dichlorosilane (30.0 ml, 0.25 mole) and thiolacetic acid (20 ml, 0.27 mole) in hexane (175 ml). After 1 day at room temperature, the mixture was filtered. The solid was washed with benzene and hexane. The washes and filtrate were combined and distilled to give 20 g (39% yield) of yellow liquid: bp 55° (3 mm); $n^{25}D$ 1.5034; d_4^{25} 1.102; λ_{max}^{hexane} 222 mμ (ε 3940), 243 (4400), and 389 (22.1); $\lambda_{max}^{CCl_4}$ 3.38 (m), 3.44 (w), 5.82 (w), 7.00 (m), 7.36 (w), 19.6 (m), 20.0 (m), 21.3 (w), 27.8 (m), 28.6 (m), 31.3 (m), and 34.5 (w) μ; $\lambda_{max}^{CS_2}$ 8.00 (s), 8.20 (s), 8.93 (w), 9.90 (s), 11.8 (s), 12.3 (m), 14.5 (w), and 15.9 (w) μ. The nmr spectrum showed two absorptions of equal intensity at τ 9.28 (Si—Me) and 7.44 (C=SMe).

Anal. Calcd for $C_6H_{12}O_2S_2Si$: C, 34.6; H, 5.8; Si, 13.5; S, 30.7; mol wt, 208.4. Found: C, 34.8; H, 5.5; Si, 13.8; S, 31.1; mol wt, 191 (cryoscopically in benzene).

Thionobenzoxytriphenylsilane was prepared by adding triethylamine (8.0 ml, 0.06 mole) to a solution of triphenylchlorosilane (14.75 g, 0.05 mole) and thiolbenzoic acid (6.9 g, 0.05 mole) in benzene (50 ml). After about 30 min, the mixture was filtered free of solids which were washed with benzene (25 ml), then with hexane until colorless, and dried to give 6.2 g of triethylamine hydrochloride (theory is 6.8 g). The benzene wash and filtrate were combined and concentrated. The residue was crystallized from heptane (50 ml) to give 15.7 g (80% yield) of yellow crystals, mp 40–50° (Fisher-Johns melting point apparatus). A portion of the crystals slowly recrystallized from cyclohexane at room temperature had the following properties: mp 96–98°; $\lambda_{max}^{CCl_4}$ 3.26 (w), 3.29 (w), 6.33 (w), 6.76 (w), 6.93 (m), 7.01 (m), 7.63 (s), 19.6 (s), and 20.8 (s) μ; $\lambda_{max}^{CS_2}$ 7.93 (s), 8.20 (s), 8.47 (w), 8.55 (m), 8.85 (s), 9.10 (sh), 9.34 (m), 9.70 (w), 12.6 (s), 13.0 (m), 13.5 (m), 14.1 (s), 14.4 (s), 14.6 (s), 15.4 (w), and 15.6 (w) μ.

Anal. Calcd for $C_{25}H_{20}OSSi$: S, 8.1; Si, 7.1. Found: S, 8.2, 8.5; Si, 6.8, 7.1.

Reactions of Thionoacetoxytrimethylsilane.—Thionoacetoxytrimethylsilane (1.48 g, 0.01 mole) and water (0.18 ml, 0.01 mole) were put in a vial and shaken vigorously. After a few minutes an exothermic reaction was observed. A small amount of water remained. The clear solution above the water was analyzed by glpc, which showed only two products, hexamethyldisiloxane and thiolacetic acid. The elution times were checked with authentic standards. The infrared spectrum of the reaction mixture showed a strong carbonyl absorption at 5.72 μ (neat).

In a similar manner thionoacetoxytrimethylsilane reacted with ethanol and acetic acid. The products with ethanol were shown by glpc to be ethoxytrimethylsilane and thiolacetic acid. The infrared spectrum showed a strong carbonyl absorption at 1750 cm^{-1}. The reaction with acetic acid was slower but was accelerated by a small amount of sodium acetate. The products, acetoxytrimethylsilane and thiolacetic acid, were identified by glpc also.

The Reactions of Carbamoyl Azides with Sulfur Nucleophiles

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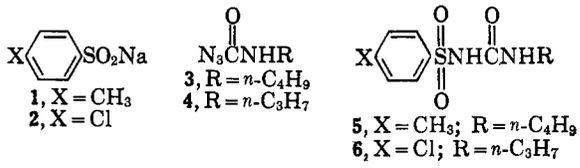
A topic of current interest is the behavior of organic azides under thermal and photolytic conditions, a field stimulated greatly by the elegant work of Lwowski and co-workers[1] on the formation and reactivity of carbethoxynitrene. These results have encouraged us to investigate the decompositions of carbamoyl azides in the presence of sulfur nucleophiles. In particular, we have considered reactions which could provide compounds of pharmaceutical interest.

(1) W. Lwowski and T. W. Mattingly, Jr., *Tetrahedron Letters*, 277 (1962), and subsequent papers.

It has been observed[2] that the decomposition of carbamoyl azides in the presence of hydroxylic solvents is accompanied by Curtius-type rearrangement. To avoid this complication, we have carried out our reactions by heating equimolar amounts of a carbamoyl azide and a sulfur compound without solvent at 125° until gas evolution ceased.

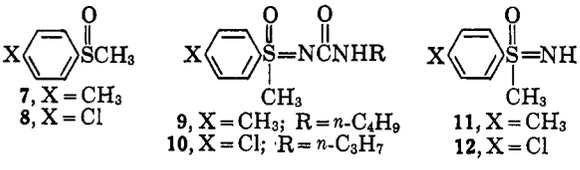
Sulfinate salts react as nucleophiles at the sulfur atom; reactions with alkyl halides, for instance, produce sulfones.[3] It was expected, therefore, that a sulfinate salt would react with a carbamoyl azide to form a sulfonylurea. When the arylsulfinate salts **1** and **2** were heated with the carbamoyl azides **3** and **4**,[4] respectively, vigorous reactions occurred, and the sulfonylureas **5** and **6** (the antidiabetic drugs tolbutamide and chlorpropamide)[5] were obtained in low yields.



1, X = CH_3
2, X = Cl

3, R = *n*-C_4H_9
4, R = *n*-C_3H_7

5, X = CH_3; R = *n*-C_4H_9
6, X = Cl; R = *n*-C_3H_7



7, X = CH_3
8, X = Cl

9, X = CH_3; R = *n*-C_4H_9
10, X = Cl; R = *n*-C_3H_7

11, X = CH_3
12, X = Cl

Horner and Christmann[6] have shown that the reaction of *p*-toluenesulfonyl azide with dimethyl sulfoxide leads to a sulfoximine derivative. Similarly, the carbamoyl azides **3** and **4** underwent gentle reactions with the sulfoxides **7** and **8**[7] to provide, in low yields, the N-carbamoylsulfoximines **9** (mp 63–64°) and **10** (mp 109–111°). The structures of the novel sulfonylurea analogs **9** and **10** were confirmed by independent synthesis from the sulfoximines **11** and **12**[8] and butyl and propyl isocyanate.

Whether these reactions proceed through nitrene intermediates or are best explained as the bimolecular additions of azides to sulfur compounds followed by loss of nitrogen has not been established.

Experimental Section[9]

1-Butyl-3-*p*-tolylsulfonylurea (5).—A mixture of 0.71 g (5.0 mmoles) of butylcarbamoyl azide[4] and 0.89 g (5.0 mmoles) of sodium *p*-toluenesulfinate was heated for 0.5 hr in a 125° oil bath. A vigorous reaction occurred. The mixture was diluted with water, made strongly basic with 1 *N* sodium hydroxide, and filtered. The filtrate was acidified with 6 *N* hydrochloric acid, and an oily solid separated. Recrystallization from ethanol provided 0.11 g (8% yield) of colorless crystals, mp 123–124° (lit.[10] mp 128–129°). The infrared spectrum was identical with that of an authentic sample.

(2) F. L. Scott, *Chem. Ind.* (London), 959 (1954); W. Lwowski, *et al.*, *Tetrahedron Letters*, 3285 (1964).

(3) A. Schöberl and A. Wagner, "Houben-Weyl-Methoden der Organischen Chemie," Vol. 9, Georg Thieme Verlag, Stuttgart, 1955, p 231.

(4) E. Oliveri-Mandala and F. Noto, *Gazz. Chim. Ital.*, **43**, 514 (1913).

(5) W. C. Cutting, "Handbook of Pharmacology," Appleton-Century-Crofts, Inc., New York, N. Y., 1964, p 374.

(6) L. Horner and A. Christmann, *Chem. Ber.*, **96**, 388 (1963).

(7) A. Cerniani and G. Modena, *Gazz. Chim. Ital.*, **89**, 843 (1959).

(8) F. Misani, T. W. Fair, and L. Reiner, *J. Am. Chem. Soc.*, **73**, 459 (1951).

(9) Melting points were determined in a Hershberg apparatus and are uncorrected. Microanalyses were performed by Mr. L. M. Brancone and staff. Nmr spectra were determined by Mr. W. Fulmor and staff on a Varian A-60 spectrometer with tetramethylsilane as an internal standard.

(10) G. Ehrhart, *Naturwissenschaften*, **43**, 93 (1956).

1-*p*-Chlorophenyl-3-propylurea (6).—A mixture of 1.00 g (7.8 mmoles) of propylcarbamoyl azide[4] and 1.55 g (7.8 mmoles) of sodium *p*-chlorobenzenesulfinate was heated for 1.5 hr in a 120° oil bath. The mixture was diluted with water, made strongly basic with 1 *N* sodium hydroxide, and filtered. The filtrate was acidified with 6 *N* hydrochloric acid, and the mixture was extracted with chloroform. The chloroform layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to a yellow oil. Crystallization from ethanol gave 0.16 g (7% yield) of colorless crystals, mp 125–127° (lit.[11] mp 127–129°). The infrared spectrum was identical with that of an authentic sample.

N-Butylcarbamoyl-S-methyl-S-*p*-tolylsulfoximine (9). **A.**—A solution of 6.8 g (0.04 mole) of S-methyl-S-*p*-tolylsulfoximine[8] and 8.0 g (0.08 mole) of butyl isocyanate in 40 ml of glyme was heated under reflux for 2 hr. The solution was concentrated to a viscous, yellow liquid, which was twice crystallized from ether to provide 4.6 g (43% yield) of colorless prisms, mp 64–67°. Another recrystallization gave the analytical sample, mp 66–68°.

Anal. Calcd for $C_{13}H_{20}N_2O_2S$: C, 58.19; H, 7.51; N, 10.44; S, 11.93. Found: C, 58.41; H, 7.26; N, 10.24; S, 11.92.

The infrared spectrum (KBr disk) exhibits bands at 2.83 (NH), 6.15 (C=O), and 8.2, 8.7, and 9.1 μ (O=S=N).

B.—A mixture of 0.71 g (5.0 mmoles) of butylcarbamoyl azide[4] and 0.77 g (5.0 mmoles) of methyl *p*-tolylsulfoxide[7] was heated for 24 hr in a 135° oil bath; a gentle evolution of gas occurred. The resultant brown oil was chromatographed on 50 g of silica gel. The fraction eluted with a 4:1 chloroform–methanol mixture contained a yellow oil, which upon crystallization from ether provided 0.10 g (8% yield) of colorless prisms, mp 63–64°. The infrared spectrum was identical with that of the sample prepared in method A above.

S-*p*-Chlorophenyl-S-methyl-N-propylcarbamoylsulfoximine (10). **A.**—A solution of 12.7 g (0.07 mole) of S-*p*-chlorophenyl-S-methylsulfoximine [bp 134–136° (0.4 mm), prepared by the method of Misani, Fair, and Reiner[8]] and 11.9 g (0.14 mole) of propyl isocyanate in 100 ml of glyme was heated under reflux for 1 hr. The solution was concentrated to a solid, which upon recrystallization from ethyl acetate gave 5.5 g (29% yield) of colorless crystals, mp 99–102°. Recrystallization provided colorless prisms, mp 109–111°.

Anal. Calcd for $C_{11}H_{15}ClN_2O_2S$: C, 48.09; H, 5.46; Cl, 12.93; N, 10.20; S, 11.66. Found: C, 48.45; H, 5.54; Cl, 13.13; N, 10.06; S, 11.77.

The infrared spectrum (KBr disk) exhibits bands at 2.97 (NH), 6.10 (C=O), and 8.2, 8.8, and 9.2 μ (O=S=N). The nmr spectrum ($CDCl_3$) shows doublets at τ 2.07 and 2.48 (2 H each, J = 8 cps, phenyl), singlets at 4.68 (1 H, NH, broad) and 6.68 (3 H, SCH_3), a quartet at 6.88 (2 H, J = 6 cps, NCH_2), a multiplet at 8.53 (2 H, CCH_2C), and a triplet at 9.12 (3 H, J = 7 cps, CCH_3).

B.—A solution of 0.87 g (5.0 mmoles) of *p*-chlorophenyl methyl sulfoxide[7] and 0.65 g (5.0 mmoles) of propylcarbamoyl azide[4] was heated for 12 hr in a 115° oil bath. The resultant brown oil was chromatographed on 50 g of silica gel. The fraction eluted with a 49:1 benzene–methanol mixture contained an oily solid, which upon recrystallization from ethyl acetate gave 0.12 g (12% yield) of colorless crystals, mp 107–108°. The infrared spectrum was identical with that of the sample prepared by method A, above.

(11) F. J. Marshall and M. V. Sigal, Jr., *J. Org. Chem.*, **23**, 927 (1958).

Elimination Reactions of *endo*-2-Norbornyl Brosylate

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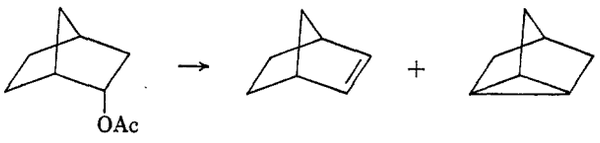
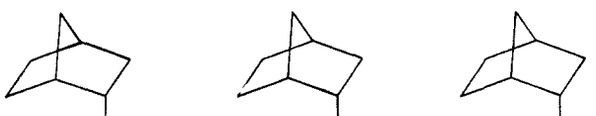
In the course of another investigation, it was necessary to convert *endo*-2-norborneol-2,3,3-d_3 or its derivative to 2,3-dideuterionorbornene without skeletal rearrangement; yet there are only a few reports in the literature[2,3] of elimination of substituents in the *endo*-2 position in the bicyclo[2.2.1]heptane series. Thus a study of such elimination reactions was undertaken.

When *endo*-2-norbornyl acetate (1) was pyrolyzed[4] at 600–615°, the major olefin product was not norbornene (2) but nortricyclene (3) in a ratio of 7:93 as



1 2 3

determined by vpc analysis. Pyrolysis[5] of methyl *endo*-2-norbornyl sulfite (4) at 250° afforded 2 and 3 in the ratio 16:84. It is interesting to note that subjection of *endo*-2-dimethylaminonorbornane (5) to either the Hofmann or Cope elimination conditions led only to the formation of norbornene (2).[3]



4 5 6

Treatment of *endo*-2-norbornyl brosylate (6) with various bases gave varying results (Table I). The bulkiest tertiary alkoxide yielded the least amount of nortricyclene (3). Under solvolytic conditions[6] (nitrobenzene) the ratio of 2 to 3 was 24:76, a ratio which is nearly the same as the equilibrium ratio using a silica–alumina catalyst at the reflux temperature.[7] Under more forcing conditions in which the *endo*-brosylate was heated with sodium iodide in acetone at 110° in a sealed tube,[8] the resulting ratio of 2 to 3

TABLE I

ELIMINATION REACTIONS OF *endo*-2-NORBORNYL BROSYLATE (6)[a]

		Composition ratio[b]	
Reaction	Solvent	2	3
1	*t*-Hexanol[c]	94	6
2	*t*-Hexanol[c,d]	92	8
3	*t*-Butyl alcohol[c]	62	38
4	α-Terpineol[c]	54	46
5	2-Octanol[c]	39	61
6	Nitrobenzene	24	76
7	*s*-Collidine	22	78
8	Acetone[e]	19	81
9	Quinoline	12	88

[a] All reactions except 8 were swept with nitrogen to collect the olefins in a Dry Ice–isopropyl alcohol bath. All reactions were run at 100–120° for 3 hr, except 8 which was run at 110° in a sealed tube for 24 hr. [b] Determined by vpc analysis using a 10% diisodecyl phthalate (8 ft × 0.25 in.) column at 45°. [c] The potassium salt was formed *in situ*. [d] Some *p*-cymene was added. [e] Sodium iodide was added.

(1) National Aeronautics and Space Administration Trainee, 1964–1966.

(2) W. E. Parham, W. T. Hunter, R. Hanson, and T. Lahr, *J. Am. Chem. Soc.*, **74**, 5646 (1952).

(3) A. C. Cope, E. Ciganek, and N. A. LeBel, *ibid.*, **81**, 2799 (1959).

(4) W. J. Bailey and H. R. Goldin, *ibid.*, **75**, 4780 (1953).

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