$NaHCO_3$, dried, and chromatographed on 30 g of Woelm neutral alumina (grade III). Ether–petroleum ether (5:95) eluted 462 mg (~50%) of deuterated camphor. Deuterium was removed from C-3 by heating the product with acetic and hydrochloric acid in a sealed tube at 150°, and the camphor-*6-endo-d*$_1$ was finally sublimed, nmr δ 0.85 (s, CH_3), 0.91 (s, CH_3), and 0.95 ppm (s, CH_3). Analysis by mass spectroscopy gave 1% d_2, 74% d_1, and 24% d_0.

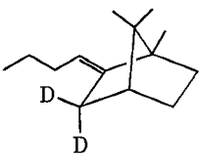
(±)-**Camphor-*6-exo-d*$_1$** (**18**).—To the solution obtained by dissolving 0.8 g of K metal in 10 ml of MeOD was added 1.94 g (~60% camphor homoenol acetate **17**) of the crude product of oxidation of tricyclene with $Pb(OAc)_4$[17] dissolved in 5 ml of MeOD and 2 ml of D_2O. After ~12 hr at room temperature the mixture was poured into water and extracted with petroleum ether. Chromatography of the crude product (1.4 g) on 40 g of Woelm neutral alumina (grade III) gave 901 mg (~97%) of deuterated camphor. Deuterium was removed from C-3 by reflux with methanolic KOH, and the camphor-*6-exo-d*$_1$ was finally sublimed at atmospheric pressure, nmr δ 0.85 (s, CH_3), 0.91 (s, CH_3), and 0.95 ppm (s, CH_3).

The stereochemistry of the D atom in each camphor-*6-d*$_1$ was proved by bromination to 3-*endo*-bromocamphor and $LiAlH_4$ reduction of the product to 3-*endo*-bromoborneol-*6-d*$_1$. In the nmr spectrum of the product from *6-exo-d*$_1$ camphor (from the basic reaction) the C-2 exo-H lacked the long range coupling to the 6-exo hydrogen which coupling was present in the product from *6-endo-d*$_1$ camphor from the acidic reaction.

d-**Camphor-*3-exo-d*$_1$** (**23**).—A solution of 7.6 g (50 mmol) of *d*-camphor in 200 ml of THF (distilled from $LiAlH_4$) under a N_2 atmosphere was treated with 40 ml (64 mmol) of 1.6 *M* *n*-butyllithium solution (Foote Mineral Co.) at room temperature for 30 min. The solution of camphor enolate was then added dropwise (stopcock in bottom of reaction flask) with stirring to a solution of 4 ml (65 mmol) of CD_3COOD and 2 ml of D_2O. After 1 hr the colorless THF solution was decanted from a white paste on the walls of the flask. The THF solution was diluted with petroleum ether, dried, filtered, and evaporated to leave 6.95 g (91%) of crude product. A 4.00-g portion was sublimed at atmospheric pressure to give 3.56 g of pure colorless crystals of *d*-camphor-3-*exo*-d_1. Analysis by mass spectroscopy gave 96.6% d_1 and 3.4% d_0. From the coupling pattern of the CHOH proton in the nmr spectrum of the derived ($LiAlH_4$) isoborneol the D is almost entirely exo.

d-**Camphor-*3,3-d*$_2$** (**24**).—A solution of 25.0 g (81 mmol) of 3,3-dibromo-*d*-camphor in 50 ml of dioxane (distilled from $LiAlH_4$) and 15 ml of CD_3COOD was stirred and heated (steam bath) with 15 g of Zn powder (B. D. H. Analar). Dilution with 200 ml of petroleum ether and 2 ml of D_2O followed by washing (H_2O), drying, and evaporation gave 11.3 g (91%) of crude product which was sublimed to yield 11.0 g of colorless feathery camphor-*3,3-d*$_2$, mp 177–178° (sealed capillary). Analysis by mass spectroscopy gave 83.5% d_2 and 16.5% d_1.

d-**Camphor-*3-endo-d*$_1$** (**25**).—This compound was prepared from 7.58 g (49 mmol) of camphor-*3,3-d*$_2$ by the procedure described above for the preparation of camphor-*3-exo-d*$_1$ except that the enolate was added to a solution of 10 ml of HOAc in 25 ml of water. There was obtained 7.05 g of crude product which consisted of ~70% camphor, ~25% of a slightly more polar (tlc) product, and ~5% of three still more polar compounds. The major contaminant was apparently the product **26** of addition of *n*-butyllithium to the carbonyl group of **24**. Chromatography of 1.6 g of the crude product on silica gel resulted in dehydration of this tertiary alcohol and elution of 382 mg of (probably) **28** together with camphor. Further elution gave 800



28

mg of camphor-*3-endo-d*$_1$ which was sublimed to give colorless crystals. Analysis by mass spectroscopy gave 94% d_1 and 6% d_0. From the coupling pattern of the CHOH proton in the nmr spectrum of the derived ($LiAlH_4$) isoborneol the D is almost entirely endo.

Registry No.—**4**, 34733-67-0; **6**, 34733-68-1; **9**, 34733-69-2; **10**, 10334-07-3; **15**, 34733-71-6; **16**, 34733-72-7; **24**, 34733-73-8; *d*-camphor-*9,9-d*$_2$, 34739-97-4.

Acknowledgment.—The financial assistance of the National Research Council of Canada is gratefully acknowledged.

Anodic Oxidations. VIII. The Anodic Oxidation of *N,N*-Dimethylmethanesulfonamide in Alcohols and in Acetic Acid

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Received January 27, 1972

The anodic oxidation of *N,N*-dimethylmethanesulfonamide has been studied in alcohols and in acetic acid, using quaternary ammonium fluoborates and nitrates as the supporting electrolytes. The structures of the products, *N*-alkoxymethyl-*N*-methylmethanesulfonamides and *N*-acetoxymethyl-*N*-methylmethanesulfonamide, were established by synthesis.

Compounds containing the grouping XCH_2Y, where Y is halogen, OH, OR, or O(C=O)R and X is S, O, or N, are effective electrophilic reagents, frequently used to introduce a new carbon–carbon bond in aromatic compounds or in aliphatic compounds containing reactive methylene or methine groups. Some typical reagents, with, *e.g.*, Y a halogen atom, are the chloromethylamines, the chloromethyl sulfides, the chloromethyl ethers, the chloromethyl amides, and the chloromethyl imides. When the electrophilic reagent is one in which the X above is the nitrogen of an amide group or an imide group, the reaction is an amidoalkylation reaction, and these reactions have been reviewed by Hellman[1] and by Zaugg and Martin.[2]

Many mechanisms are possible for these reactions, but the most common is the acid-catalyzed $A_{AL}1$ mechanism[3] in which the rate-determining step is the formation of the ion I. The most active reagents are

$$-XCH_2^+ \longleftrightarrow \underset{I}{-\overset{+}{X}=CH_2}$$

(1) H. Hellman in "Newer Methods of Preparative Organic Chemistry," Vol. II, W. Foerst, Ed., Academic Press, New York, N. Y., 1963.

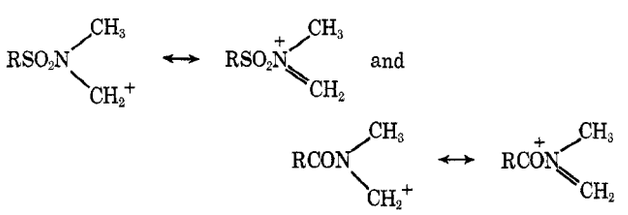
(2) H. E. Zaugg and W. B. Martin, *Org. React.*, **14**, 52 (1965).

(3) S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Org. Chem.*, **31**, 133 (1966).

those in which X is the oxygen of an ether or the nitrogen of an amine. The least active are those in which X is the nitrogen of an imide, and intermediate reactivity is shown by reagents in which X is sulfur or an amide nitrogen.

The half-wave oxidation potentials for the compounds $-XCH_3$[4] parallel the reactivities of the compounds $-XCH_2Y$ discussed above. The order of increasing oxidation potential is amines < sulfides < amides. Oxidation potentials are not available for imides, but *N*-methylimides do not react under conditions where *N*,*N*-dimethylamides are successfully formyloxylated in an electrooxidation.[5]

It has been suggested[3] that the enhanced reactivity of the amine derivatives, R_2NCH_2Y, is due to the absence of both the carbonyl group and the amide resonance in the former and that, in the imides, $(RCO)_2NCH_2Y$, the additional carbonyl decreases the reactivity still further. These considerations make the anodic oxidation of an *N*,*N*-dimethylsulfonamide a subject of interest. In the anodic oxidations of an *N*,*N*-dimethylsulfonamide and an *N*,*N*-dimethylcarbonamide the product-forming intermediates are the ions shown, but the barrier to internal rotation



about the N–S bond of a sulfonamide is small in magnitude compared to the barrier to internal rotation about the N–CO bond of a carbonamide.[6] One might, therefore, expect the anodic oxidation of an *N*,*N*-dimethylsulfonamide to be more facile than the oxidation of an *N*,*N*-dimethylcarbonamide and to show oxidation behavior approaching that of an *N*,*N*-dimethylamine. In the present work the anodic oxidation of *N*,*N*-dimethylmethanesulfonamide has been studied. The oxidation products have been isolated, and their structures have been established by synthesis.

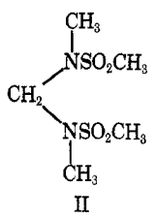
Results and Discussion

The chemistry of the sulfonamide oxidations proved to be very similar to that observed for the carbonamides. Anodic oxidation of *N*,*N*-dimethylmethanesulfonamide in methanol, ethanol, or 1-butanol, with either a quaternary ammonium nitrate or tetrafluoroborate as supporting electrolyte, resulted in the respective *N*-alkoxymethyl-*N*-methylmethanesulfonamides. These products proved to be somewhat more difficult to isolate than the corresponding products from *N*,*N*-dimethylformamide, but only because the difference in boiling point between starting material and product is much smaller in the sulfonamide case.

The structures of these *N*-alkoxymethyl-*N*-methylmethanesulfonamides were confirmed by synthesis. *N*-Methylmethanesulfonamide was treated with formaldehyde to give the hydroxymethyl derivative, which was, in turn, converted to *N*-acetoxymethyl-*N*-methylmethanesulfonamide with acetic anhydride and pyridine. Treatment of the *N*-acetoxymethyl compound with a catalytic quantity of sulfuric acid in the appropriate alcohols gave the desired *N*-alkoxymethyl compounds. It was also possible to interchange alkoxymethyl groups by treatment with acid and an alcohol. In addition, the reaction of an *N*-alkoxymethyl-*N*-methylmethanesulfonamide with anisole in the presence of acid gave a mixture of the ortho and para isomers of *N*-methyl-*N*-methoxybenzylmethanesulfonamide, both of which could be prepared independently by known reactions.

N-Acetoxymethyl-*N*-methylmethanesulfonamide is a somewhat unstable compound which decomposes, in part, during distillation at reduced pressure or within a few days on standing at room temperature. It was shown to be the product formed by electrooxidation of *N*,*N*-dimethylmethanesulfonamide in acetic acid by chemically converting the initially formed *N*-acetoxymethyl compound to a known alkoxymethyl compound and determining, by vpc analysis, the amount of this latter compound obtained.

The decomposition product of the *N*-acetoxymethyl derivative is 2,4-dimethanesulfonyl-2,4-diazapentane (II). It may also be obtained by anodic oxidation of



II

N,*N*-dimethylmethanesulfonamide in water, with ammonium fluoborate as the supporting electrolyte, or by heating *N*-methylmethanesulfonamide and paraformaldehyde in the molar ratio of 2:1 with a catalytic quantity of concentrated hydrochloric acid in a sealed tube at 120°.

Preparative electrooxidations from which the products were isolated are described in the Experimental Section. It was most convenient to do these electrolyses at constant current, a technique which permits the rapid passage of sizable amounts of charge with relatively simple equipment, even with nonaqueous solvents such as acetic acid.

With authentic samples of the oxidation products available, it was possible to study these oxidations by determining the product formed by analytical vpc rather than by isolation. The results are collected in Table I. These experiments used 140 ml of solvent, 0.05 mol of the supporting electrolyte, and 0.10 mol of the sulfonamide. The current was usually the maximum one which could conveniently be maintained constant in the cell used, and the amount of charge passed in each experiment was 0.112 faraday.

The results in Table I are very similar to results obtained in a comparable set of experiments with *N*,*N*-dimethylformamide.[7] Studies of the sulfonamide oxidation by cyclic voltammetry further confirm the

(4) For tables of the appropriate potentials, see C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970, Chapters 9 and 12.

(5) S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Org. Chem.*, **31**, 128 (1966).

(6) R. M. Moriarty, *Tetrahedron Lett.*, 509 (1964); *J. Org. Chem.*, **30**, 600 (1965).

(7) E. J. Rudd, M. Finkelstein, and S. D. Ross, *J. Org. Chem.*, **37**, 1763 (1972).

TABLE I

ANODIC OXIDATION OF *N,N*-DIMETHYLMETHANESULFONAMIDE AT CONSTANT CURRENT

Solvent	Supporting electrolyte	Current, A	Product	Registry no.	Coulombic yields, %
Methanol	Tetraethylammonium fluoborate	2.0	$CH_3SO_2N(CH_3)CH_2OCH_3$	34825-76-8	81.3
Methanol	Ammonium nitrate	2.0	$CH_3SO_2N(CH_3)CH_2OCH_3$		64.3
Ethanol	Tetra-*n*-butylammonium fluoborate	1.0	$CH_3SO_2N(CH_3)CH_2OC_2H_5$	34825-77-9	74.7
Ethanol	Tetraethylammonium nitrate	1.0	$CH_3SO_2N(CH_3)CH_2OC_2H_5$		59.1
1-Butanol	Tetra-*n*-butylammonium fluoborate	0.5	$CH_3SO_2N(CH_3)CH_2OnC_4H_9$	34825-78-0	89.3
1-Butanol	Tetraethylammonium nitrate	0.5	$CH_3SO_2N(CH_3)CH_2OnC_4H_9$		77.3
Acetic acid	Tetra-*n*-butylammonium fluoborate	1.0	$CH_3SO_2N(CH_3)CH_2OOCCH_3$	34825-79-1	53.9
Acetic acid	Tetraethylammonium nitrate	1.0	$CH_3SO_2N(CH_3)CH_2OOCCH_3$		66.1

similarity in oxidation behavior for the two amides. These measurements were carried out in acetonitrile, using 0.3 *M* tetraethylammonium perchlorate as the supporting electrolyte, a Ag/Ag^+ (0.1 *M*) reference electrode, and a platinum wire working electrode of 0.05 cm^2 area. The current–voltage curves for a solution containing 8×10^{-3} *M* *N,N*-dimethylmethanesulfonamide and 8×10^{-3} *M* tetraethylammonium nitrate are shown in Figure 1, in which two distinct oxidation peaks are to be noted. At sweep speeds below 150 mV sec^{-1} the peak potential [V *vs.* $E(Ag/Ag^+)$ (0.1 *M*)] is 2.07–2.08 V for *N,N*-dimethylmethanesulfonamide, and the peak potential for the oxidation of nitrate ion occurs at a potential more than 0.5 V less anodic than that for the amide.

Still further corroboration for this similarity in oxidation behavior is afforded by competition experiments. Mixtures of the two amides (0.064 mol of each) in methanol (150 ml) were oxidized, passing 0.112 faraday of charge, with tetraethylammonium nitrate (0.05 mol) as the supporting electrolyte and with tetra-*n*-butylammonium fluoborate (0.05 mol) as the supporting electrolyte; the ratios of the two products formed, the *N*-methoxymethylformamide to the *N*-methoxymethylsufonamide, were determined. In both experiments the coulombic yield of oxidation products exceeded 95%, and the ratio of oxidation products was 1.58 with the nitrate and 1.40 with the fluoborate. This small preference for oxidation of *N,N*-dimethylformamide is consistent with its slightly lower oxidation potential.

N,N-Dimethylformamide and *N,N*-dimethylmethanesulfonamide are quite similar, both in the nature of the products formed by anodic oxidation and in the potentials at which these reactions occur. The anticipated difference in behavior between these two amides was thus not realized. The expectation was based on the relative absence of amide resonance in the sulfonamide. This would make the electrons on nitrogen more available for transfer to the electrode. Neglected, however, was the very large electron-withdrawing effect of the SO_2 group. This latter effect, larger than that due to the carbonyl group of the carbonamide, would operate in the opposite direction. In the sulfonamide case the two competing effects largely cancel one another. A better correlation with the oxidation potentials would very probably be obtained with either the ionization potentials[8,9] or the energies of the highest occupied molecular orbitals for these

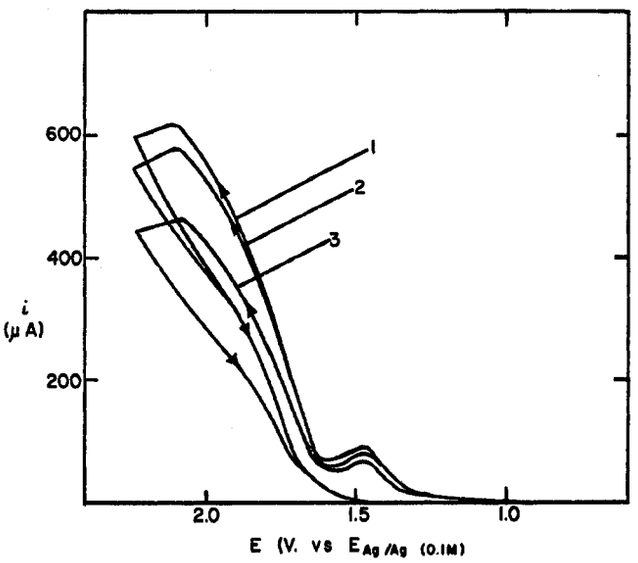
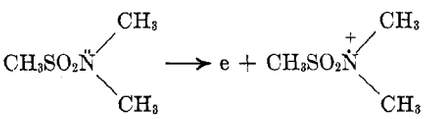


Figure 1.—Cyclic voltammetric studies in acetonitrile containing 0.3 *M* tetraethylammonium perchlorate for the electrooxidation of *N,N*-dimethylmethanesulfonamide ($\cong 8 \times 10^{-3}$ *M*) and nitrate anion ($\cong 8 \times 10^{-3}$ *M* tetraethylammonium nitrate). The sweep rates are 250 mV sec^{-1} for 1, 200 mV sec^{-1} for 2, and 125 mV sec^{-1} for 3.

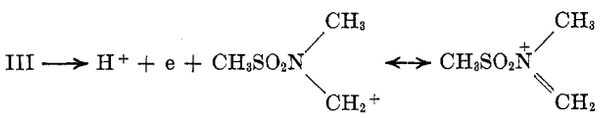
two amides.[9,10] Unfortunately, neither type of data is available.

As demonstrated previously in the case of *N,N*-dimethylformamide,[7] two mechanisms are available for the anodic oxidation of *N,N*-dimethylmethanesulfonamide. In the one, the primary reaction is an electron transfer from the sulfonamide to give a cation radical, III.



III

In a subsequent step or steps III can lose a proton and transfer an additional electron to the electrode to give the ion IV.



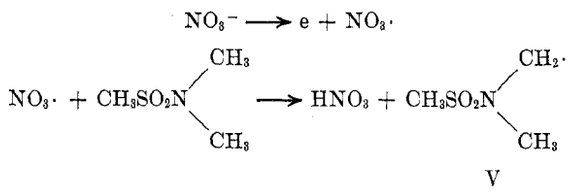
IV

(8) E. S. Pysh and N. C. Yang, *J. Amer. Chem. Soc.*, **85**, 2124 (1963).

(9) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, Chapter 7.

(10) G. J. Hoijtink, *Recl. Trav. Chim. Pays-Bas*, **77**, 555 (1958).

In the other, the initiating reaction is an electron transfer from nitrate ion to give a nitrate radical, which abstracts a hydrogen atom from the substrate to give V.



V

An additional electron transfer to the anode from V again results in the product-forming cation IV. With a nitrate salt as the supporting electrolyte, both mechanisms can operate, with the hydrogen atom abstraction mechanism becoming significant when the concentration of nitrate ion is comparable in magnitude to or larger than the concentration of the sulfonamide.

Experimental Section

Materials.—Preparations of tetraethylammonium nitrate,[11] tetraethylammonium fluoborate,[12] and tetrabutylammonium fluoborate[7] have been described.

N,N-Dimethylmethanesulfonamide[13,14] was prepared in 92% yield by treating anhydrous dimethylamine in dry benzene with methanesulfonyl chloride, bp 110° (12 mm), mp 49–51° from chloroform–hexane.

N-Methylmethanesulfonamide[15] was prepared in 66% yield by adding methanesulfonyl chloride dropwise, with stirring and cooling, to an excess of 40% aqueous methylamine. The reaction mixture was saturated with sodium chloride, and the product was extracted with methylene chloride, bp 104–107° (0.35 mm), n^{23}D 1.4514.

Preparative Electrochemical Reactions.—Two types of electrochemical preparations were run. In the first, the objective was to actually isolate the oxidation products; in the second, the objective was to determine the coulombic efficiency of the electrochemical reaction, and the products were determined analytically. The same equipment was suitable for both types of experiment. The electrolysis cell consisted of a water-jacketed, 200-ml beaker, fitted with a magnetic stirring bar, a thermometer, and a Teflon cover to which were attached two platinum electrodes, 0.025 cm thick, 2.5 cm wide, immersed to a depth of 7 cm and at a separation of 2 cm. Current was supplied by a voltage-regulated d.c. power supply. Descriptions of the reactions in the first category follow.

***N*-Methoxymethyl-*N*-methylmethanesulfonamide.**—A solution of *N,N*-dimethylmethanesulfonamide (12.3 g, 0.1 mol) and tetraethylammonium fluoborate (10.9 g, 0.05 mol) in methanol (150 ml) was electrolyzed at a constant current of 2.0 A until 0.112 faraday of charge was passed. Methanol was removed with the water pump, and ether (200 ml) was added. The fluoborate salt, which precipitated, was recovered by filtration, the ether was removed, and the residue was distilled. The crude product, 13.4 g, bp 68–73° (0.05 mm), was found to be impure by vpc. It proved difficult to separate product from starting material, and even after another distillation, the product was less than 70% pure by vpc analysis. Some additional purification was effected with a Model A-700 Aerograph Autoprep, fitted with a column, 20 ft × 0.375 in., packed with 30% SE-30 on 45/60 Chromosorb W, and maintained at a temperature of 230°. The purified product has n^{23}D 1.4453.

Anal. Calcd for $C_4H_{11}NO_3S$: C, 31.37; H, 7.24; S, 20.90. Found: C, 31.22, 30.56; H, 7.39, 7.45; S, 21.29, 21.77.

In spite of the above satisfactory results, analysis by vpc indicates that this product is only 80% pure.

***N*-Ethoxymethyl-*N*-methylmethanesulfonamide.**—A solution of *N,N*-dimethylmethanesulfonamide (24.6 g, 0.2 mol) and tetrabutylammonium fluoborate (16.5 g, 0.05 mol) in ethanol (150 ml) was electrolyzed at 1 A until 0.224 faraday of charge was passed. The work-up was the same as that described above. The crude product, 16.6 g (88% coulombic yield), had bp 116–121° (12 mm) and n^{23}D 1.4433. A sample redistilled for analysis had bp 129–130° (15 mm) and n^{22}D 1.4434.

Anal. Calcd for $C_5H_{13}NO_3S$: C, 35.91; H, 7.84; S, 19.17. Found: C, 35.53; H, 8.11; S, 19.52.

***N*-*n*-Butoxymethyl-*N*-methylmethanesulfonamide.**—A solution of *N,N*-dimethylmethanesulfonamide (24.6 g, 0.2 mol) and tetrabutylammonium fluoborate (16.5 g, 0.05 mol) in 1-butanol (140 ml) was electrolyzed at a constant current of 0.5 A until 0.224 faraday of charge was passed. The work-up described above resulted in 14.3 g (65.3% coulombic yield) of product, bp 85–91° (0.35 mm), n^{24}D 1.4438. A sample redistilled for analysis had bp 91° (0.35 mm) and n^{23}D 1.4439. Analysis by vpc indicated that this sample was 97% pure.

Anal. Calcd for $C_7H_{17}NO_3S$: C, 43.05; H, 8.77; S, 16.42. Found: C, 43.56; H, 8.99; S, 16.97.

2,4-Dimethanesulfonyl-2,4-diazapentane.—A solution of ammonium fluoborate (10.4 g, 0.1 mol) and *N,N*-dimethylmethanesulfonamide (12.3 g, 0.1 mol) in water (150 ml) was electrolyzed at 2 A until 0.20 faraday of charge was passed. The solution was saturated with sodium chloride and extracted with methylene chloride (3 × 250 ml). Removal of the methylene chloride and crystallization from acetone yielded 4.58 g of product, mp 174–177°. The aqueous layer was distilled at the water pump, and the residue was digested with acetone to yield an additional 1.32 g of product. The total yield was 5.90 g (51% coulombic yield). A sample recrystallized from acetone for analysis had mp 175–177°.

Anal. Calcd for $C_5H_{14}N_2O_4S_2$: C, 26.08; H, 6.13; N, 12.16; S, 27.79. Found: C, 26.50; H, 6.25; N, 11.93; S, 28.11.

For the experiments of the second type, in which the products formed were determined by vpc analysis but not isolated, the solutions electrolyzed contained 0.05 mol of the supporting electrolyte, 0.10 mol of *N,N*-dimethylmethanesulfonamide, and 140 ml of either acetic acid or the appropriate alcohol. The amount of charge passed was 0.112 faraday in each experiment. The results are compiled in Table I.

Since the electrooxidation products of *N,N*-dimethylmethanesulfonamide had not been prepared previously, these same products were synthesized using known chemical reactions. The preparations described below served both as proofs of structure and sources of authentic material.

***N*-Acetoxymethyl-*N*-methylmethanesulfonamide.**—A mixture of *N*-methylmethanesulfonamide (21.6 g, 0.2 mol), paraformaldehyde (6.2 g, 0.207 mol), and potassium carbonate (0.3 g) in ethanol was refluxed for 1 hr. The ethanol was removed with the water pump. Pyridine (25 ml) and acetic anhydride (40 ml) were added, and the mixture was left standing for 24 hr. The excess reagents were removed with the water pump, and the crude product was distilled at 0.04 mm, yield 19.6 g (54%), bp 100–101°, n^{22}D 1.4518. A sample redistilled for analysis had bp 97° (0.015 mm) and n^{24}D 1.4505.

Anal. Calcd for $C_6H_{11}NO_4S$: C, 33.14; H, 6.12; N, 7.73. Found: C, 32.97; H, 6.21; N, 7.94.

The residue from the first distillation above yielded, after two crystallizations from acetone, 1.0 g of 2,4-dimethanesulfonyl-2,4-diazapentane, mp 176–178°.

The *N*-acetoxymethyl-*N*-methylmethanesulfonamide is unstable at room temperature and is slowly converted on standing to 2,4-dimethanesulfonyl-2,4-diazapentane.

***N*-Ethoxymethyl-*N*-methylmethanesulfonamide.**—Concentrated sulfuric acid (1.5 ml) was added to a solution of *N*-acetoxymethyl-*N*-methylmethanesulfonamide (43 g, 0.237 mol) in ethanol (500 ml). The solution was left standing overnight. Pyridine (65 ml) was added, and the ethanol was removed by distillation. The residue was taken up in ether (1 l.), and the solution was extracted with water (2 × 100 ml). The ether solution was dried over magnesium sulfate; the ether was removed, and the crude product was distilled at 0.02 mm, yield 29.3 g (74%), bp 65°, n^{23}D 1.4429.

Anal. Calcd for $C_5H_{13}NO_3S$: C, 35.91; H, 7.84; N, 8.38. Found: C, 35.66; H, 7.88; N, 8.26.

***N*-*n*-Butoxymethyl-*N*-methylmethanesulfonamide.**—The above procedure applied to a solution of *N*-acetoxymethyl-*N*-methylmethanesulfonamide (45.3 g, 0.25 mol) in 1-butanol (500 ml) gave 23.4 g (48%) of product, bp 85–95° (0.1–0.02 mm), n^{24}D 1.4451. On redistillation this product had bp 80° (0.01 mm) and n^{23}D 1.4460. Crystallization of the residue from the

(11) S. D. Ross and M. M. Labes, *J. Amer. Chem. Soc.*, **79**, 4155 (1957).
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first distillation from acetone yielded 1.8 g of 2,4-dimethanesulfonyl-2,4-diazapentane.

N-Methoxymethyl-N-methylmethanesulfonamide.—A solution of N-n-butoxymethyl-N-methylmethanesulfonamide (6.1 g, 0.0313 mol) in methanol (50 ml) was treated with concentrated sulfuric acid (3 drops), and the mixture was left standing for 5 hr. The reaction mixture was dissolved in anhydrous ether (250 ml), and the solution was stirred with sodium carbonate to neutralize the acid. Filtration of the solid, removal of the solvents, and distillation at 0.01 mm yielded 3.6 g (75%) of a product, bp 52–56°, which gave a single peak on vpc.

Anal. Calcd for $C_4H_{11}NSO_3$: C, 31.37; H, 7.24; S, 20.90. Found: C, 31.27; H, 7.34; S, 21.51.

N-Methoxymethyl-N-methylmethanesulfonamide was also obtained in 44% yield from the reaction of N-acetoxymethyl-N-methylmethanesulfonamide with methanol.

2,4-Dimethanesulfonyl-2,4-diazapentane.—A mixture of N-methylmethanesulfonamide (21.6 g, 0.2 mol), paraformaldehyde (3 g, 0.1 mol), and concentrated hydrochloric acid (0.5 ml) was heated in a sealed tube at 120° for 24 hr. The yield was 15.3 g (66.5%), mp 176–178° after two crystallizations from acetone.

Anal. Calcd for $C_5H_{14}N_2O_4S_2$: C, 26.08; H, 6.13; S, 27.84. Found: C, 26.36; H, 6.24; S, 28.26.

Reaction between N-Ethoxymethyl-N-methylmethanesulfonamide and Anisole.—A solution of the sulfonamide (5 g, 0.03 mol) in anisole (30 ml) was treated with concentrated sulfuric acid (1.5 ml). After 2.5 hr the mixture was added to ether (300 ml), and the ether solution was extracted with water (2 × 100 ml). Both the aqueous extract and the ether solution gave products. The aqueous extract was taken to dryness, and the residue was crystallized from acetone, yielding 1.18 g (34.2%) of 2,4-dimethanesulfonyl-2,4-diazapentane, mp 173–176°. The ether solution was washed twice with saturated sodium bicarbonate solution and then once with water. The solution was dried over magnesium sulfate, the ether and anisole were removed by distillation, and the residue was analyzed by vpc. The products found were: N-methyl-N-p-methoxybenzylmethanesulfonamide, 1.43 g (20.8%); N-methyl-N-o-methoxybenzylmethanesulfonamide, 0.72 g (10.5%); and a third, unidentified component, 0.43 g.

N-Methyl-N-p-methoxybenzylmethanesulfonamide.—N-Methyl-N-p-methoxybenzylamine was prepared by the procedure described by Cromwell and Hoeksema,[16] except that platinum oxide was used as the catalyst for the reduction. A solution of methanesulfonyl chloride (4.7 g, 0.041 mol) in benzene (20 ml) was added dropwise, with magnetic stirring, to a solution of the above amine (12.2 g, 0.081 mol) in benzene (50 ml) in a two-necked, 250-cc, round-bottomed flask. After the addition, more benzene (50 ml) was added, and stirring was continued for 15 min. Separation of the precipitate and removal of solvent and excess reagents by distillation with the water pump gave the crude product, which was crystallized from ethyl acetate–hexane, yield 8.45 g (90%), mp 74–75°.

Anal. Calcd for $C_{10}H_{15}NO_3S$: C, 52.38; H, 6.59; N, 6.11. Found: C, 51.94; H, 6.63; N, 5.93.

N-Methyl-N-o-methoxybenzylmethanesulfonamide.—The above procedure gave the ortho isomer in 94% yield, mp 45–48°.

Anal. Calcd for $C_{10}H_{15}NSO_3$: C, 52.38; H, 6.59; N, 6.11. Found: C, 51.59; H, 6.50; N, 5.94.

Registry No.—N,N-Dimethylmethanesulfonamide, 918-05-8; 2,4-dimethanesulfonyl-2,4-diazapentane, 34825-80-4; N-methyl-N-p-methoxybenzylmethanesulfonamide, 34825-81-5; N-methyl-N-o-methoxybenzylmethanesulfonamide, 34825-82-6.

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Effect of Activating Group on Trans Stereoselectivity of Thiolate Additions to Activated Acetylenes

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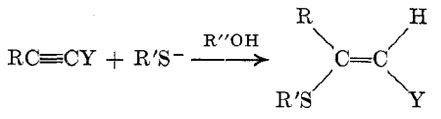
Received February 8, 1972

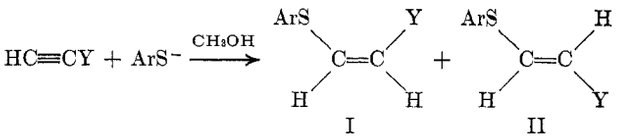
The degree of trans stereoselectivity for nucleophilic additions of arylthiols to negatively substituted acetylenic compounds of the type HC≡CY in methanol is dependent on the nature of the activating group Y, decreasing where Y is a carbonyl-containing group.

Some years ago there was noted a strong tendency for base-catalyzed additions of thiols to acetylenic compounds activated by electron-withdrawing groups to proceed in a trans fashion in protic media[1] (*e.g.*, thiolate attack at the β carbon and protonation at the α carbon occurring from opposite sides).



This "rule" of trans nucleophilic addition has since been confirmed by many workers.[2] Recently, however, several authors have reported violations of this rule; a competing cis-addition process was postulated.[3] Some of the claimed violations could be rationalized as resulting from post-isomerization of the kinetically favored trans-addition product (possessing the *Z*, or cis, configuration) to the more stable *E* (trans) isomer,[3b,c] while others could have resulted from the intermediacy of resonance-stabilized or equilibrating carbanions in aprotic solvents.[3a,d]

Work commenced in this laboratory to determine the limitations of the rule of trans-nucleophilic addition. Where violations were found, it was desirable to determine the factors promoting a competitive cis-addition



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