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BASE-INDUCED α-NITRATION OF SULFONAMIDES

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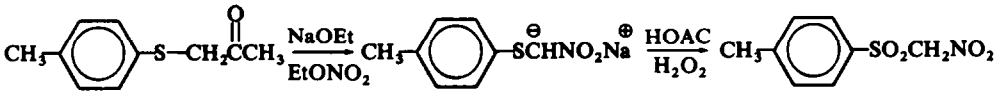
Abstract—A general procedure has been devised for the preparation of α-nitrosulfonamides. Benzylic sulfonamides, and a wide variety of N,N-dialkylalkanesulfonamides may be converted to the corresponding nitrosulfonamides via displacement by a sulfonamide-stabilized carbanion on an alkyl nitrate.

IN OUR continuing studies[1] of the chemistry and synthetic utility of sulfur-stabilized carbanions, i.e.

$$\text{sulfur—}\overset{|}{\underset{|}{\text{C}}}\text{:}^{\ominus} + \text{AB} \rightarrow \text{sulfur—}\overset{|}{\underset{|}{\text{C}}}\text{—A} + \text{B:}^{\ominus}$$

(where AB = —COCl,[2] —$\overset{|}{\underset{|}{\text{C}}}$—X,[3] X_2,[4] $RSO_3\emptyset$,[5] O_2N—OR[6]), we have found base-induced nitrations with alkyl nitrates* to be a useful general approach to α-nitrosulfonamides.†

Although the synthesis of α-nitrosulfonamides has only recently been realized, and knowledge of the parent α-nitrosulfonic acids is very limited,[7,8] other α-nitrosulfur compounds have previously been prepared. Arndt and Rose[9] utilized the base-induced nitration of a β-ketosulfide in the preparation of *p*-toluenesulfonylnitromethane, **11**,



10 **11**

This method was also used by Hunig and Bose[10] for the preparation of methylsulfonylnitromethane from methyl mercaptoacetone. Kharasch and Cameron[11] devised an alternate synthesis of α-nitrosulfides via the reaction of sulfenyl halides with the salts of nitroalkanes. The α-nitrosulfides produced were oxidized to the corresponding α-nitrosulfones. A more direct method, however, for the preparation of α-nitrosulfones consists of the displacement by an aryl or alkyl sulfinate salt on a halonitroalkane.[11,12]

* α-Nitration of sulfur-stabilized carbanions has been realized not only with sulfonamides but also with sulfones, sulfoxides, etc.—J. E. Parr, Ph.D. Thesis, Purdue University, 1967, and other unpublished work in this department, some in collaboration with Professor H. Feuer.

† The preparation of $\phi CH(NO_2)SO_2NMe_2$ has been described by a like method.[7]

An additional method for the preparation of α-nitrosulfur compounds was devised by Backer[13] when he demonstrated that *tris*-sulfonylmethanes could be nitrated using a mixture of concentrated nitric and sulfuric acids.

The preceding methods for the preparation of α-nitrosulfides or sulfones appear less applicable to α-nitrosulfonamides. Instead the more promising procedure involving a strong base and an alkyl nitrate[14] to effect the desired conversion was utilized. This method for the introduction of a nitro grouping into an organic moiety has been extensively applied to other active methylene groups such as simple nitriles, ketones and amides.[15]

A sulfonamide-stabilized carbanion reacts with an alkyl nitrate to afford the α-nitrosulfonamide. The following mechanistic pathway may be operative. If R or R′ in **12** is hydrogen, then the additional step, forming

$$RR'CHSO_2NR''_2 + \overset{\ominus}{B}: \xrightarrow[0°]{THF} RR'\overset{\ominus}{C}SO_2NR''_2$$

12

$$\mathbf{12} + O_2N{-}OEt \xrightarrow[-30°]{THF} RR'C(NO_2)SO_2NR''_2 + \overset{\ominus}{O}Et$$

the anion of the nitro compound, **13** occurs. However, it can be concluded that

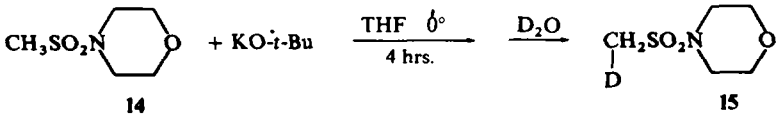
$$\begin{matrix} NO_2 \\ | \\ RCHSO_2NR''_2 \end{matrix} + \overset{\ominus}{O}Et \rightarrow R\overset{\ominus}{C}(NO_2)SO_2NR''_2 + EtOH$$

13

the formation of the stable anion, **13**, is not a necessary driving force in the reaction, since tertiary systems such as **6** and **8**, in which the formation of **13** is not possible, may easily be prepared, (Table 1).

While potassium t-butoxide has been found to be an adequate base for benzylic systems, it was necessary to use the stronger base, n-butyllithium for the aliphatic sulfonamides.

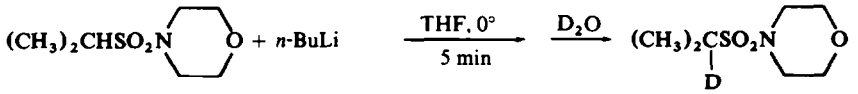
The greater effectiveness of n-butyllithium in forming the anion was demonstrated through quenching experiments. For example, treatment of **14** with potassium t-butoxide followed by deuterium oxide gave **15**, which was shown, by mass spectrometry, to be only 18% α-monodeuterated.



14 **15**

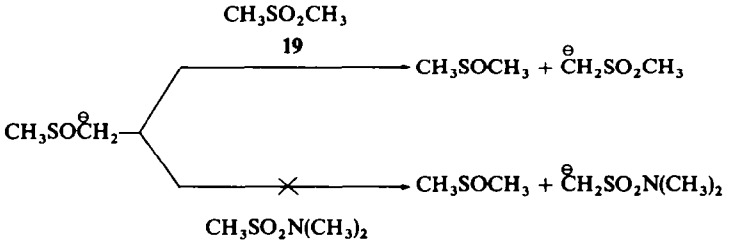
In contrast, when **14** was treated with an equal molar amount of *n*-butyllithium for five minutes and then similarly quenched with deuterium oxide, **15** was 77% α-monodeuterated. Even the tertiary system, **16**, was 77% metallated when it was treated with

n-butyllithium. Furthermore, the need for a powerful base to form the anion from a simple sulfonamide is consistent with the observations of Corey and Chaykovsky,[16]



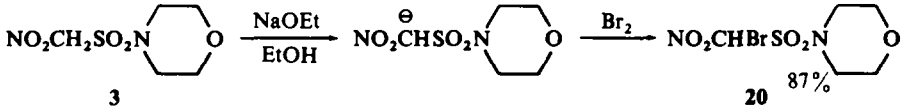
16

who showed that N,N-dimethylmethanesulfonamide, **18**, is less acidic than dimethyl sulfone, **19**, through a study of the following competition.



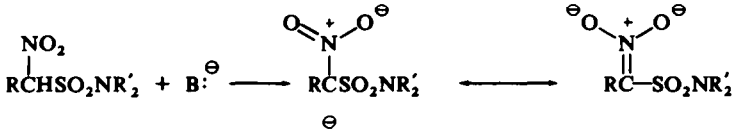
In the benzylic systems higher yields of α-nitrosulfonamide are obtained with potassium t-butoxide as base rather than n-butyllithium. It has been shown that the nature of the cation affects the basicity of the anion,[17] and it may be expected that if organo-alkalies, such as **12**, exist as ion pairs in organic solvents, e.g. tetrahydrofuran, the cation with the greater electron attracting ability would lower the nucleophilicity of the anion. This effect should be most pronounced in a reaction in which a great deal of nucleophilic "push" is needed, i.e. those reactions involving poor leaving groups. Since alkoxide is a poor leaving group, this may explain the moderate yields obtained when n-butyllithium was utilized.*

Several reactions of the α-nitrosulfonamides have been studied. Those α-nitrosulfonamides possessing at least one α hydrogen can be brominated in good yield.



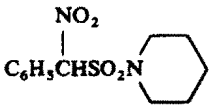
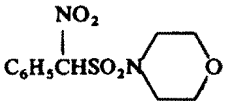
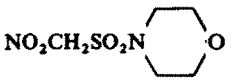
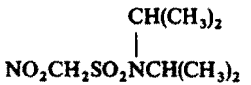
3 20 87%

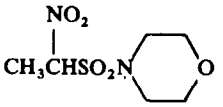
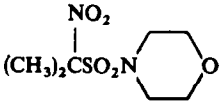
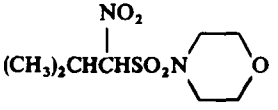
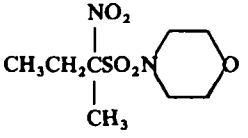
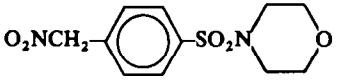
The ambident nitronate anion[18] formed from treatment of an appropriate α-nitrosulfonamide



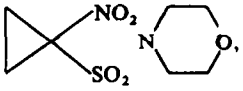
* A similar "cation effect" has been found when a sulfone was nitrated using either lithium or potassium bases. See footnote* on page 181.

TABLE 1. α-NITROSULFONAMIDES

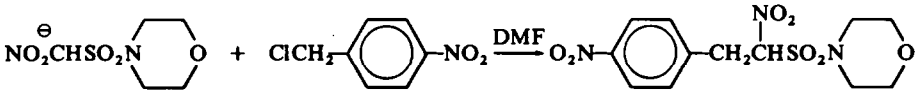
No.	Compound	mp(bp)	Yield[a]	Calcd. %				Found %			
				C	H	N	S	C	H	N	S
1		81–82°	64[b]	50·75	5·67	9·85	11·26	50·64	5·84	9·87	11·21
2		(146–148/0·01)	66[b]	46·20	4·85	9·78	11·18	45·92	4·62	9·53	11·41
3		106–107°	31[c]	28·58	4·79	13·30	15·20	28·86	4·87	13·46	14·95
4		93–94°	25[c]	37·44	7·19	12·50	14·27	37·73	7·12	12·28	14·32

5		95–96°	36[c]	32·13	5·39	12·50	14·28	32·40	5·48	12·71	14·20
6		158–159°	46[c]	32·25	5·98	11·76	13·55	35·35	6·10	11·53	13·66
7		48–49°	39[c]	38·30	6·40	11·10	12·60	38·34	6·57	11·16	12·24
8		85–86°	35[c,d]	38·30	6·39	11·11	12·60	38·54	6·50	11·08	12·43
9		136–137°	21[c]	46·14	4·93	9·78	11·18	46·17	5·10	9·71	11·23

[a] Isolated, purified material. [b] KO-t-Bu used as base. [c] n-BuLi used as base. [d] Purified via Silica Gel column.

Note added in proof. The scope of this synthetic procedure has been extended by the preparation of the following compounds: $\phi CH(NO_2)SO_2N(CH_3)\phi$, m.p. 93–94°; $\phi CH(NO_2)SO_2NHC(CH_3)_3$, m.p. 99–100°; $CH_3CH_2CH(NO_2)SO_2N$  O, m.p. 76–77°, and  O, m.p. 114–115·5°; see L. W. Christensen, Ph.D. Thesis, Purdue University, 1969, for experimental details.

with base, did not afford an alkylation product when treated with an alkyl halide such as benzyl chloride. The only pure product isolated when **3** was treated in the preceding manner was benzaldehyde. This may arise via initial oxygen alkylation followed by decomposition of the unstable nitronate ester.[19] However, when the anion of **3** was treated with *p*-nitrobenzyl chloride in DMF a good yield of the C-alkylation product was obtained.



21 **22**

These divergent results suggest that the C-alkylation product arises via a route other than direct displacement. This transformation may proceed by a radical anion mechanism as has been proposed for C-alkylation of simpler aliphatic nitro compounds with ortho or para nitrobenzyl halides.[20]

To date, we have been unable to effect a condensation of a nitro-anion such as **21** with a Michael acceptor system. This unexpected lack of reactivity for a nitro-anion may be due to a combination of the steric effects of the sulfonyl grouping[21] and the stability of the anion itself.

In light of the recent report describing a thiophenoxide displacement on a halomethyl sulfone,[22] nitration of a sulfonamide was attempted via nitrite anion attack on a bromomethanesulfonamide in DMF.[23] Most of the starting bromomethanesulfonamide was recovered unchanged. If the analogous α-halosulfone reaction[22] proceeds by attack on halogen, displacing a sulfonyl stabilized carbanion i.e.

$$Nu\!:\! + Br\!-\!CH_2SO_2R \rightarrow [Nu\!-\!Br + \overset{\ominus}{C}H_2SO_2R],$$

then the lack of reactivity in the α-halosulfonamides may reflect the increased basicity of the $\overset{\ominus}{C}H_2SO_2NR_2$ carbanion (poorer leaving group) as compared to the $\overset{\ominus}{C}H_2SO_2R$ carbanion. However, if the displacement proceeds by nucleophilic attack on carbon, the lack of reaction in the present system may simply reflect the decreased nucleophilicity of the nitrite ion as compared to the thiophenoxide anion.[24]

EXPERIMENTAL

All m.ps are uncorrected. Mass spectra were recorded on a Hitachi RMU-6A instrument using a heated inlet system. The NMR spectra were obtained in $CDCl_3$ using a Varian A-60 spectrometer with TMS=O. The NMR spectral data are reported as chemical shift (multiplicity, integrated intensity), with s, d, t, q, m referring to singlet, doublet, triplet, quartet and multiplet, respectively. Microanalyses were performed by Dr. C. S. Yeh and staff.

Reagents. t-BuOK was purchased from MSA Corporation and purified by sublimation. n-BuLi was used as a 1·6M soln in hexane purchased from Foote Mineral Corporation. Reagent grade THF was distilled from LAH prior to use. $EtNO_3$ was obtained commercially as were the amines and also methane, ethane, α-toluene and *p*-toluenesulfonyl chlorides. 2-Propanesulfonyl chloride and 2-butanesulfonyl chloride were prepared according to known procedures.[25]

General procedure for preparation of sulfonamides. To a soln of 0·13 mole Et_3N (Matheson, Coleman and Bell), and 0.13 mole secondary or primary amine in 200 ml THF stirred under N_2 and cooled to 0° was slowly added a soln of 0·12 mole alkanesulfonyl chloride in 50 ml THF. The mixture was stirred for

1 hr, and the precipitated $Et_3N \cdot HCl$ filtered off. The filtrate was evaporated *in vacuo* and the resulting solid recrystallized from 90% EtOH.

Morpholine α-toluenesulfonamide. α-Toluenesulfonyl chloride (19·07 g, 0·10 mole) afforded 20·0 g (83%) morpholine α-toluenesulfonamide, m.p. 174–175°; NMR: δ 3·16 (m, 4), 3·64 (m, 4), 4·29 (s, 2), 7·50 (s, 5).

Piperidine α-toluenesulfonamide. α-Toluenesulfonyl chloride (23·8 g, 0·125 mole) gave 23·9 (80%) piperidine α-toluenesulfonamide, m.p. 136–137°; NMR δ 1·53 (m, 6), 3·14 (m, 4), 4·21 (s, 2), 7·46 (s, 5).

Morpholine methanesulfonamide. Methanesulfonyl chloride (11·4 g, 0·10 mole) afforded 10·5 g (63%) morpholine methanesulfonamide, m.p. 93–94°; NMR: δ 2·83 (s, 3), 3·23 (m, 4), 3·80 (m, 4).

N,N-*Diisopropylmethanesulfonamide.* Methanesulfonyl chloride (22·9 g, 0·40 mole) afforded 13·0 g (36%) N,N-diisopropylmethanesulfonamide, m.p. 72–73°; NMR δ 1·32 (d, 6), 2·88 (s, 3), 3·83 (m, 2).

Morpholine ethanesulfonamide. Ethanesulfonyl chloride (25·8 g, 0·20 mole) afforded 27·0 g (76%) morpholine ethanesulfonamide, m.p. 60–61°; NMR: δ 1·35 (t, 3), 3·05 (q, 2), 3·29 (m, 4), 3·75 (m, 4).

Morpholine 2-propanesulfonamide. 2-Propanesulfonyl chloride (14·0 g, 0·096 mole) afforded 10·3 g (53%) morpholine 2-propanesulfonamide, b.p. 109–110 at 1·0 mm Hg; NMR δ 1·35 (d, 6), 3·35 (m, 5), 3·78 (m, 4).

Morpholine 2-butanesulfonamide. 2-Butanesulfonyl chloride (16·5 g, 0·105 mole) gave 16·8 g (77%) morpholine 2-butanesulfonamide, m.p. 73–75°; NMR: δ 1·01 (t, 3), 1·35 (d, 3), 1·65 (m, 2), 3·0 (m, 1), 3·38 (m, 4), 3·78 (m, 4).

Morpholine 2-methyl-1-propanesulfonamide. 2-Methyl-1-propanesufonyl chloride (25·0 g, 0·16 mole), afforded 15·7 g morpholine 2-methyl-1-propanesulfonamide, m.p. 84–86°; NMR: δ 1·16 (d, 6), 2·30 (m, 1), 2·83 (d, 2), 3·29 (m, 4), 3·81 (m, 4).

Morpholine p-toluenesulfonamide. p-Toluenesulfonyl chloride (47·7 g, 0·25 mole) gave 29·1 g (49%) morpholine *p*-toluenesulfonamide, m.p. 149–150°; NMR: δ 2·43 (s, 3), 3·00 (m, 4), 3·75 (m, 4), 7·52 (q, 4).

General procedure for the base-induced nitration of benzylic, primary, and secondary aliphatic sulfonamides (**1–5, 7**). To 0·05 mole sulfonamide in 300 ml dry THF at 0° under N_2 was added 0·055 mole n-BuLi (1·6M in hexane).* After 15 min the soln was cooled to −30° and 0·06 mole $EtNO_3$ slowly added. After stirring at −30° for 4 hr, the mixture was cooled to −50° and acidified with 0·055 mole glacial AcOH. The soln was filtered, the solid washed with THF, and the combined filtrates were evaporated *in vacuo*, usually leaving a yellow oil. This oil was cooled to induce crystallization. The resulting solid was extracted with 10% aq NaOH, filtered, and the filtrate acidified (pH 6) with glacial AcOH. The solid was recrystallized from EtOH affording pure starting sulfonamide. Upon cooling the acidic filtrate, α-nitrosulfonamide separated as a solid, was filtered, dried and recrystallized from 90% EtOH. The acidic soln was extracted with $CHCl_3$ and the extracts evaporated *in vacuo* to yield additional α-nitrosulfonamide.

Piperidine α-nitrotoluenesulfonamide (**1**). Piperidine α-toluenesulfonamide (8·0 g, 0·033 mole), afforded 5·95 g of **1** (Table 1); NMR δ 1·53 (s, 6), 3·23 (s, 4), 6·49 (s, 1), 7·65 (m, 5).

Morpholine α-nitrotoluenesulfonamide (**2**). Morpholine α-toluenesulfonamide (5·5 g, 0·023 mole), gave 4·46 g of **2**, (Table 1); NMR: δ 3·24 (m, 4), 3·57 (m, 4), 6·59 (s, 1), 7·58 (m, 5).

Morpholine nitromethanesulfonamide (**3**). Morpholine methanesulfonamide (20·0 g, 0·121 mole), afforded 7·9 g of **3** (Table 1); NMR: δ 3·48 (m, 4), 3·78 (m, 4), 5·54 (s, 2). 9·5 g (48%) of starting sulfonamide was also recovered.

N,N-*Diisopropylnitromethanesulfonamide* (**4**). N,N-Diisopropylmethanesulfonamide (12·0 g, 0·067 mole) gave 3·8 g of **4** (Table 1); NMR: δ 1·40 (d, 12), 3·90 (m, 2), 5·55 (s, 2). 2·5 g (21%) of starting sulfonamide was recovered.

Morpholine 1-Nitroethanesulfonamide (**5**). Morpholine ethanesulfonamide (15·0 g, 0·084 mole), afforded 6·40 g of **5** (Table 1); NMR: δ 1·95 (d, 3), 3·45 (m, 4), 3·75 (m, 4), 5·59 (q, 1). 1·8 g (12%) of starting sulfonamide was recovered.

Morpholine 1-nitro-2-methylpropanesulfonamide (**7**). Morpholine 2-methylpropanesulfonamide (10·0 g, 0·048 mole) afforded 4·6 g of **7**, (Table 1); NMR: δ 1·18 (q, 6), 2·80 (m, 1), 3·60 (m, 8), 5·34 (d, 1). 3·2 g (32%) of the starting sulfonamide was also recovered.

Morpholine 2-nitro-2-propanesulfonamide (**6**). To morpholine 2-propanesulfonamide (5·0 g, 0·026 mole), in 150 ml dry THF at 0° under N_2, was added 0·029 mole n-BuLi. After stirring for 15 min, the heterogeneous soln was cooled to −35° and $EtNO_3$ (2·63 g, 0·029 mole) added slowly. An exothermic reaction occurred (temp increase of 15–20°). After the addition was complete the orange reaction mixture was stirred

* In the case of benzylic sulfonamides, **1** and **2**, sublimed KO–*t*-Bu was used as the base, and the time allowed for carbanion formation was increased to 12 hrs.

for 10 min,* cooled to $-50°$ and glacial AcOH (1·80 g, 0·03 mole) added dropwise. After allowing the reaction mixture to warm to room temp, it was filtered, the solid washed with THF and the combined filtrates evaporated *in vacuo* affording a light yellow solid. Recrystallization from 90% EtOH gave 2·8 g of **6** (Table 1); NMR: δ 2·02 (2, 6), 3·60 (m, 4), 3·80 (m, 4).

Morpholine 2-nitro-2-butanesulfonamide (**8**). Morpholine 2-butanesulfonamide (2·0 g, 9·7 mmole), afforded, via procedure identical to that used for the preparation of **6**, a red oil which would not crystallize on cooling. The oil was chromatographed on a 100 cc Silica Gel Column using hexane–benzene (1:1) then EtOAc as eluents. The fractions eluted with EtOAc contained 0·95 g of **8**. Recrystallization from 95% EtOH afforded 0·88 g of **8**, (Table 1); NMR: δ 0·97 (t, 3), 1·88 (s, 3), 2·38 (m, 2), 3·60 (m, 8).

Morpholine p-nitromethylbenzenesulfonamide (**9**). Morpholine *p*-toluenesulfonamide, (6·8 g, 0·028 mole) gave, via a procedure identical to that used for the preparation of **6**, 1·2 g of **9** (Table 1); NMR: δ 3·12 (m, 4), 3·83 (m, 4), 5·69 (s, 2), 7·93 (m, 4). Also 2·0 g (30%) of starting sulfonamide was recovered.

Morpholine bromonitromethanesulfonamide (**20**). To 100 ml abs EtOH at room temp was added 0·345 g Na. When all the Na had dissolved, **3**, (2·73 g, 13·0 mmole) was added and the soln was allowed to stir for 6 hr. Br_2 (2·40 g, 15·0 mmole) in 20 ml abs EtOH was added dropwise and the resulting light yellow soln stirred overnight. The EtOH was removed *in vacuo* and the resulting white solid taken up in 50 ml water. The water soln was extracted with 5 × 25 ml diethyl ether and the ether layer dried over Na_2SO_4. Evaporation of the filtered ether layer afforded a white solid, which was dried, recrystallized from 90% EtOH to give 2·58 g (87%) of **20**, m.p. 114–115° NMR: δ 3·75 (m, 8), 6·90 (s, 1). (Found: C, 21·07, H, 3·30; N, 9·99; Br, 27·47; S, 11·30. Calcd. for $C_5H_9BrN_2O_5S$: C, 20·78; H, 3·14; N, 9·71; Br, 27·64; S, 11·09%).

Morpholine 1-nitro 2-p-nitrophenylethanesulfonamide (**22**). To 50 ml dry benzene under N_2, **3** (2·5 g, 0·012 mole) was added. To this soln was added a suspension of 57% NaH in mineral oil (0·602 g, 0·143 mole). After stirring for 0·50 hr, excess NaH was destroyed by adding a few drops EtOH. The product was collected and dried to give 2·80 g (100%) of the Na salt of **3**, m.p. 203° (violent dec). To a stirred soln of the above salt (2·09 g, 0·009 mole) in 30 ml dry DMF at 50° (under N_2) was added, over a period of 30 min, a soln of *p*-nitrobenzyl chloride (1·5 g, 8·7 mmole) in 15 ml dry DMF. After addition was complete, the reaction mixture was stirred for 6 hr, cooled, and diluted with 150 ml water. This mixture was extracted with diethyl ether (6 × 30 ml), the ether extracts washed with water and dried over Na_2SO_4. Evaporating the ether afforded a solid which was shown by NMR to be a mixture of **3** and **22**. The solid was chromatographed on Silica Gel using hexane–benzene and EtOAc as eluents. The fractions eluted with EtOAc gave 1·73 g (57%) of **22**, m.p. 151–152°; NMR: δ 1·20 (d, 2), 3·52 (m, 8), 5·55 (m, 1), 7·30 (m, 2), 8·15 (m, 2). (Found: C, 42·21; H, 4·29; N, 12·23. Calcd. for $C_{12}H_{15}N_3O_7S$: C, 41·87; H, 4·38; N, 12·13%).

Attempted reaction of benzyl chloride with sodium salt of morpholine nitromethanesulfonamide. In a procedure identical to that described for the preparation of **22**, benzyl chloride (1·11 g, 8·76 mmole) afforded 0·39 g of a colorless oil which was identified by its IR spectrum and 2,4 DNP derivative as benzaldehyde, (42%). No other product could be isolated.

Deuteration of morpholine methanesulfonamide. To morpholine methanesulfonamide (1·65 g, 0·01 mole), in 50 ml dry THF at 0° was added *n*-BuLi (0·011 mole). After stirring for 5 min the mixture was quenched with D_2O (2·0 g, 0·10 mole). The soln was acidified with glacial AcOH (0·72 g, 0·012 mole) filtered, the filtrate evaporated *in vacuo* to give a white solid, which, upon recrystallization from benzene–hexane, afforded 1·20 g (73%) of **15**, m.p. 93–94°. The mass spectrum indicated 77% α-monodeuteration. A similar experiment carried out using t-BuOK as the base and allowing the time for carbanion formation to extend to 4 hr afforded 0·40 g (30%) of **15**, the mass spectrum of which indicated 18% α-monodeuteration.

Morpholine bromomethanesulfonamide. Bromomethanesulfonyl chloride (8·12 g, 0·08 mole), via the general procedure for the preparation of sulfonamides, afforded 14·3 g (73%) morpholine bromomethanesulfonamide, m.p. 133–135°; NMR: δ 3·58 (m, 4), 3·83 (m, 4), 4·55 (s, 2). (Found: C, 24·50; H, 3·95; S, 13·19. Calcd. for $C_5H_{10}BrNO_3S$: C, 24·58; H, 4·14; S, 13·12%).

Attempted reaction of morpholine bromomethanesulfonamide with sodium nitrite. In 35 ml dry DMF at room temp (under N_2) was placed morpholine bromomethanesulfonamide (6·1 g, 0·025 mole), and $NaNO_2$ (2·58 g, 0·0375 mole). After stirring at room temp for 12 hr, the reaction mixture was poured into 200 ml cold water. A solid ppt was filtered off, dried and recrystallized from 95% EtOH to give 2·75 g of starting sulfonamide (identical IR spectra). Ether extraction of the DMF-water mixture afforded an additional 1·60 g of starting sulfonamide (71% recovery).

* Longer reaction times produced lower yields or only intractable oils.

Increasing the reaction temp to 45° and reaction time to 24 hr produced no change in product formation (76% recovery of starting sulfonamide).

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