_5$[b]	$C_6H_5CH(NO_2)SO_2C_6H_5$	36
p-$CH_3C_6H_4SO_2CH_2C_6H_5$[a]	*p*-$CH_3C_6H_4SO_2CH(NO_2)C_6H_5$ (**2**)	79
$(C_6H_5CH_2)_2SO_2$[a]	$C_6H_5CH_2SO_2CH(NO_2)C_6H_5$ (**3**)	82
$(C_6H_5CH_2)_2SO_2$[b]	$C_6H_5CH_2SO_2CH(NO_2)C_6H_5$	40
$(C_6H_5CH_2)_2SO_2$[c]	$C_6H_5CH_2SO_2CH(NO_2)C_6H_5$	9
$C_6H_5CH_2SO_2C_2H_5$[a]	$C_6H_5CH(NO_2)SO_2C_2H_5$ (**4**)	42
$(n\text{-}C_3H_7)_2SO_2$[d]	$n\text{-}C_3H_7SO_2CH(NO_2)CH_2CH_3$[e] (**5**)	39
$(n\text{-}C_4H_9)_2SO_2$[d]	$n\text{-}C_4H_9SO_2CH(NO_2)CH_2CH_2CH_3$ (**6**)	79
$(n\text{-}C_4H_9)_2SO_2$[a]	$n\text{-}C_4H_9SO_2CH(NO_2)CH_2CH_2CH_3$	33
$(CH_3)_2SO_2$[d]	$CH_3SO_2CH_2NO_2$ (**7**)	37
$n\text{-}C_3H_7SO_2C_6H_5$[a]	$CH_3CH_2CH(NO_2)SO_2C_6H_5$ (**8**)	8
$CH_3SO_2C_6H_5$[b]	$NO_2CH_2SO_2C_6H_5$ (**9**)	22
p-$CH_3C_6H_4SO_2CH(CH_3)_2$[b]	*p*-$CH_3C_6H_4SO_2C(CH_3)_2NO_2$ (**10**)	19
$CH_2(CH_2)_3SO_2CH_2$[d]	$CH_2(CH_2)_3SO_2CHNO_2$ (**11**)	17

[a] KO-*t*-Bu–THF. [b] *n*-BuLi–THF. [c] *n*-BuLi–TMEDA. [d] K-NH_2–NH_3. [e] Nmr ($CDCl_3$) δ 1.13 (t, 6, CH_3), 1.5–2.6 (m, 4, $\mathbf{CH_2}CH_3$), 2.8–3.4 (m, 2, $\mathbf{CH_2}SO_2$), and 5.5 (q, 1, $\mathbf{H}CNO_2SO_2$); ir (Nujol) 1577 (NO_2), 1351–1333 and 1153 cm^{-1} (SO_2); calcd mol wt, 195.2; found mol wt, 195.7; however, elemental analysis indicated that impurities were present.

The nitration of alkyl sulfones by treatment with potassium *t*-butoxide in THF produced only low yields of nitration products. However, yields were substantially increased when nitration was performed with the potassium amide–liquid ammonia system[2e] (Table II). The maximum yields were obtained when 3 equiv of potassium amide to 4.5 equiv of alkyl nitrate were employed. Acidification with ammonium chlo-

Table II

Nitration of *n*-Butyl Sulfone with Amyl Nitrate (Potassium Amide–Liquid Ammonia)

KNH_2, mol	Time of anion formation, hr	$AmONO_2$ mol	Acidifying agent	Yield, %	Recovered sulfone
0.11	0.5	0.15	CH_3CO_2H	41.8	35.0[a]
0.11	12.0	0.15	CH_3CO_2H	39.4	35.1[a]
0.2	2.0	0.3	CH_3CO_2H	58.7[b]	20.7[a]
0.2	2.0	0.3	$NH_4Cl(s)$	65.0[b]	23.2[b,c]
0.3	2.0	0.45	$NH_4Cl(s)$	78.8[b]	12.2[b,c]
0.4	2.0	0.6	NH_4Cl	77.3[b]	2.1

[a] The recovered sulfone was obtained by recrystallization from an ether–petroleum ether mixture. [b] Average value of two experiments. [c] The sulfone was recovered by distillation *in vacuo*.

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(1) (a) W. E. Truce and G. D. Madding, *Tetrahedron Lett.*, 3681 (1966). (b) W. E. Truce, C. R. Robbins, and E. M. Kreider, *J. Amer. Chem. Soc.*, **88**, 4027 (1966). (c) W. E. Truce and V. V. Badiger, *J. Org. Chem.*, **29**, 3277 (1964). (d) W. E. Truce, and L. W. Christensen, *Tetrahedron*, **25**, 181 (1969). (e) W. E. Truce and L. B. Lindy, *J. Org. Chem.*, **26**, 1463 (1961); W. E. Truce and R. Lagally, Abstracts of the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

(2) (a) H. Feuer, J. W. Shepherd, and C. Savides, *J. Amer. Chem. Soc.*, **78**, 4364 (1956); (b) H. Feuer and C. Savides, *ibid.*, **81**, 5826 (1959); (c) H. Feuer and B. F. Vincent, Jr., *J. Org. Chem.*, **29**, 939 (1964); (d) H. Feuer and P. M. Pivawer, *ibid.*, **31**, 3152 (1966); (e) H. Feuer, A. M. Hall, S. Golden, and R. L. Reitz, *ibid.*, **33**, 3622 (1968).

(3) (a) H. Wieland, P. Garbisch, and J. J. Chavan, *Justus Liebigs Ann. Chem.*, **461**, 298 (1928); (b) W. Wislicenus and R. Grutzner, *Chem. Ber.*, **42**, 1930 (1909).

(4) B. Loev, F. Kowalo, I. M. Fried, and M. M. Goodman, *Tetrahedron Lett.*, 817 (1968).

(5) J. Troger and E. Nolte, *J. Prakt. Chem.*, **101**, 136 (1920).

(6) H. J. Backer, *Rec. Trav. Chim.*, **68**, 838 (1949).

(7) (a) F. Arndt and J. D. Rose, *J. Chem. Soc.*, 147 (1935); (b) S. Hunig and O. Bose, *Justus Liebigs Ann. Chem.*, **579**, 23 (1953).

(8) Since initial carbanion formation was complete for both bases, the decreased yield with *n*-butyllithium may be a consequence of the cation being lithium rather than potassium; this cation effect has been noted and discussed by others, *e.g.*, (a) M. Hamell and R. Levine, *J. Org. Chem.*, **15**, 162 (1950), and (b) A. A. Morton, *Chem. Rev.*, **35**, 1 (1944).

ride, rather than glacial acetic acid, was found also to give higher yields. Excess alkyl nitrate was necessary to prevent loss of product by destruction of the alkyl nitrate by the base[2e] (eq 2). When dimethyl sulfone

$$\mathrm{RONO_2 + KNH_2 \longrightarrow K^+OR^- + O_2NNH_2} \quad (2)$$

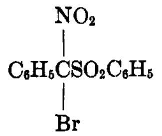
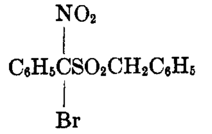
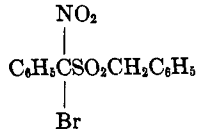
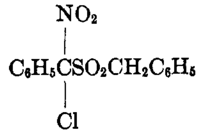
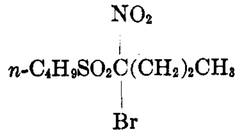
was subjected to the same nitration conditions potassium amide–liquid ammonia, followed by acidification with ammonium chloride or glacial acetic acid, only the potassium salt, **12**, of nitromethyl methyl sulfone (**7**) was obtained. Careful acidification of **12** with dry hydrogen chloride in ether at −5° produced a 37% yield of **7** (eq 3).

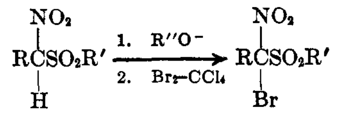
$$\mathrm{CH_3SO_2CH_3} \xrightarrow[\text{3. NH}_4\text{Cl or HOAc}]{\text{1. KNH}_2\ \text{2. AmONO}_2} \underset{\mathbf{12}}{[\mathrm{CH_3SO_2CHNO_2}]^-\mathrm{K}^+} \xrightarrow[\text{ether, }-5^\circ]{\text{HCl}} \underset{\mathbf{7}}{\mathrm{CH_3SO_2CH_2NO_2}} \quad (3)$$

Halogenation of α-nitro sulfones proceeded in excellent yields (Table III). Treatment of a nitro sulfone with sodium alkoxide followed by addition of bromine in carbon tetrachloride at 0° afforded maximum yields of products (eq 4). Bromination of **12** yielded the dibromo rather than the monobromo product (eq 5).

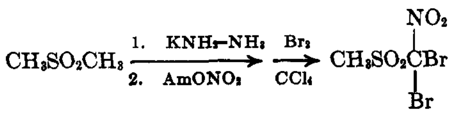
TABLE III

HALOGENATION OF α-NITRO SULFONES

Product	Halogenating agent	Yield, %
 $\mathrm{C_6H_5\overset{NO_2}{\underset{Br}{C}}SO_2C_6H_5}$	Br_2–CCl_4	97
 $\mathrm{C_6H_5\overset{NO_2}{\underset{Br}{C}}SO_2CH_2C_6H_5}$	Br_2–THF	82
 $\mathrm{C_6H_5\overset{NO_2}{\underset{Br}{C}}SO_2CH_2C_6H_5}$	NBS	80
 $\mathrm{C_6H_5\overset{NO_2}{\underset{Cl}{C}}SO_2CH_2C_6H_5}$	NCS	73
 $n\text{-}\mathrm{C_4H_9SO_2\overset{NO_2}{\underset{Br}{C}}(CH_2)_2CH_3}$	Br_2–CCl_4	86
$\mathrm{CH_3SO_2CBr_2NO_2}$	Br_2–CCl_4	32



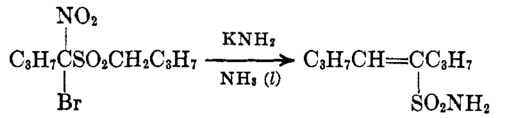
$$\mathrm{R\overset{NO_2}{\underset{H}{C}}SO_2R'} \xrightarrow[\text{2. Br}_2\text{–CCl}_4]{\text{1. R}''\text{O}^-} \mathrm{R\overset{NO_2}{\underset{Br}{C}}SO_2R'} \quad (4)$$



$$\mathrm{CH_3SO_2CH_3} \xrightarrow[\text{2. AmONO}_2]{\text{1. KNH}_2\text{–NH}_3} \xrightarrow[\text{CCl}_4]{\text{Br}_2} \mathrm{CH_3SO_2\overset{NO_2}{\underset{Br}{C}}Br} \quad (5)$$

Halogenation of α-nitrobenzylic sulfones was readily carried out with N-halosuccinimides in refluxing carbon tetrachloride.

Recently the Ramberg–Bäcklund rearrangement of α-halo sulfones has received considerable attention.[9] Treatment of α-nitro-α-bromo-*n*-butyl butyl sulfone with potassium amide in liquid ammonia to yield 4-octene-4-sulfonamide probably proceeded through an analogous pathway (eq 6).



$$\mathrm{C_3H_7\overset{NO_2}{\underset{Br}{C}}SO_2CH_2C_3H_7} \xrightarrow[\text{NH}_3\ (l)]{\text{KNH}_2} \mathrm{C_3H_7CH{=}\underset{SO_2NH_2}{C}C_3H_7} \quad (6)$$

Experimental Section[10]

Reagents.—*n*-Butyllithium was obtained as a 1.6 *M* solution in hexane from Foote Mineral Corp. Potassium *t*-butoxide was purchased from MSA Corp and purified by sublimation. Reagent grade THF was distilled from lithium aluminum hydride prior to use. Ethyl nitrate was purchased from Eastman Organic Chemicals and amyl nitrate (a mixture of *n*-amyl and isoamyl nitrates) was graciously donated by Ethyl Corp. The sulfones were either obtained commercially or prepared by oxidation of the commercially available sulfides with hydrogen peroxide and glacial acetic acid.

General Procedure for the Base-Induced Nitration of Sulfones. A.—The sulfone (0.1 mol) was dissolved in 400 ml of freshly dried THF and the system was flushed with dry nitrogen. Sublimed potassium *t*-butoxide (0.125 mol) was added and stirring continued at room temperature for 4 hr. After cooling to −35°, 0.15 mol of alkyl nitrate was added dropwise and stirring was continued 4 hr. Glacial acetic acid (0.2 mol) was added dropwise and the reaction mixture was allowed to warm to 25°. After the potassium acetate was filtered off, the solvent was removed *in vacuo*, the crude α-nitro sulfone was treated with 10% aqueous sodium hydroxide, and starting material was removed by filtration. Then the aqueous solution was cooled to 0° and carefully acidified with glacial acetic acid, and the α-nitro sulfone was filtered.

B.—The sulfone (0.1 mol) in 400 ml of freshly dried THF under nitrogen was cooled to −35° and 0.1 mol of *n*-butyllithium in hexane was added. After the mixture had stirred for 15 min, 0.125 mol of alkyl nitrate was added dropwise and stirring was continued for 4 hr. The subsequent work-up was carried out as in procedure A.

C.—In a dry 500-ml flask, flushed with nitrogen, were placed 0.3 g-atom of potassium in 250 ml of anhydrous ammonia and a small crystal of $\mathrm{Fe(NO_3)_3\cdot 9H_2O}$. Stirring was continued until the blue slurry had turned gray, at which time 0.1 mol of sulfone in 50 ml of dry THF was added with stirring at −33° over a 5-min period. After the mixture had stirred for 2 hr, 0.45 mol of amyl nitrate was added[11] over a period of 5 min and the reaction mixture was stirred an additional 10 min. The reaction mixture was cooled to −50° and 0.4 mol of solid ammonium chloride was slowly added. The ammonia was replaced with anhydrous ether over a 6-hr period and the solution was acidified with 0.16 mol of glacial acetic acid. The residue, after filtration and removal of solvent, was treated in the same manner as described in procedure A to obtain pure product.

α-Nitrobenzyl Phenyl Sulfone (1). A.—Benzyl phenyl sulfone (24 g, 0.103 mol) was treated according to procedure A with potassium *t*-butoxide (15 g, 0.135 mol) and ethyl nitrate (22 g,

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[9] (a) L. Ramberg and B. Bäcklund, *Ark. Kemi Mineral. Geol.*, **13A**, No. 27 (1940); *Chem. Abstr.*, **34**, 4725 (1940). (b) L. A. Paquette, *J. Amer. Chem. Soc.*, **86**, 4089 (1964). (c) L. A. Carpino and L. V. McAdams, *ibid.*, **87**, 5804 (1965). (d) L. A. Paquette, *Accounts Chem. Res.*, **1**, 209 (1968). (e) F. G. Bordwell, J. M. Williams, Jr., and B. B. Jarris, *J. Org. Chem.*, **33**, 2026 (1968).

[10] All melting points are uncorrected. The nmr spectra were obtained using a Varian A-60 spectrophotometer. Microanalyses were performed by Dr. C. S. Yeh and staff. Molecular weights were determined with a vapor phase osmometer, Model 301A.

[11] Care must be exercised in the addition of the first few drops of alkyl nitrate to prevent violent reaction.

0.252 mol). Recrystallization from ethanol gave 22.3 g (81%) of **1**: mp 137–139°; nmr ($CDCl_3$) δ 6.50 (s, 1, $HCNO_2SO_2$) and 7.1–7.8 (m, 10, aromatic H).

Anal. Calcd for $C_{13}H_{11}NSO_4$: C, 56.32; H, 4.00; N, 5.05; S, 11.54; mol wt, 277. Found: C, 56.25; H, 4.17; N, 5.04; S, 11.40; mol wt, 280.

B.—When benzyl phenyl sulfone (10 g, 0.043 mol) was treated according to procedure B with *n*-butyllithium in hexane (0.052 mol) and ethyl nitrate (6.4 g, 0.07 mol), 4.3 g (36%) of **1** was isolated.

α-Nitrobenzyl *p*-Tolyl Sulfone (2).—*p*-Tolyl benzyl sulfone (24.6 g, 0.1 mol) was treated according to procedure A with potassium *t*-butoxide (16.8 g, 0.15 mol) and ethyl nitrate (14.6 g, 0.16 mol). Recrystallization from ethanol gave 23 g (79%) of **2**: mp 162–163°; nmr ($CDCl_3$) δ 2.45 (s, 3, $C_6H_4CH_3$), 6.41 (s, 1, $HCNO_2SO_2$), and 7.39 (m, 9, aromatic H).

Anal. Calcd for $C_{14}H_{13}NSO_4$: C, 57.80; H, 4.47; N, 4.82; S, 11.0; mol wt, 291. Found: C, 57.66; H, 4.48; S, 11.03; mol wt, 296.

α-Nitrobenzyl Benzyl Sulfone (3). A.—Benzyl sulfone (64.64 g, 0.262 mol) was treated according to procedure A with potassium *t*-butoxide (32.6 g, 0.290 mol) and ethyl nitrate (24.7 g, 0.272 mol). Recrystallization from absolute ethanol gave 62.5 g (82%) of **3**: mp 153–154°; nmr ($CDCl_3$) δ 4.6 (q, 2, SO_2CH_2), 6.2 (s, 1, $HCNO_2SO_2$), and 7.35 (m, 10, aromatic H).

B.—To a solution of *n*-butyllithium (0.048 mol) in 300 ml of dry THF under nitrogen was added TMEDA (5.57 g, 0.048 mol) dropwise at 5°. After stirring for 30 min, the solution was cooled to −20° and benzyl sulfone (10 g, 0.0423 mol) dissolved in 100 ml of THF was added dropwise. The solution was stirred for 30 min at −35° and ethyl nitrate (6.83 g, 0.075 mol) was added. After 4 hr the reaction mixture was acidified with glacial acetic acid and **3** was isolated (9%).

Anal. Calcd for $C_{14}H_{13}NSO_4$: C, 57.72; H, 4.50; N, 4.81; S, 10.98; mol wt, 291.3. Found: C, 57.55; H, 4.66; N, 4.72; S, 11.14; mol wt, 293.

α-Nitrobenzyl Ethyl Sulfone (4).—Benzyl ethyl sulfone (9.2 g, 0.05 mol) was treated according to procedure A with potassium *t*-butoxide (11.2 g, 0.1 mol) and ethyl nitrate (10.0 g, 0.11 mol). The product was purified by chromatography on a silica gel column eluting with CH_2Cl_2. Recrystallization from ether gave 4.8 g (42%) of **4**: mp 50–51°; nmr ($CDCl_3$) δ 1.15 (t, 3, CH_2CH_3), 3.25 (q, 2, CH_2CH_3), 6.45 (s, 1, $HCNO_2SO_2$), and 7.45 (m, 5, aromatic H).

Anal. Calcd for $C_9H_{11}NSO_4$: C, 47.15; H, 4.84; N, 6.11; S, 13.99. Found: C, 47.35; H, 5.11; N, 6.20; S, 14.05.

1-Nitrobutyl Butyl Sulfone (6). A.—According to procedure C, *n*-butyl sulfone (17.8 g, 0.1 mol) was treated with potassium amide (0.3 mol) and amyl nitrate (59.9 g, 0.45 mol). Distillation of the product gave 17.6 g (78.8%) of **6**: bp 110–112° (0.5 mm); $n^{20}D$ 1.4690–1.4700; ir (film) 2981 and 2880 (CH), 1569 (NO_2), and 1141 cm^{-1} (SO_2); nmr (CCl_4) δ 5.33 (q, 1, $HCNO_2SO_2$), 3.17 (t, 2, H_2CSO_2), 2.1–2.6 (m, 2, H_2CCHNO_2), 1.2–2.1 (m, 6, CH_2), and 0.78–1.2 (t, 6, CH_3).

Anal. Calcd for $C_8H_{17}NO_4S$: C, 43.0; H, 7.69; N, 6.28; S, 14.34. Found: C, 43.19; H, 7.67; N, 6.06; S, 14.44.

B.—By treating *n*-butyl sulfone (8.9 g, 0.05 mol) according to procedure A with potassium *t*-butoxide (8.4 g, 0.075 mol) and amyl nitrate (6.8 g, 0.05 mol), there was obtained 3.70 g (33.2%) of **6**.

Nitromethyl Methyl Sulfone (7).—To a suspension of potassium amide (0.3 mol) in 250 ml of liquid ammonia, 9.4 g (0.1 mol) of methyl sulfone was slowly added at −33°, and the reaction mixture was stirred for 2 hr. Then, 59.9 g (0.45 mol) of amyl nitrate was rapidly added (5 min). Stirring was continued for 10 min more; then the ammonia was replaced by anhydrous ether at room temperature. During this time the yellow, crude potassium salt **12** precipitated. The reaction mixture was cooled to −5° and anhydrous hydrogen chloride was introduced for 2 hr. The solid material was removed by filtration, and ether and HCl were removed *in vacuo*. The remaining liquid was dissolved in 50 ml of ether and the solution was extracted with water. After the ether was removed *in vacuo*, the remaining liquid was dissolved in 25 ml of absolute ethanol. On the addition of 350 ml of petroleum ether (bp 60–70°), 5.2 g (37%) of **7** precipitated. Recrystallization from methanol followed by sublimation at −30° (0.2 mm) gave pure **7**: mp 51.5–52.5°; ir (KBr) 3028–2950 (CH), 1569–1558 (NO_2), 1332 and 1178–1137 cm^{-1} (SO_2); nmr (d_6-DMSO) δ 3.39 (s, 3, O_2SCH_3) and 6.49 (s, 2, $O_2SCH_2NO_2$).

Anal. Calcd for $C_2H_5NO_4S$: C, 17.26; H, 3.62; N, 10.01; S, 23.00. Found: C, 17.48; H, 3.60; N, 9.95; S, 22.89.

1-Nitropropyl Phenyl Sulfone (8).—Phenyl *n*-propyl sulfone (27.65 g, 0.15 mol) was treated according to procedure A with potassium *t*-butoxide (22.4 g, 0.2 mol) and ethyl nitrate (20 g, 0.22 mol). Recrystallization from methanol gave an 8% yield of **8**: mp 58–60°; nmr ($CDCl_3$) δ 1.05 (t, 3, CH_2CH_3), 2.3 (m, 2, CH_2), 5.4 (q, 1, SO_2CHNO_2), and 7.5–7.9 (m, 5, aromatic H).

Anal. Calcd for $C_9H_{11}NO_4S$: C, 47.17; H, 4.84; N, 6.11; S, 13.96; mol wt, 229. Found: C, 47.16; H, 4.71; N, 5.82; S, 13.85; mol wt, 230.

1-Nitromethyl Phenyl Sulfone (9).—Phenyl methyl sulfone (5.0 g, 0.032 mol) was treated according to procedure B with *n*-butyllithium (0.035 mol) and ethyl nitrate (3.46 g, 0.038 mol). Recrystallization from 95% ethanol afforded 1.48 g (22%) of **9**: mp 150–150.5° (lit.[7] mp 151°); nmr ($CDCl_3$) δ 5.82 (s, 2, CH_2) and 7.70 (m, 5, aromatic H).

(α-Nitroisopropyl) *p*-Tolyl Sulfone (10).—*p*-Tolyl isopropyl sulfone (7.93 g, 0.04 mol) was treated according to procedure B with *n*-butyllithium (0.042 mol) and ethyl nitrate (4.0 g, 0.044 mol). The nitration mixture was acidified after 5 min. Purification on a silica gel column (eluent, CH_2Cl_2) gave 1.82 g (19%) of **10**: mp 110.5–111°;[12] nmr ($CDCl_3$) δ 1.98 (s, 6, *i*-$PrCH_3$), 2.50 (s, 3, $C_6H_4CH_3$), and 7.68 (m, 4, aromatic H).

Anal. Calcd for $C_{10}H_{13}NO_4S$: C, 49.50; H, 5.38; N, 5.76; S, 13.20. Found: C, 49.68; H, 5.62; N, 5.80; S, 13.06.

2-Nitrotetrahydrothiopyran 1,1-Dioxide (11).—Tetrahydrothiopyran 1,1-dioxide (6.7 g, 0.05 mol) was treated according to procedure C with potassium amide (0.15 mol) and amyl nitrate (30 g, 0.225 mol) to obtain 1.6 g (17%) of **11**: mp 136–137°; nmr ($CDCl_3$) δ 1.8 (m, 4, CH_2), 2.45 (m, 2, CH_2CHNO_2), 3.50 (m, 2, CH_2SO_2), and 6.20 (q, 1, $CHNO_2$).

Anal. Calcd for $C_5H_9NO_4S$: C, 33.5; H, 5.08; N, 7.81; S, 17.85. Found: C, 33.54; H, 5.03; N, 7.51; S, 17.55.

α-Bromo-α-Nitrobenzyl Phenyl Sulfone.—Sodium (0.23 g, 0.01 g-atom) was dissolved in 150 ml of absolute ethanol and 2.8 g (0.01 mol) of **1** was added. After the mixture had stirred for 7 hr at room temperature, bromine dissolved in ethanol was added dropwise until a yellow color persisted and the reaction mixture was stirred overnight. Removal of solvent, extraction with water, and recrystallization from ethanol gave 3.4 g (97%) of the brominated nitro compound, mp 90–91°.

Anal. Calcd for $C_{13}H_{10}BrNO_4S$: C, 43.87; H, 2.81; N, 3.93; S, 8.95; Br, 22.45. Found: C, 43.93; H, 3.04; N, 3.74; S, 9.07; Br, 22.78.

1-Bromo-1-nitrobutyl Butyl Sulfone.—To a suspension of sodium methoxide (1.4 g, 0.026 mol) in 100 ml of anhydrous ether, 5.8 g (0.026 mol) of **6** was slowly added at 0°. After the mixture had stirred for 3 hr, a 5% solution of bromine in carbon tetrachloride was slowly added over a 6-hr period until the bromine color persisted. The solution was concentrated and extracted with aqueous base and dilute acetic acid. Distillation yielded 6.75 g (86%) of product: bp 110–112° (0.5 mm); $n^{20}D$ 1.5002; ir (film) 2949 and 2862 (CH), 1581 (NO_2), and 1379–1290 and 1156 cm^{-1} (NO_2 and SO_2); nmr (CCl_4) δ 3.08–3.91 (m, 2, CH_2SO_2), 2.30–3.08 (m, 2, CH_2CBrNO_2), 1.28–2.30 (m, 6, CH_2), and 0.78–1.28 (t, 6, CH_3).

Anal. Calcd for $C_8H_{16}BrNO_4S$: C, 31.79; H, 5.34; Br, 26.40; N, 4.63; S, 10.60. Found: C, 31.96; H, 5.40; Br, 26.60; N, 4.44; S, 10.37.

Dibromonitromethyl Methyl Sulfone.—To the crude potassium salt **12** was added a 5% solution of bromine in carbon tetrachloride at 0° until the color of bromine persisted (6 hr). The solution was filtered and solvent was removed *in vacuo*. The residue was taken up in ether and extracted with water, the ether was removed, and the residue was recrystallized from a 1:3 ether–carbon tetrachloride mixture to yield 4.0 g (32%) of dibromonitromethyl methyl sulfone, mp 165–168°. Subliming at 80° (0.2 mm) gave the analytical sample: mp 167–168°; ir (KBr) 3030 and 2941 (CH), 1588 (NO_2), and 1343–1207 and 1156 cm^{-1} (NO_2 and SO_2); nmr ($CDCl_3$) δ 3.67 (s, 3, O_2SCH_3).

Anal. Calcd for $C_2H_3Br_2NO_4S$: C, 8.10; H, 1.02; Br, 53.85; N, 4.72; S, 10.80. Found: C, 7.89; H, 1.00; Br, 53.66; N, 4.78; S, 10.97.

α-Bromo-α-nitrobenzyl Benzyl Sulfone. A.—Under a nitrogen atmosphere at −40°, **3** (5.83 g, 0.02 mol) was added to a solution of 2.24 g (0.02 mol) of potassium *t*-butoxide in 75 ml of

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[12] This experiment was performed by L. W. Christensen, Ph.D. Thesis, Purdue University, 1969.

THF. After stirring for 3.5 hr, this solution was added slowly to 2.19 ml (0.04 mol) of bromine dissolved in 100 ml of dry THF at −40°. Stirring at this temperature was continued for 4 hr and then the solution was allowed to warm to 25°. The solvent was removed *in vacuo;* the residue was taken up in 200 ml of chloroform and extracted with water. After the extract was dried ($MgSO_4$) and decolorized with charcoal, the solvent was removed. The remaining oil crystallized on standing at 0° and was recrystallized from ethanol to yield 6.01 g (81.3%) of α-bromo-α-nitrobenzyl benzyl sulfone, mp 108–109°.

B.—In 500 ml of Spectrograde carbon tetrachloride was suspended 10 g (0.0342 mol) of **3** and 13 g (0.07 mol) of N-bromosuccinimide. The suspension was refluxed under nitrogen and irradiated with a sun lamp for 14 hr. After chilling, the solution was filtered, the solvent was removed *in vacuo,* and the residue was recrystallized from ethanol to give 9.6 g (80%) of α-bromo-α-nitrobenzyl benzyl sulfone.

Anal. Calcd for $C_{14}H_{12}BrNO_4S$: C, 45.42; H, 3.27; N, 3.78; Br, 21.58; S, 8.66; mol wt, 370.2. Found: C, 45.52; H, 3.50; N, 3.68; Br, 21.70; S, 8.65; mol wt, 372.

α-Chloro-α-nitrobenzyl Benzyl Sulfone.—Compound **3** (5 g, 0.0171 mol) and N-chlorosuccinimide (4.55 g, 0.0342 mol) dissolved in 250 ml of carbon tetrachloride were refluxed and irradiated under nitrogen for 19 hr. Cooling, filtration, and removal of solvent yielded an oil. Eluting through a silica gel column with chloroform and recrystallizing from ethanol gave 4.1 g (73%) of α-chloro-α-nitrobenzyl benzyl sulfone, mp 81–82°.

Anal. Calcd for $C_{14}H_{12}ClNO_4S$: C, 51.6; H, 3.72; N, 4.30; Cl, 10.9; S, 9.85. Found: C, 51.8; H, 3.81; N, 4.38; Cl, 10.95; S, 10.09.

4-Octene-4-sulfonamide.—Stirring 9.0 g (0.03 mol) of 1-bromo-1-nitrobutyl butyl sulfone with potassium amide (0.09 mol) in 150 ml of liquid ammonia for 1 hr at −33° gave a brown solution. Solid ammonium chloride (0.1 mol) was slowly added at −50°, the ammonia was replaced by ether, and glacial acetic acid was added until the ether solution was neutral. After filtration, the ether layer was concentrated to 40 ml and extracted with two 30-ml portions of 10% aqueous potassium hydroxide. The aqueous layer was acidified with acetic acid and extracted with ether. The extract was concentrated to 30 ml and 30 ml of petroleum ether (bp 60–70°) was added. Further concentration to 40 ml and cooling gave 2.2 g (40%) of colorless crystals, mp 94.5–97°. Recrystallization from a 1:1 benzene–petroleum ether (60–70°) mixture and subsequent sublimation at 80° (0.2 mm) gave pure product: mp 97–98°; ir (KBr) 3330 and 3213 (NH_2), 2940 (CH), and 1317 and 1167 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 6.64 (t, 1, HC=C), 5.07 (s, 2, NH_2), 1.90–2.60 (m, 4, CH_2C=C), 1.17–1.90 (m, 4, CH_2), and 0.76–1.17 (t, 6, CH_3).

Anal. Calcd for $C_8H_{17}NO_2S$: C, 50.19; H, 8.96; N, 7.36; S, 16.86. Found: C, 49.98; H, 9.06; N, 7.11; S, 16.91.

Registry No.—**1,** 21272-78-6; **2,** 21272-79-7; **3,** 21272-80-0; **4,** 21272-81-1; **6,** 21272-82-2; **7,** 21272-83-3; **8,** 21272-84-4; **9,** 21272-85-5; **10,** 21272-86-6; **11,** 21272-87-7; α-bromo-α-nitrobenzyl phenyl sulfone, 21272-88-8; 1-bromo-1-nitrobutyl butyl sulfone, 21272-89-9; dibromonitromethyl methyl sulfone, 21272-90-2; α-bromo-α-nitrobenzyl benzyl sulfone, 21272-91-3; α-chloro-α-nitrobenzyl benzyl sulfone, 21272-92-4; 4-octene-4-sulfonamide, 21272-93-5.

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The Isomerization of the Xylenes Using Zeolite Catalysts

M. A. LANEWALA AND A. P. BOLTON

Union Carbide Corporation, Linde Division, Molecular Sieve Department, Tonawanda, New York 14150

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The isomerization of the xylenes, catalyzed by partially multivalent metal cation exchanged, partially decationized Type Y zeolites, is invariably accompanied by transalkylation, and the degree of isomerization is proportional to the extent of transalkylation. An equilibrium distribution of the xylenes is obtained when over 50% transalkylation has occurred in agreement with calculated values. Data from the transalkylation of the trimethylbenzenes with benzene indicated that this reaction proceeds *via* a bimolecular mechanism. Such a mechanism, involving a diphenylalkane-type transition state, is proposed for xylene isomerization and satisfactorily accounts for the observed results.

The isomerization of the xylenes has received considerable attention in the literature, and the xylenes are used as model compounds in the elucidation of reaction mechanisms for the positional isomerization of alkylaromatics. The usually accepted mechanism[1] involves the addition of a proton, furnished by an acid catalyst, to the alkylbenzene at the ring carbon holding the alkyl group, followed by a 1,2 shift of the methyl group. However, such a mechanism neglects to account for the presence of transalkylation products which are considered to be derived from side reactions. Unseren and Wolf[2] have shown that 1,2 shifts can only compete with the transalkylation reactions, and Allen, Yats, and coworkers[3,4] have shown that the product isomers derived from the isomerization of alkylaromatics can be due to both intra- and intermolecular reactions, the individual contributions being a function of the structure of the alkylaromatic. Recent work on the isomerization of the diethylbenzenes[5] and *t*-butylphenols[6] has shown that a mechanism for positional isomerization *via* transalkylation satisfactorily accounts for the occurrence of transalkylated products. The objective of this study was to follow closely the composition of the transalkylation products formed during the isomerization of xylenes with a crystalline catalyst derived from a Type Y zeolite and determine the role of transalkylation in this reaction.

Results

Initial experiments showed that the isomerization of the xylenes over a zeolite catalyst is accompanied by a transalkylation reaction. To determine the extent of

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(1) A. P. Lien and D. A. McCauley, *J. Amer. Chem. Soc.*, **74**, 6246 (1952).

(2) E. Unseren and A. P. Wolf, *J. Org. Chem.*, **27**, 1509 (1962).

(3) R. H. Allen, L. D. Yats, and D. S. Erley, *J. Amer. Chem. Soc.*, **82**, 4853 (1960).

(4) R. H. Allen, *ibid.*, **82**, 4856 (1960).

(5) A. P. Bolton, M. A. Lanewala, and P. E. Pickert, *J. Org. Chem.*, **33**, 1513 (1968).

(6) A. P. Bolton, M. A. Lanewala, and P. E. Pickert, *ibid.*, **33**, 3415 (1968).