methoxy singlets of the (*E*)- and (*Z*)-hydroximoyl chlorides were integrated at a sweep width of 100 Hz. The first-order rate constants and the Hammett value were calculated by a least-squares evaluation of the data and the error limits were calculated at the 95% confidence level.

Rate of $^{36}Cl^-$ Exchange with (*Z*)-*O*-Methylbenzohydroximoyl Chloride (2a). Eight samples (100 mg each) of **2a** were dissolved in 0.210 molal $H^{36}Cl$–dioxane (10.3 g) which had been thermostated at 39.5 °C. Each reaction was quenched by pouring the reaction mixture into 0.20 M sodium hydroxide (25 mL). The hydroximoyl chloride was extracted with ether (4 × 10 mL) and the ether extracts were washed with water (4 × 10 mL) and dried over anhydrous magnesium sulfate. The magnesium sulfate was filtered by gravity and the filter paper and the magnesium sulfate were thoroughly washed with ether. The ether was removed by means of rotary evaporation and the residue was dissolved in 5 mL of scintillation fluid [3.0 g of 2,5-diphenyloxazole and 0.3 g of 1,4-bis(5-phenyloxazol-2-yl)-benzene/L of toluene]. Each sample was counted three times (10 min each time) with either a Beckman Model 1650 or a Beckman Model LS 9000 liquid scintillation counter using a ^{32}P window. The raw activity data were corrected for counting efficiencies and a blank was run without **2a** in order to correct for background radioactivity. A 1.03-g and 2.06-g sample of the $H^{36}Cl$–dioxane solution in 5 mL of scintillation fluid was counted in order to obtain the initial activity of this solution. The rate constant was calculated by a least-squares evaluation of the data and the error was estimated at the 95% confidence level.

Incorporation of $^{36}Cl^-$ during $H^{36}Cl$-Catalyzed Isomerization of (*E*)-*O*-Methylbenzohydroximoyl Chloride (1a). A 100-mg sample of **1a** was dissolved in 0.210 molal $H^{36}Cl$–dioxane (10.3 g) which had been thermostated at 39.5 °C. The solution was kept at 39.5 °C for 80 min and then quenched by addition of 0.20 M sodium hydroxide (25 mL). The reaction mixture was worked up as described above. In the experiment which was run to only one half-life a larger sample of **1a** (393 mg) was dissolved in 10.3 g of 0.210 molal $H^{36}Cl$–dioxane solution. This reaction was quenched with 0.20 M sodium hydroxide and the reaction mixture was worked up in the usual way. The residual mixture of **1a** and **2a** was separated by PGLC (20% SE-30 on Chromosorb W, 30 ft × 0.375 in. column).

Acknowledgment. We gratefully acknowledge support of this work by a grant from the Robert A. Welch Foundation and by a Texas Woman's University Institutional Research Grant. We are also grateful to Dr. James E. Hardcastle for his assistance with the radioassays.

Registry No. 1a, 41071-34-5; **1b**, 41071-36-7; **1c**, 57139-26-1; **1d**, 57139-27-2; **1e**, 57139-29-4; **1f**, 57139-30-7; **2a**, 41071-35-6; **2b**, 41071-37-8; **2c**, 57139-33-0; **2d**, 57139-34-1; **2e**, 57139-36-3; **2f**, 57139-37-4.

Deamination via Nitrogen Derivatives of Sulfonic Acids: *N*-Alkyl-*N*-nitroso-4-toluenesulfonamides, *N*-Alkyl-*N*-nitro-4-toluenesulfonamides, and *N*-Alkyl-*N'*-(4-toluenesulfonyloxy)diimide *N*-Oxides

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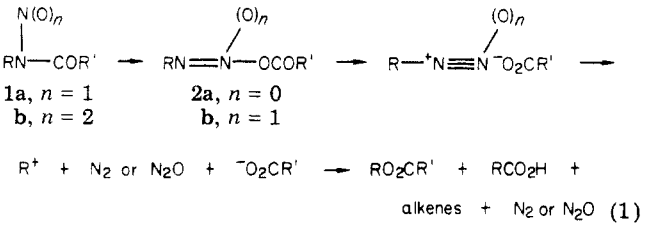
Received September 11, 1980

The thermal decomposition of several *N*-alkyl-*N*-nitroso-4-toluenesulfonamides, *N*-alkyl-*N*-nitro-4-toluenesulfonamides, and *N*-alkyl-*N'*-(4-toluenesulfonyloxy)diimide *N*-oxides was undertaken to determine whether the basicity of the negatively charged counterion in deamination reactions was a reaction variable. The nitrososulfonamides decompose following first-order kinetics to give the corresponding esters with retention of configuration. The reaction characteristics are very similar to those of the *N*-nitrosocarboxamides, and the reaction mechanisms are presumably very similar also. The *N*-nitrosulfonamides required high temperatures for decomposition, and they gave an anomalous set of products: amide (by denitration) and olefins, but no nitrous oxide or toluenesulfonate esters. The *N'*-toluenesulfonoxydiimide *N*-oxides, isomeric to the nitrosulfonamides, proved to be surprisingly stable compounds; they decompose by first-order kinetics to yield the corresponding esters and nitrous oxide.

The rate-determining step in the thermal decomposition of *N*-nitroso and *N*-nitrocarboxamides of primary alkylamines **1** is a rearrangement to the diazo or diazoxy ester **2**, respectively; subsequent fast steps lead to the corresponding ester, olefin products, and nitrogen or nitrous oxide (eq 1).[1-4] The range of products, the stereochemical course of the reaction (principally retention of configuration in R), and the extent of scrambling of ^{18}O in the carboxylate groups are virtually the same whether nitrogen or nitrous oxide is the gas molecule formed and also whether the *E* or *Z* isomer of **2a** is the reaction intermediate.[5] The present study, involving the rearrangement of nitroso- and nitrosulfonamides, was designed to determine whether the basicity of the counterion (carboxylate vs. sulfonate) was a reaction variable.



(1) White, E. H. *J. Am. Chem. Soc.* **1955**, *77*, 6014.

(2) Huisgen, R. *Justus Liebigs Ann. Chem.* **1951** *574*, 184.

(3) Hey, D. H.; Stuart-Webb, J.; Williams, G. H. *J. Chem. Soc.* **1952**, 4657.

(4) White, E. H.; Woodcock, D. J. "The Chemistry of the Amino Group"; S. Patai, Ed.; Wiley: New York, 1968; Chapter 8.

(5) White, E. H.; Ryan, T. J.; Field, K. W. *J. Am. Chem. Soc.* **1972**, *94*, 1360.

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Table I. Composition of Nitrososulfonamides and *N'*-(4-Toluenesulfonoxy)diimide *N*-Oxides

(A) *N*-Alkyl-*N*-nitroso-4-toluenesulfonamides

compd	temp, °C	solvent	ester yield, %	10^4k, s^{-1}
3a	81	cyclohexane[a]	56[b]	1.3[c]
	79	carbon tetrachloride	50[b]	3.3
3b	40	methylene chloride	19	1.4
	40	*n*-pentane	10	1.1
	40	acetonitrile	9	0.79

(B) *N'*-(4-Toluenesulfonoxy)diimide *N*-Oxides

compd	temp, °C	ester yield, %	$t_{1/2}$, h (at 61 °C)
11a[e]	61-100[d]	9-14	99
11b[e]	61	74	27

[a] Concentration 7.8×10^{-2} M; runs in all other solvents had concentrations of = $(1.8\text{-}3.1) \times 10^{-2}$ M. [b] Contains ~10% of the *sec*-butyl isomer;[6] varying amounts of butenes, 4-toluenesulfonic acid, and up to 22% of *N*-*n*-butyl-4-toluenesulfonamide were also formed. [c] A half-life of 6 min was reported for 3a in chlorobenzene at 94.2 °C.[9] [d] Butenes (55%) were also formed (see Experimental Section for isomer distribution). [e] The solvent was chloroform.

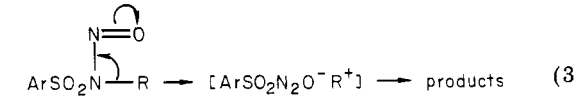
Results

Nitrososulfonamides. *N*-*n*-Butyl-*N*-nitroso-4-toluenesulfonamide (**3a**)[6] and *N*-*sec*-butyl-*N*-nitroso-4-toluenesulfonamide (**3b**) were prepared by nitrosation of the corresponding sulfonamides with dinitrogen tetraoxide.[7,8] Each compound, upon warming, decomposed to give the corresponding ester, alkene, and nitrogen (eq 2).

$$\underset{\textbf{3a, R = } n\text{-butyl}\quad \textbf{b, R = } sec\text{-butyl}}{CH_3C_6H_4SO_2N(NO)R} \xrightarrow[\text{slow}]{\Delta} \underset{\textbf{4}}{[CH_3C_6H_4SO_2ON{=}NR]} \rightarrow \underset{\textbf{5}}{[CH_3C_6H_4SO_3^-N_2^+R]} \longrightarrow CH_3C_6H_4SO_3R + N_2 + CH_3C_6H_4SO_3H + \text{alkenes} \quad (2)$$

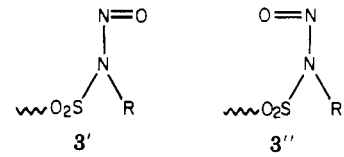
This result is in agreement with the report of Hey and DeBoer on the formation of toluenesulfonate esters from several nitrososulfonamides of primary alkylamines[9] and with our preliminary study of **3a**.[6] To Maximize ester yields (Table I), an excess of sodium carbonate was generally included to neutralize the 4-toluenesulfonic acid formed since in the absence of base, extensive denitrosation of the nitrososulfonamide occurred.[6]

The thermolysis will be treated in the framework of the reaction mechanism (eq 2) shown to hold for the nitrosocarboxamides.[1-4] The small rate difference between the *n*-butyl and *sec*-butyl isomers (Table I), effectively the same as in the nitrosobenzamide series,[10] would appear to eliminate from consideration a direct ionization mechanism (eq 3), which had been considered but ruled out in the decomposition of the nitrosocarboxamides.[14]

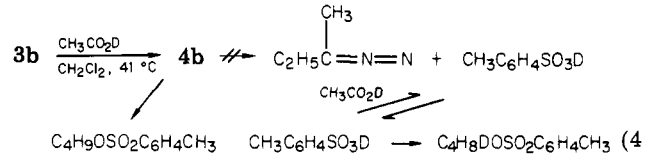


(3)

The decomposition of the *N*-nitrososulfonamides followed first-order kinetics (slow step is rearrangement to **4**),[1,4] and the rate constants (and ester yields) were little influenced by the solvent (Table I). Interestingly, the rates of rearrangement of the nitrososulfonamides (Table I) are similar to the rates of rearrangement of the corresponding *N*-nitrosobenzamides[12] to within a factor of ~15 (the decomposition rates of the nitrosocarboxamides are also relatively insensitive to the nature of the solvent). The effect of bulky R groups in increasing the rates of decomposition and the alkene yields was also approximately the same in the carboxamide and sulfonamide series. Bulky R groups increase decomposition rates by shifting the equilibrium between rotational isomers **3'** and **3''** in the direction favoring the *Z* form (**3''**) required for the rearrangement to **4**.[12,13]



The formation of *sec*-butyl 4-toluenesulfonate in the decomposition of *N*-*sec*-butyl-*N*-nitroso-4-toluenesulfonamide (**3b**) does not proceed through 2-diazobutane (eq 4)[15] as shown by the lack of deuterium incorporation in



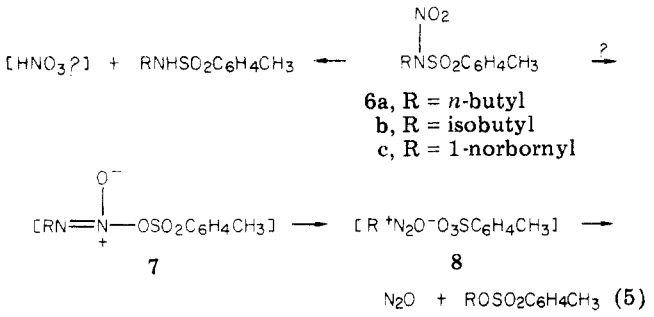
(4)

the ester produced when a threefold excess of acetic acid-*O*-*d* was present in the reaction medium. Analysis of the product ester by ^1H NMR indicated that the methine proton of the *sec*-butyl group at δ 4.51 integrated correctly for one proton. In addition, the mass spectrum of the ester, in comparison with that of the authentic "protio" sample, showed that no detectable amount of deuterium had been incorporated. Thus, the tosyl ester is formed in methylene chloride by the ionization pathway of eq 2. The conversion of *sec*-butylnitrososulfonamide **3b** to *sec*-butyl tosylate proceeded with 71% retention of configuration (29% inversion). The ester yield and the extent of retention of configuration observed in the decomposition of nitrososulfonamide **3b** are quite similar to those reported for the conversion of *N*-*sec*-butyl-*N*-nitrosobenzamide to *sec*-butyl benzoate (11% yield; 66% overall retention of configuration).[1] These results, in conjunction with the kinetic work, indicate that the mechanism of decomposition of the *N*-nitrosotoluene-

(6) White, E. H. *J. Am. Chem. Soc.* **1955**, *77*, 6011.
(7) White, E. H. *J. Am. Chem. Soc.* **1955**, *77*, 6008.
(8) White, E. H.; Aufdermarsh, C. A.; Jr. *J. Am. Chem. Soc.* **1961**, *83*, 1179.
(9) Hey, D. H.; DeBoer, T. J. *Recl Trav. Chim. Pays-Bas* **1954**, *73*, 686.
(10) The ratio of decomposition rates for the *n*-butyl and *sec*-butyl isomers in hydrocarbon solvents at 81 and 40 °C, respectively, is about 1; in the *N*-nitrosobenzamide series, the ratio for the *n*-butyl and isopropyl derivatives in 1,2,4-trimethylbenzene at 80 and 40 °C, respectively (by extrapolation from 70 and 30 °C, respectively), is also about 1 (solvent effects and the rate differences between *sec*-butyl and isopropyl derivatives are expected to be small).[11-13]
(11) Heyns, K.; Bebenburg, W. v. *Justus Liebigs Ann. Chem.* **1955**, *595*, 55-68.
(12) Huisgen, R. and H. Reimlinger, *Justus Liebigs Ann. Chem.* **1956**, *599*, 161-182.
(13) White, E. H.; Dolak, L. A. *J. Am. Chem. Soc.* **1966**, *88*, 3790.
(14) White, E. H.; Dzadzic, P. M. *J. Org. Chem.* **1974**, *39*, 1517.
(15) Nitrosamides of primary carbinamines in *nonpolar* solvents do decompose via diazoalkanes (*Streitwieser*, A.; Schaeffer, W. D. *J. Am. Chem. Soc.* **1957**, *79*, 2893. White, E. H.; Aufdermarsh, C. A., Jr *Ibid.* **1961**, *83*, 1174).

sulfonamides closely parallels the mechanism of decomposition of the *N*-nitrosocarboxamides. It appears that in deamination reactions, the basicity of the counterion has little effect on the course of the reaction, at least in solvents of low polarity.[16]

***N*-Nitrosulfonamides.** In an attempt to gain further insight into the mechanism of deamination of the sulfonamides, several *N*-nitrotoluenesulfonamides [R = *n*-butyl (**6a**), isobutyl (**6b**), and 1-norbornyl (**6c**)], prepared by nitration of the amides, were thermolyzed (eq 5). As in



6a, R = *n*-butyl
b, R = isobutyl
c, R = 1-norbornyl

(5)

the *N*-nitroso-4-toluenesulfonamide decompositions, an excess of sodium carbonate was generally used to neutralize any *p*-toluenesulfonic acid formed. The *N*-nitrotoluenesulfonamides proved to be rather stable compounds, and relatively high temperatures were required for decomposition. In general, only products of denitration and elimination were detected. Toluenesulfonyl esters may well have been formed from **6a,b**, but they were found to decompose under the thermolysis conditions that were used. *N*-Isobutyl-*N*-nitrosulfonamide **6b** at 130 °C in chlorobenzene for 20 h yielded 50% each of the corresponding amide and toluenesulfonic acid (alkenes not analyzed), and at 100 °C in chloroform for 29 days (~3 half-lives) it yielded 17% of a mixture of butenes, in addition to the acid and amide. Decomposition of the *n*-butyl compound **6a** gave similar results. The norbornyl analogue **6c**, at 98 °C in methylene chloride for 16 h in the absence of sodium carbonate, gave 4-toluenesulfonic acid, *N*-norbornyl-4-toluenesulfonamide (15%), 1-norbornyl chloride (13%), and minor amounts of several compounds, but no toluenesulfonyl ester, norbornane, or nitrous oxide as determined from the infrared spectra of the products [although nitrous oxide will react with alkenes, higher temperatures are normally required (200–400 °C)].[17]

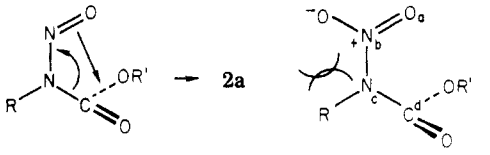
The recovered amide presumably stems from a denitration reaction catalyzed by unscavenged toluenesulfonic acid (acid-catalyzed denitrations of nitroamines[18] and denitrosations of nitrosoamides[7] are known). The alkenes might have originated in ion pair **8** (eq 5) since higher temperatures are known to favor alkene formation from the corresponding ion pairs in the decomposition of the *N*-nitrosocarboxamides.[1] However, some type of elimination

(16) At the completion of the present work, we learned of unpublished results of Professor D. Arigoni and Dr. A. Gautier (Eidgenössische Technische Hochschule, Zurich, Switzerland) which suggest that an effect of the basicity of the counterion in deamination may have been detected. The *N*-nitrososulfonamide of chiral methylamine was shown to decompose to methyl toluenesulfonate with inversion of configuration. This result was interpreted in terms of a displacement reaction stemming from a rearrangement of the diazonium tosylate ion pairs. Primary alkyl nitrosocarboxamides react largely via the corresponding diazoalkanes,[15] presumably because of the high energy of primary carbonium ions and the high basicity of carboxylate ions (however, results for *N*-methylnitrosoamides, specifically, are not available). We thank Professor C. A. Townsend (The Johns Hopkins University) for bringing the Arigoni and Gautier results to our attention.

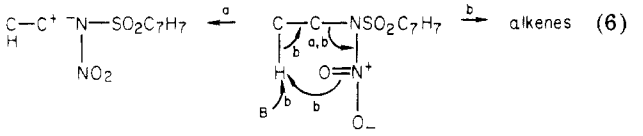
(17) Buckley, G. D.; et al. *J. Chem. Soc.* **1951**, 2999, 3009, 3016.

(18) Ingold, C. K. "Structure and Mechanism in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1953; pp 625–628.

Chart I. Comparison of Nonbonded Interactions in the Rearrangement of *N*-Nitroso- and *N*-Nitrocarbamates

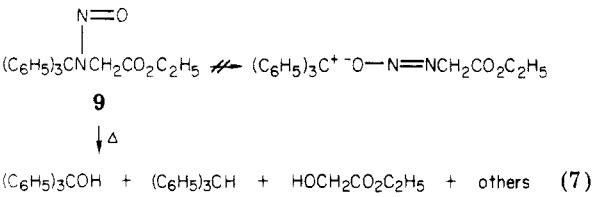


(path b) or ionization (path a) directly from **6** might be involved (eq 6). An attempt to devise a model reaction



(6)

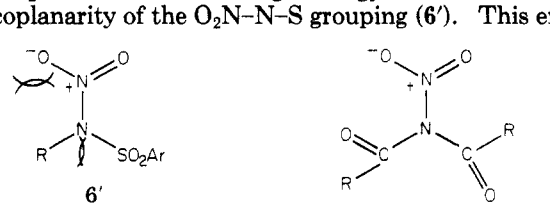
for the ionization mode in a nonamide series (eq 7) was



(7)

unsuccessful, as the product composition suggested that several concurrent decomposition modes were being followed. Of all the products formed in the decomposition of the nitrosulfonamides, norbornyl chloride is the only one reasonably assigned to ion pair intermediates such as **8**, since the chloride is the major product in the decomposition in methylene chloride of the corresponding nitroso and nitrocarbamates for which such intermediates are reasonably firmly established.[19]

The *N*-nitrosulfonamides exhibit a pronounced reluctance to rearrange to the diazoxy ester **7**. We estimate that the half-life of decomposition of compound **6a** in chlorobenzene (and also in isooctane) is 300 h at 100 °C, whereas the half-life of rearrangement of the nitroso analogue (**3a**) at the same temperature is ~0.1 h. In contrast, in the carbamate series with primary alkyl groups, the *N*-nitro derivatives rearranged only about an order of magnitude more slowly than the corresponding *N*-nitroso compounds.[13] A large rate difference favoring the *N*-nitroso derivative was observed in the carbamate series ($NO/NO_2 \simeq 10^8$) for sterically crowded derivatives (e.g., for *N*-*tert*-alkyl derivatives). The relative stability of the nitro derivatives in the carbamate series with bulky R groups was believed to result from nonbonded interactions of the nitro and R groups, which force the nitro group out of the b,c,d plane (Chart I); a coplanar a,b,c,d system appears to be required for maximum rates of rearrangement.[13] A similar explanation may account for the extreme stability of the *N*-nitrosulfonamides. The larger size of SO_2Ar vs. CO_2R' could lead to a high-energy barrier for achieving coplanarity of the O_2N–N–S grouping (**6'**). This effect of

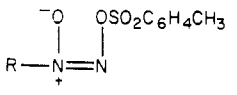


the sulfonyl group might stem from its compression of the

(19) White, E. H.; McGirk, R. H.; Aufdermarsh, C. A., Jr.; Tiwari, H. P.; Todd, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 8107.

R–N–N angle and/or from its influence on the conformations of the R group, in some of which the alkyl group blocks the coplanarity of the O_2N–N–S grouping required for rearrangement (Chart I). Compound **10** (R = CH_3)[20] is also a surprisingly stable nitroamide ($t_{1/2} \approx 10$ h at 100 °C in toluene), and difficulty in reaching coplanarity of the O_2NNC system may similarly be the reason for the stability.

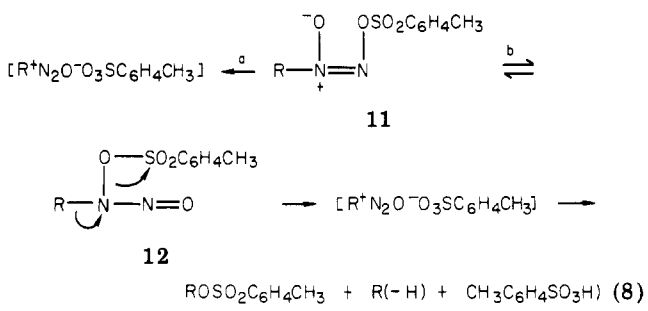
(4-Toluenesulfonyloxy)diimide *N*-Oxides. *N*-Isobutyl-*N'*-(4-toluenesulfonyloxy)diimide *N*-oxide (**11a**), an



11a, R = isobutyl
b, R = benzyl

isomer of compound **6b**, and the benzyl analogue (**11b**) were prepared from the corresponding alkylnitrosohydroxylamine salts and toluenesulfonyl chloride.[21] The overall structure and the cis relationship of the oxygens in analogues of **11** (R = phenyl[22] and 2-adamantyl[23]) have been definitively established by X-ray analysis. The surprising stability of these compounds, considering their structure, has been noted.[22] Compounds **11a,b** decompose in chloroform by first-order kinetics, forming the corresponding esters, alkenes, and nitrous oxide (Table I).[23] No hexachloroethane is formed, and the product distribution suggests an ionic reaction pathway.

If direct ionization were involved (eq 8, path a), these compounds could serve as an interesting bridge between solvolysis and deamination.[22] However, the relatively small rate difference observed for R = isobutyl vs. benzyl (~1/4) suggests that the more complex decomposition of eq 8b

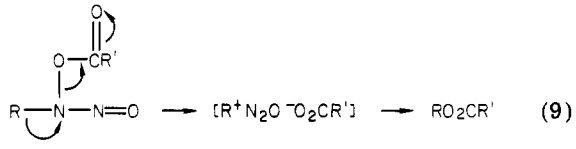


11

12

$$ROSO_2C_6H_4CH_3 + R(-H) + CH_3C_6H_4SO_3H \quad (8)$$

is involved. ^{18}O-labeling experiments showed that the phenyl analogue (**11**, R = C_6H_5) decomposes by this pathway;[24] further, the carboxylic amide analogue of **12**, compound **13**, is exceedingly labile, and it is known to decompose directly as shown in eq 9.[22,25] Further labeling



13

(9)

experiments will be required, however, to determine whether direct ionization of **11** might occur in polar solvents, especially in cases where relatively stable carbonium ions can be formed.

Experimental Section

Proton magnetic resonance spectra were recorded at 100 MHz in deuteriochloroform (Merck 99.7% deuterated) with Me_4Si as an internal standard by using a JEOLCO MH-100 spectrophotometer. Infrared spectra were obtained in carbon tetrachloride with a Perkin-Elmer 457 grating spectrophotometer. Optical rotations were measured in a 1-dm, water-jacketed cell by using a Perkin-Elmer 141 polarimeter. Mass spectra were recorded with a Hitachi Perkin-Elmer RMU-6 with an ionization potential of 70 eV. The ultraviolet *N*-oxide spectra were recorded on a Varian 635 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories. Melting points were measured on a Thomas-Hoover apparatus and are uncorrected.

Thermal reactions were carried out in Pyrex tubes sealed either under vacuum (10^{-3} torr) at liquid nitrogen temperatures or under an atmosphere of purified nitrogen. Cyclohexane and *n*-pentane (Fisher, Certified ACS grade) and chloroform (Baker, reagent grade) were passed through columns of basic alumina (Woelm, activity I) before use. Methylene chloride (Baker, reagent grade) was distilled from phosphorous pentoxide under nitrogen. Other solvents were used as received. Quantitative kinetic data were obtained by monitoring the disappearance of the *N*-nitroso absorbance at 396 nm for **3a** and at 411 nm for **3b**.

Acetic Acid-*O-d*. A mixture of acetic anhydride (25.5 g, 250 mmol) and deuterium oxide (99.7% deuterated, 5 g, 250 mmol) in a dried 50-mL flask was stirred under a nitrogen atmosphere overnight. The mixture was distilled under nitrogen, and the center fraction was collected; bp 117–118 °C. Analysis by NMR indicated ≥96% O-deuteration.

***sec*-Butyl 4-toluenesulfonate** was prepared and purified by the procedure of Schleyer[27] to yield a clear oil: ^1H NMR ($CDCl_3$) δ 7.52 (m, 4 H), 4.51 (m, 1 H), 2.38 (s, 3 H), 1.51 (m, 2 H), 1.19 (d, J = 7.3 Hz, 3 H), and 0.78 (t, J = 7.9, 3 H); IR (CCl_4) 1380, 1190, 1180, 910 cm^{-1}.

***N*-*n*-Butyl-4-toluenesulfonamide** was prepared from toluenesulfonyl chloride and a 50% molar excess of *n*-butylamine. The product was washed with water, dried, and recrystallized from an ethanol–hexane solution to produce off-white crystals: 91% yield; mp 42.8–44 °C (lit.[28] mp 41–42.5 °C); ^1H NMR ($CDCl_3$) δ 7.55 (m, 4 H), 5.3 (br s, 1 H), 2.95 (br t, 2 H), 2.4 (s, 3 H), 1.50–0.74 (m, 7 H); IR (CCl_4) 3280,1390, 1175 cm^{-1}.

***N*-*sec*-Butyl-4-toluenesulfonamide** was prepared by the procedure given for the *n*-butyl isomer. Following purification, white crystals were obtained: mp 56–57 °C (lit.[29] mp 54–55 °C); ^1H NMR ($CDCl_3$) δ 7.52, (m, 4 H), 5.70 (br d, J = 8.1 Hz, 1 H), 3.12 (m, 1 H), 2.40 (s, 3 H), 1.40 (m, 2 H), 1.00 (d, J = 7.8 Hz, 3 H), 0.80 (t, J = 7.9 Hz, 3 H); IR (CCl_4) 3280, 1325, 1160 cm^{-1}.

(*S*)-(+)-*N*-*sec*-Butyl-4-toluenesulfonamide. *sec*-Butylamine was resolved as its bitartrate salt as described by Thomé.[30] Following treatment of the salt in aqueous sodium hydroxide, the amine was dried and distilled in a short-path apparatus under nitrogen: bp 63.5 °C; $[\alpha]^{22.5}_D$ +5.34°. An optical purity of 69% was determined by interplating the rotation of $[\alpha]^{20}_D$ +7.48° (neat) reported by Bruck[31] and $[\alpha]^{25}_D$ +8.10° (neat) reported by Smith.[32]

(20) Diels, O.; Borgwardt, E. *Chem. Ber.* **1920**, *53*, 152.
(21) Stevens, T. E. *J. Org. Chem.* **1964**, *29*, 311.
(22) White, E. H.; Todd, M. J.; Ryan, T. J.; Sieber, A. A. F. *Tetrahedron Lett.* **1970**, *51*, 4467–4472.
(23) Adamantyl azoxytoluene-*p*-sulfonate has been reported to solvolyze in alcohols by first-order kinetics to yield adamantanol and the corresponding ethers. We thank Dr. H. Maskill for a preprint of their work (Maskill, H.; Murray-Rust, P.; Thompson, J. T.; Wilson, A. A. *J. Chem. Soc., Chem. Commun.* **1980**, 788.
(24) Neiman, L. A.; Smolyakov, V. S.; Nekrasov, Y. S.; Shemyakin, M. V. *Tetrahedron* **1970**, *26*, 4963.
(25) Product distributions, yields, and stereochemical changes occurring in the decomposition of **13** and in the decomposition of the corresponding *N*-nitrosoamides[4,5] are essentially the same, indicating that similar ionic intermediates are involved in the two cases (Ryan, T. J.; Dzadzic, P. M., unpublished work. See also ref 26).
(26) E. H. White and D. W. Grisley, *J. Am. Chem. Soc.* **1961**, *83*, 1191.
(27) Schleyer, P. v. R. In "Reagents for Organic Synthesis"; Fieser, L. F., Fieser, M., Eds.; Wiley: New York, **1967**; Vol. 1, p 1180.
(28) Lange, N. A.; Forker, G. M. "Lange's Handbook of Chemistry", 10th ed.; McGraw-Hill: New York, 1967; p 714.
(29) Pope, W. J.; Gibson, C. S. *J. Chem. Soc.* **1912**, *101*, 1702.
(30) Thomé, L. G. *Chem. Ber.* **1903**, *36*, 582.
(31) Bruck, P.; Denton, I. N.; Lamberton, A. H. *J. Chem. Soc.* **1956**, 921.

(S)-(+)-N-sec-Butyltoluenesulfonamide was prepared by the procedure given for the n-butyl analogue; it was purified by two sublimations [53–60 °C (10^{-3} torr)] to yield a white crystalline material: mp 54.3–58.5 °C; $[\alpha]^{21}_D$ +1.77° (c 0.96, EtOH) (calculated value for optically pure form 2.57°);[33] IR and NMR spectra were identical with those of the DL form.

Anal. Calcd for $C_{11}H_{17}NO_2S$: C, 58.12; H, 7.54; N, 6.16; S, 14.10. Found: C, 58.15; H, 7.70; N, 6.06; S, 13.98.

N-Isobutyl-4-toluenesulfonamide was prepared by the procedure used for the n-butyl analogue. The product was purified by recrystallization from an ethanol–hexane solution, netting white crystals in 93% yield: mp 77 °C (lit.[34] mp 78 °C); ^{1}H NMR ($CDCl_3$) δ 7.56 (m, 4 H), 5.38 (br t, J = 6.3 Hz, 1 H), 2.79 (t, J = 6.3 Hz, 2 H), 2.42 (s, 3 H), 1.74 (m, 1 H), 0.86 (d, J = 7.1 Hz, 6 H); IR (CCl_4) 3260, 1360, 1163 cm^{-1}.

N-(1-Norbornyl)-4-toluenesulfonamide. 1-Norbornylamine hydrochloride (589 mg, 4.0 mmol) was added to 15 mL of a 10% sodium hydroxide solution. Toluenesulfonyl chloride (780 mg, 4.0 mmol, sublimed before use) was added in one portion to the amine, and the flask was shaken periodically for 5 h. A white solid precipitated. An additional 45 mL of sodium hydroxide solution was added, and the mixture was warmed on a steam bath to dissolve most of the material. The solution was filtered while hot and made acidic with concentrated hydrochloric acid. The white precipitate (240 mg, 0.09 mmol; mp 95–96 °C; 24% yield, other runs up to 65%) was collected by filtration and recrystallized from ether/petroleum ether; mp 96.5–97.5 °C.

This material gave one spot on TLC (silica gel/benzene): ^{1}H NMR ($CDCl_3$) δ 7.79 (m, 4 H), 5.34 (br s, 1 H), 2.42 (s, 3 H), 2.16–0.91 (m, 11 H); IR (CH_2Cl_2) 3360, 2950, 2915, 2870, 1600, 1400, 1325, 1160, 1135, 1095 cm^{-1}.

Anal. Calcd for $C_{14}H_{19}NO_2S$: C, 63.40; H, 7.17; N, 5.28; S, 12.08. Found: C, 63.46; H, 7.15; N, 5.02; S, 11.84.

N-n-Butyl-N-nitroso-4-toluenesulfonamide (3a) was prepared by nitrosation of the amide with dinitrogen tetraoxide as described by White and Aufdermarsh.[8] The product was identified by its ^{1}H NMR spectrum, which exhibited signals at δ 7.61 (m, 4 H), 3.7 (br t, 2 H), 2.4 (s, 3 H), and 1.60–0.6 (m, 7 H), and by the IR spectrum (CCl_4): 1510, 1390, 1175 cm^{-1}.

Kinetic Measurements. The decompositions of nitrososulfonamides **3a,b**, freshly purified by chromatography on neutral alumina, were followed spectrophotometrically at 395 nm (central band of the n,π triplet) in degassed solvents which had previously been passed through a column of neutral alumina; a tenfold excess of anhydrous sodium carbonate was present in each run. No induction periods were observed, and the reactions were first order for at least 2 half-lives. The half-lives of the nitrososulfonamides and toluenesulfonoxydiimides were determined from the decrease of various absorptions in the IR and NMR spectra.

N-sec-Butyl-N-nitroso-4-toluenesulfonamide (3b) was prepared by the method of White and Aufdermarsh.[8] The product was a yellow oil: ^{1}H NMR ($CDCl_3$, internal Me_4Si) δ 7.56 (m, 4 H), 4.60 (m, 1 H), 2.4 (s, 3 H), 1.76 (m, 2 H), 1.28 (d, J = 7.5, 3 H), 0.76 (t, J = 8.0, 3 H); IR (CCl_4) 1510, 1375, 1195, 1175 cm^{-1}.

Decomposition of N-n-Butyl-N-nitroso-4-toluenesulfonamide (3a) in Cyclohexane. Freshly prepared N-n-butyl-N-nitrosotosylamide (1.0 g, 3.9 mmol) was decomposed under nitrogen for 14 h at 81 °C (ca. 9 half-lives) in 50 mL of purified cyclohexane containing anhydrous sodium carbonate (4.2 g, 40 mmol). The sodium salts were filtered, and the reaction mixture was concentrated at reduced pressure. The weight of this material coupled with an analysis of the IR and NMR spectra indicated the product to be a mixture of n-butyl tosylate (504 mg, 2.2 mmol, 56%) and N-n-butyl-4-toluenesulfonamide (192 mg, 0.85 mmol, 22%).

Decomposition of N-sec-Butyl-N-nitroso-4-toluenesulfonamide (3b) in Methylene Chloride. Compound **3b** (2.6 g, 10 mmol), anhydrous sodium carbonate (12.0 g, 107 mmol), and 110 mL of purified methylene chloride were heated under a nitrogen atmosphere for 17 h at 40 °C (ca. 10 half-lives). Following the workup, analysis as for the n-butyl case indicated that the sulfur-containing products consisted of sec-butyl tosylate (443 mg, 1.9 mmol, 19%) and N-sec-butyl-4-toluenesulfonamide (260 mg, 1.1 mol. 11%).

Decomposition of (S)-(+)-N-sec-Butyl-N-nitroso-4-toluenesulfonamide. (S)-(+)-N-sec-Butyl-4-toluenesulfonamide (69% optically pure) was nitrosated by the procedure outlined above. The product (2.56 g, 10.0 mmol) was dissolved in 150 mL of methylene chloride containing sodium carbonate (11 g, 100 mmol). The decomposition was carried out at 40 °C for 15 h (ca. 9 half-lives). A major product, (S)-(+)-sec-butyl 4-toluenesulfonate, was purified by chromatography on silica gel (Bio-Rad, 100–200 mesh), eluting with hexane–carbon tetrachloride (95/5) (the ester was shown to be stable to the workup conditions). The product was identified by its IR and NMR spectra; $[\alpha]^{25}_D$ +1.67° (c 4.90, EtOH) (calculated value if starting amide had been optically pure 2.42°). Since dextrorotatory amine, tosylamide, alcohol, and tosyl ester all have the same configuration[35,36] and since optically pure sec-butyl toluenesulfonate gives $[\alpha]^{20}_D$ +5.80° (c 5.00, EtOH),[35] the reaction had proceeded with 42% net retention of configuration (71% retention and 29% inversion).

Anal. Calcd for $C_{11}H_{16}O_3S$: C, 57.87; H, 7.06. Found: C, 57.90; H, 6.92.

Decomposition of N-sec-Butyl-N-nitroso-4-toluenesulfonamide (3b) in the Presence of Acetic Acid-O-d. Freshly prepared N-sec-butyl-N-nitroso-4-toluenesulfonamide (2.56 mg, 10 mmol) was thermolyzed in the presence of a threefold excess of acetic acid-O-d in 150 mL of methylene chloride at 41 °C for 17 h. Acetic acid and 4-toluenesulfonic acid were removed by washing with a 5% sodium bicarbonate solution (3 × 25 mL). The reaction mixture was dried over a mixture of sodium sulfate and sodium carbonate and concentrated under reduced pressure. The sec-butyl tosylate was purified by chromatography on a column of silica gel, eluting with hexane–carbon tetrachloride (95/5). Analysis by ^{1}H NMR indicated that the methine proton of the sec-butyl group, δ 4.51, integrated correctly for one proton. In addition, the mass spectrum of the sec-butyl 4-toluenesulfonate produced from this experiment compared with that of an authentic "protio" sample showed that the sample contained no deuterium.

N-n-Butyl-N-nitro-4-toluenesulfonamide (6a) was prepared by a modification of the procedure described by White and Grisley for the synthesis of N-nitrocarboxamides.[26] N-n-Butyl-4-toluenesulfonamide (2.27 g, 10.0 mmol) was added to 7 mL of 70g nitric acid at 0 °C. Sulfuric acid (98%, 7.4 g, 75 mmol) was added dropwise, and the reaction mixture was stirred for an additional 45 min at 0 °C. The mixture was poured onto ice (ca. 30 g), extracted with ether (3 × 25 mL), washed with 5% sodium bicarbonate (3 × 10 mL), and dried over magnesium sulfate. The crude product was concentrated under reduced pressure and chromatographed on silica gel, eluting with hexane–benzene (90/10 v:v).

Following recrystallization from hexane–ether (95/5 v:v), white crystals were obtained: 2.12 g (78% yield); mp 35.5–37 °C; ^{1}H NMR ($CDCl_3$) δ 7.63 (m, 4 H), 4.22 (br t, 2 H), 2.45 (s, 3 H), 2.00–0.8 (m, 7 H); IR (CCl_4) 1575, 1380, 1190, 1175 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}O_4N_2S$: C, 48.52; H, 5.92. Found: C, 48.36; H, 5.90.

N-Isobutyl-N-nitro-4-toluenesulfonamide (6b) was prepared in 23% yield by the above procedure: mp 40–41.5 °C; IR (CCl_4) 2950, 1565, 1375, 1280, 1195, 1180 cm^{-1}; NMR ($CDCl_3$) δ 7.65 (m, 4 H) 4.08 (d, J = 7.5 Hz, 2 H), 2.45 (s, 3 H), 2.18 (m, 1 H), 1.04 (d, J = 7.8 Hz, 6 H).

Anal. Calcd for $C_{11}H_{16}N_2O_4S$: C, 48.51; H, 5.92; N, 10.30. Found: C, 48.61; H, 6.02; N, 10.33.

N-(1-Norbornyl)-N-nitro-4-toluenesulfonamide (6c). N-(1-Norbornyl)-4-toluenesulfonamide was nitrated by the procedure of White, Chen, and Dolak,[37] modified in that the reaction solution was only allowed to warm to 0 °C. Fuming nitric acid

(32) Smith, H. E.; Cook, S. L.; Warren, M. E., Jr. J. Org. Chem. 1964, 29, 2265.
(33) Tosylamide prepared from sec-butylamine ($[\alpha]^{20}_D$ −1.25 (c ~4.7, H_2O)) was reported to give $[\alpha]^{20}_D$ +0.20° (c ~3.2, EtOH).[29]
(34) Shriner, R. L.; Fuson, R. C.; Curtin, D. Y. "The Systematic Identification of Organic Compounds", 5th ed.; Wiley: New York, 1965.
(35) Mills, J. A.; Klyne, W. "Progress in Stereochemistry"; Academic Press: New York, 1954; Vol. 1, Chapter 5, p 195.
(36) Kenyon, J.; Phillips, H.; Pittman, V. P.; Shackleton, R. B.; Kahn, D. E.; Yorston, F. H.; Cochinaras, N. E. J. Chem. Soc. 1935, 1072.
(37) White, E. H.; Chem, M. C.; Dolak, L. A. J. Org. Che. 1966, 31, 3038.

(1.5 mL, sp gr 1.59–1.60) was added to acetic anhydride (10 mL) at −60 °C. *N*-(1-Norbornyl)-4-toluenesulfonamide (369 mg, 1.4 mmol) dissolved in 5 mL of acetic anhydride was added dropwise to the nitric acid solution at −60 °C. The solution was allowed to warm to 0 °C, and then it was pumped on with a water aspirator to remove excess nitric acid. The mixture was poured into 50 mL of an ice–water mixture, and after the mixture was stirred for 5 min, the aqueous layer was extracted with two 50-mL portions of ether. The ether washings were combined and washed with two 50-mL portions of a saturated sodium bicarbonate solution and then with a 50-mL portion of water. After the ether solution was dried over sodium sulfate, the mixture was filtered and stripped on a rotary evaporator to yield a yellow oil. It the oil had the odor of acidic anhydride, the washing procedure was repeated. The oil was then added to an ice–water mixture, and the white sludge which formed was recrystallized from ether/petroleum ether to yield 43 mg (0.14 mmol, 10%) of pure *N*-(1-norbornyl)-*N*-nitro-4-toluenesulfonamide, mp 98–99 °C dec. Additional product (55 mg, 0.18 mmol, 13% was recovered from the mother liquors: IR (CH_2Cl_2) 2950, 2925, 2872, 1575, 1370, 1295–1265, 1190, 1178, 1135, 1090, 810, 650 cm^{-1}; NMR ($CDCl_3$) δ 2.42–1.15 (m, 11 H), 2.46 (s, 3 H), 7.35 and 7.92 (dd, 4 H).

Anal. Calcd for $C_{14}H_{18}N_2O_4S$: C, 54.19; H, 5.80; N, 9.03. Found: C, 54.24; H, 6.00; N, 8.93.

The decomposition of compound **6c** was carried out in degassed solvents (three freeze–thaw cycles) in sealed tubes. The analysis of products was carried out by means of (1) NMR, with *n*-octyl acetate as an internal standard, (2) infrared spectra, and (3) GLC as described in ref 19.

Decomposition of *N*-Isobutyl-*N*-nitro-4-toluenesulfonamide (6b) in Chloroform. *N*-Isobutyl-*N*-nitro-4-toluenesulfonamide (39 mg, 0.14 mmol), anhydrous sodium carbonate (23 mg, 0.22 mmol), and 2 mL of purified chloroform were placed in a Pyrex tube and degassed on a vacuum line by three freeze–pump–thaw cycles. The tube was sealed under vacuum and thermolyzed in an oil bath at 100 °C for 28 days.

Gas chromatographic analysis (silver nitrate/30% DEGS) of the volatiles indicated a mixture of isobutylene, *trans*-2-butene, and *cis*-2-butene in the relative ratio of 0.9/1/0.7 and a total amount of olefins of 14% (0.02 mmol).[38] The nonvolatile residue was examined by TLC (silica gel, Merck PF 254, benzene) and IR spectroscopy which indicated a mixture of *N*-isobutyl-4-toluenesulfonamide (12 mg, 0.05 mmol, 36%) and starting material, *N*-isobutyl-*N*-nitro-4-toluenesulfonamie (6 mg, 0.02 mmol, 16%).

Nitrosation of Ethyl *N*-(Triphenylmethyl)glycinate. Sodium acetate (3.0 g, 37 mmol) was slurried in 10 mL of dry ethanol-free chloroform. Dinitrogen tetraoxide (ca. 2 mL, 30 mmol) was condensed into the slurry at −60 °C. Ethyl *N*-(triphenylmethyl)glycinate[40] (1.73 g, 5 mmol) in 30 mL of chloroform was added dropwise to the slurry at −50 °C. After the mixture was stirred for $^1/_2$ h, additional dinitrogen tetraoxide (ca. 30 mmol) was added. The mixture was allowed to come to room temperature over a 3-h period.

After removal of the sodium acetate by filtration, the chloroform solution was washed with two 50-mL portions of water, dried over $MgSO_4$, and filtered. Evaporation yielded 1.50 g of a white solid, mp 146–157 °C dec (with gas evolution). Recrystallization from benzene–isooctane yielded samples with 2 °C melting point ranges falling within the overall range of 140–150 °C; the IR spectra and R_f values by TLC of the various samples were identical. A 145–147 °C sample gave the following data: IR ($CHCl_3$) 3050, 3000, 2975, 1745, 1600, 1499, 1450, 1105, 1035 cm^{-1}; NMR ($CDCl_3$) δ 1.23 (t, 3 H, J = 7.2 Hz), 3.80 (s, 2 H), 4.17 (q, 2 H, J = 7.0 Hz), 7.1–7.7 (m, 15 H).

Anal. Calcd for $C_{23}H_{22}N_2O_3$: C, 73.62; H, 5.92; N, 7.48: Found: C, 73.76; H, 5.97; N, 7.47.

Decomposition of Ethyl *N*-Nitroso-*N*-(triphenylmethyl)glycinate (9). Solutions of **9** (0.1 M) in chloroform (15 h at 90 °C) and in chlorobenzene (13 h at 144 °C) showed little decomposition. In the absence of solvent and in a sealed tube under vacuum (4 h at 180 °C), the compound gave ethyl glycolate (10%), triphenylmethane (16%), triphenylcarbinol (43%), a crystalline solid (mp 166–169 °C), and small amounts of several other products.

Ethyl *N*-(Carboethoxy)-*N*-nitrocarbamate (10). This compound was prepared in a 3% yield from ethyl *N*-nitrocarbamate by the method of Diels and Borgwardt:[20] bp 38 °C (0.05 torr); IR (CH_2Cl_2) 1815, 1785, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.48 (q, J = 7 Hz, 4 H), 1.40 (t, J = 7 Hz, 6 H); ^1H NMR (C_6H_6) δ 3.94 (q, J = 7 Hz, 4 H), 0.90 (t, J = 7 Hz, 6 H). [In comparison, $C_2H_5O_2CNFCO_2C_2H_5$ gives signals at δ 4.40 and 1.38.][41] Decomposition of **10** in toluene at 110 °C yielded carbon dioxide, nitrous oxide, diethyl carbonate, and the diethyl ester of iminodicarboxylic acid.

***N*-Isobutyl-*N'*-(4-toluenesulfonyloxy)diimide *N*-oxide (11a)** was prepared from the reaction of tosyl chloride with the potassium salt of *N*-isobutyl-*N*-nitrosohydroxylamine in methylene chloride by the method of Stevens.[21] The product was recrystallized from methylene chloride/petroleum ether or ether/cyclohexane to give pale yellow crystals: 52% yield; mp 44.5–45 °C; IR ($CHCl_3$) 1510, 1395, 1195, 1182, 1098, 890 cm^{-1}; UV (EtOH) λ_{max} 228 nm (log ϵ 4.30), 231 (sh, 4.29), 263 (2.92), 274 (2.67); NMR (CCl_4) δ 0.85 (d, J = 7 Hz, 6 H), 2.4 (m, 1 H, 2.46 (s, 3 H), 3.87 (s, J = 7 Hz, 2 H), 7.37 (d, J = 9 Hz, 2 H), 7.84 (d, J = 9 Hz, 2 H).

Anal. Calcd for $C_{11}H_{16}N_2O_4S$: C, 48.51; H, 5.92; N, 10.30. Found: C, 48.78; H, 6.08; N, 10.47.

Decomposition of *N*-Isobutyl-*N'*-(4-toluenesulfonyloxy)-diimide *N*-Oxide in Chloroform. *N*-Isobutyl-*N*-(tosyloxy)diimide *N*-oxide (47 mg, 0.2 mmol), anhydrous sodium carbonate (27 mg, 0.2 mmol), and purified chloroform were added to a Pyrex tube and sealed under vacuum after three freeze–pump–thaw cycles. The tube was placed in an oil bath at 100 °C for 14 days. The tube was opened, and the volatiles of the reaction mixture were distilled into a liquid nitrogen trap. Gas chromatographic analysis (30% silver nitrate on DEGS and Apiezon L on 60–80 mesh Chromosorb W) indicated the presence of isobutylene, *trans*-2-butene, and *cis*-2-butene in the ratio of 2.1/1.0/2.0 with a total volume of 2.5 mL at STP (0.11 mmol, 55%).[38] The nonvolatiles were diluted with chloroform, washed with water, and dried over magnesium sulfate to yield 6 mg (0.03 mmol, 13%) of a clear oil identified by IR and TLC (silica gel, benzene) as isobutyl tosylate.

***N*-Benzyl-*N'*-(4-toluenesulfonoyloxy)diimide *N*-oxide (11b)** was prepared from the reaction of tosyl chloride with the ammonium salt of *N*-benzyl-*N*-nitrosohydroxylamine in methylene chloride. The product was decolorized with activated charcoal and recrystallized twice from an ether–petroleum ether solution to give white crystals: 14% yield; mp 90.5–91.5 °C (lit.[21] mp 92 °C); ^1H NMR ($CDCl_3$) δ 7.63 (m, 4 H), 7.34 (s, 5 H), 5.16 (s, 2 H), 2.48 (s, 3 H); IR ($CHCl_3$) 3020, 1600, 1520, 1400, 1200, 1185, 1095, 910 cm^{-1}.

This compound was decomposed in chloroform at 61 °C under the conditions described for the isobutyl analogue **11a**.

Acknowledgment. Research funding was provided by the National Science Foundation (Grant No. GP-8993) and the National Institutes of Health (Grant No. GM-21450).

Registry No. 3a, 5457-56-7; **3b**, 75934-48-4; **4** (R = Bu), 75934-60-0; **6a**, 75934-49-5; **6b**, 75934-50-8; **6c**, 75934-51-9; **9**, 75934-52-0; **10**, 75934-53-1; **11a**, 31753-82-9; **11b**, 25370-91-6; acetic acid-*O*-*d*, 758-12-3; *sec*-butyl 4-toluenesulfonate, 715-11-7; *N*-(*n*-butyl)-4-toluenesulfonamide, 1907-65-9; *N*-(*sec*-butyl)-4-toluenesulfonamide, 23705-40-0; (*S*)-(+)-*N*-(*sec*-butyl)-4-toluenesulfonamide, 75934-54-2; *N*-isobutyl-4-toluenesulfonamide, 23705-38-6; *N*-(1-norbornyl)-4-toluenesulfonamide, 75934-55-3; *n*-butylamine, 109-73-9; *sec*-butylamine, 13952-84-6; 1-norbornylamine hydrochloride, 75934-56-4; *n*-butyl tosylate, 778-28-9; (*S*)-(+)-*N*-(*sec*-butyl)-*N*-nitroso-4-

(38) The alkenes from **6b** and **11a** are more highly rearranged than those obtained in the decomposition of an analogue in the carboxylate series, *N*-isobutyl-*N*-nitrosoacetamide.[39] The excess isomerization observed in our work is probably a result of secondary reactions of the alkenes with toluenesulfonic acid, which is produced in the reaction (the scavenging of acids by solid sodium carbonate in organic solvents is not a rapid process).

(39) Friedman, L.; Bayless, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 1790–1794.

(40) Amiard, G.; Heymès, R.; Velluz, L. *Bull. Soc. Chim. Fr.* **1955**, *22*, 191.

(41) Grakauskas, V.; Baum, K. *J. Am. Chem. Soc.* **1969**, *91*, 1679.

toluenesulfonamide, 75934-57-5; (S)-(+)-sec-butyl 4-toluenesulfonate, 50896-54-3; isobutylene, 115-11-7; trans-2-butene, 624-64-6; cis-2-butene, 590-18-1; ethyl N-(triphenylmethyl)glycinate, 18514-46-0; ethyl glycolate, 623-50-7; triphenylmethane, 519-73-3; triphenylcarbinol, 76-84-6; ethyl N-nitrocarbamate, 626-37-9; N-isobutyl-N-nitrosohydroxylamine potassium salt, 75934-58-6; isobutyl tosylate, 4873-56-7; N-benzyl-N-nitrosohydroxylamine ammonium salt, 75934-59-7.

Nuclear Magnetic Resonance Studies of Some 2-(Group 4B)-Substituted 1,3-Dithianes

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Received July 10, 1980

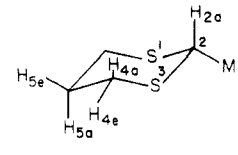
A number of 1,3-dithianes substituted with trimethylsilyl, stannyl, and plumbyl groups at the 2-position have been synthesized and their ^1H and ^{13}C NMR spectra obtained. Examination of chemical shifts, low-temperature spectra, and metal-^{13}C coupling constants in certain 2,2-disubstituted 1,3-dithianes lead to the conclusion that these metalloidal groups have a much greater equatorial preference (at C-2) in 1,3-dithiane than in cyclohexane. For example, trimethylplumbyl, with an *A* value of 0.7 kcal/mol in cyclohexane, has an *A* value at C-2 in 1,3-dithiane in excess of 2 kcal/mol, whereas for simple alkyl groups, comparable *A* values are found for both systems. These results are related to the very large equatorial preference (>6 kcal/mol) of a 2-lithio group in 1,3-dithiane. Inter alia it is shown that electrophilic substitution by trimethyltin chloride on 5-*tert*-butyl-2-lithio-1,3-dithiane proceeds with overall retention of configuration.

We have reported conformational *A* values for various metal and metalloidal groups attached to the cyclohexane ring,[1-3] utilizing both direct (low-temperature ^{13}C NMR) and indirect methods. Various investigations have reported *A* values for a number of substituents in heterocyclic ring systems,[4] and data are now available for the 1,3-dithiane system.[5-11] The general conclusion was that for 2-substituted 1,3-dithianes the *A* values for alkyl and phenyl groups were very similar to those for the corresponding cyclohexanes. It seemed a worthwhile exercise, therefore, to examine a number of 2-metallo-1,3-dithianes from the viewpoint of conformational preference so that comparisons with the cyclohexane system could be made. This was particularly interesting, in view of the studies of Eliel[12-14] which demonstrated that a 2-lithio group had a very large equatorial preference (*A* value >6 kcal/mol) in 1,3-dithiane, whereas comparably polar groups (e.g., MgX and Mg) in cyclohexane[15] lack such a large preference (*A* values from 0.50 to 0.80 kcal/mol depending on solvent etc.), and HgX actually has a slight axial preference[2,3] (*A* $\approx$ -0.2 kcal/mol). In this report, we discuss the NMR characteristics of various 2-M-1,3-dithianes, where M is a group 4B metal or metalloid, and draw conclusions regarding the magnitude of their conformational preference. While this work was in its early stages, Cane, Graham, and Vancea[16] reported the synthesis of some group 4B-substituted 1,3-dithianes and their iron tetracarbonyl complexes, but the major thrust of their work was in a different direction.

Results and Discussion

We initially prepared the series of 2-X-1,3-dithianes, where X = CH_3, C_6H_5, $Si(CH_3)_3$, $Ge(CH_3)_3$, $Sn(CH_3)_3$, and $Pb(CH_3)_3$, and recorded their ^1H and ^{13}C NMR spectra under ambient conditions. These data are shown in Table I.

The general features of the ^1H spectra of 2-substituted 1,3-dithianes have been discussed,[5,6,17,18] and accurate values of the various coupling constants are available. In the present context, we note the sharp appearance of the H_2 resonance ($W_{1/2}$ not greater than 1.5 Hz) for the compounds in Table I. This indicates quite strongly the predominantly equatorial nature of the substituent, because long-range couplings from $H_{4,6}$ or H_5 to H_{2axial} are known to be much smaller than the significant (1-2 Hz) H_{2e}-$H_{4,6e}$ or H_{5e}-H_{2e} couplings (see I).[5,19] The latter then cause equatorial protons H_{2e} to be much broader ($W_{1/2} \approx$ 4 Hz), which is not the case here.



I

(1) W. Kitching, D. Doddrell, and J. B. Grutzner, *J. Organomet. Chem.*, **107**, C5 (1976).
(2) F. A. L. Anet, J. Krane, W. Kitching, D. Doddrell, and D. Praeger, *Tetrahedron Lett.*, 3255 (1974).
(3) P. R. Barron, D. Doddrell, and W. Kitching, *J. Organomet. Chem.*, **132**, 339 (1977).
(4) See, for example: (a) F. G. Riddell, *Qt. Rev. Chem. Soc.*, **21**, 364 (1967); (b) C. Romers, C. Altonia, H. R. Buys, and E. Havinga, *Top. Stereochem.*, **4** (1972).
(5) E. L. Eliel and R. O. Hutchins, *J. Am. Chem. Soc.*, **91**, 2703 (1969).
(6) H. T. Kalff and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **85**, 467 (1966).
(7) H. Friebolin, S. Kabuss, W. Maier, and A. Luttringhaus, *Tetrahedron Lett.*, 683 (1962).
(8) R. J. Abraham and W. A. Thomas, *J. Chem. Soc.*, 335 (1965).
(9) T. Sugawara, H. Iwamura and M. Oki, *Bull. Chem. Soc. Jpn.*, **47**, 1496 (1974).
(10) K. Arai and M. Oki, *Tetrahedron Lett.*, 2183 (1975).
(11) K. Pihlaja, *J. Chem. Soc., Perkin Trans. 2*, **2**, 890 (1974).
(12) E. Eliel, A. A. Hartmann, and A. G. Abatjoglou, *J. Am. Chem. Soc.*, **96**, 1807 (1974).
(13) A. G. Abatjoglou, E. L. Eliel, and L. F. Kuyper, *J. Am. Chem. Soc.*, **99**, 8262 (1977).
(14) L. F. Kuyper and E. L. Eliel, *J. Organomet. Chem.*, **156**, 245 (1978).
(15) F. R. Jensen and K. L. Nakamaye, *J. Am. Chem. Soc.*, **90**, 3248 (1968).
(16) D. J. Cane, W. A. G. Graham, and L. Vancea, *Can. J. Chem.*, **56**, 1538 (1978).
(17) H. R. Buys, *Recl. Trav. Chim. Pays-Bas*, **89**, 1244 (1970).
(18) (a) J. Martin and J. B. Robert, *Org. Magn. Reson.*, **7**, 76 (1975). (b) E. L. Eliel, V. S. Rao, F. W. Vierhapper, and G. Z. Jvaristi, *Tetrahedron Lett.*, 4339 (1975)
(19) K. C. Ramey and J. Messick, *Tetrahedron Lett.*, 4423 (1965).

0022-3263/81/1946-0558$01.00/0