

lated to function in the activation of substrate and in the activation of indole to permit the reverse reaction.

Experimental Section

Melting points were usually taken with sealed evacuated capillaries and are corrected. Analyses were performed by Galbraith Laboratories, Inc. Ultraviolet spectra were recorded with Bausch and Lomb 505. Rates were measured from the ultraviolet absorption with the aid of a time-rate accessory connected to a Honeywell 10-mv recorder. Temperature regulation was maintained with the constant-temperature cell holder connected with a circulating thermostat. Infrared and nmr spectra were obtained with the Perkin-Elmer 21 and Varian A-60 instruments, respectively. Gas chromatography was performed with an F & M 700 instrument with thermal conductivity detector. Columns were $\frac{1}{8}$ in. \times 6 ft Hi-Pak, 10% silicone rubber. Chromatographs were run at a temperature of 220°, with helium pressure of 30 psi. Under these conditions the indole I ($R_1 = o\text{-Cl}$) retention time was 8.5 min, and the thioether-indole III ($R_1 = o\text{-Cl}$; $R_2 = \text{Ph}$) retention time was 6.3 min. The indolenine I, indole II, and phenyl thioether adduct III ($R_1 = o\text{-Cl}$) have been described.² The ultraviolet spectrum of the latter is reported here in comparison with the benzyl thioether-indole (see text, Results).

***p*-Methoxyphenyl(2-methyl-3H-indolylidene)methane Hydrochloride.** Compound I ($R_1 = p\text{-CH}_3\text{O}$), was prepared according to Burr and Gortner,¹⁶ and was twice recrystallized from methanol-ether. The yield of elongated golden crystals was 35%, mp 188–189° (lit.¹⁶ 181°); infrared $\nu_{\text{max}}^{\text{KBr}}$ 3450, 2630, 2410, 1580, 1555, 1480, and 1435 cm^{-1} . *Anal.* Calcd for $\text{C}_{17}\text{H}_{16}\text{ClNO}$: C, 71.44; H, 5.64. Found: C, 71.43; H, 5.80.

***p*-Methoxyphenyl(2-methyl-3-indolyl)methane.** Indolenine I ($R_1 = p\text{-CH}_3\text{O}$), 0.5 g, was added to a solution of 0.17 g of NaBH_4 in 50 ml of dimethylformamide. After ether extraction, washing, and recrystallization from ethyl acetate-heptane, fine colorless crystals were obtained, mp 119–120°; infrared $\nu_{\text{max}}^{\text{KBr}}$ 3330 (sharp), 1622 (weak), 1605, 1580, 1485, and 1460 cm^{-1} . *Anal.* Calcd for $\text{C}_{17}\text{H}_{17}\text{NO}$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.22; H, 6.94; N, 5.56. Gas chromatography showed a single peak with retention time of 14.4 min.

***p*-Nitrophenyl(2-methyl-3H-indolylidene)methane Hydrochloride.** This was similarly prepared from *p*-nitrobenzaldehyde and 2-methylindole.¹⁶ Yellow-brown crystals separated from the reaction mixture and were washed with ethyl acetate. The yield was

(16) G. O. Burr and R. A. Gortner, *J. Am. Chem. Soc.*, **46**, 1224 (1924).

66–69%, mp 205–210° dec. The material apparently decomposed during attempts at recrystallization from ethyl acetate. Spectra were: infrared $\nu_{\text{max}}^{\text{KBr}}$ 3400, 2420, 1625, 1600, 1570, and 1515 cm^{-1} ; ultraviolet $\lambda_{\text{max}}^{\text{EtOH}}$ 278 $\text{m}\mu$ (ϵ 17,200), 290 $\text{m}\mu$ shoulder (ϵ 13,600), and 340 $\text{m}\mu$ shoulder (ϵ 1700). *Anal.* Calcd for $\text{C}_{16}\text{H}_{13}\text{ClN}_2\text{O}_2$: C, 63.90; H, 4.36; Cl, 11.79; N, 9.32. Found: C, 63.75; H, 4.53; Cl, 11.68; N, 9.11.

***p*-Nitrophenyl(2-methyl-3-indolyl)methane.** Indolenine I ($R_1 = p\text{-NO}_2$), 0.12 g, was added to a solution of 0.1 g NaBH_4 in 5 ml of dimethylformamide. After ether extraction and alumina chromatography, yellow crystals were obtained, mp 117–118°; infrared $\nu_{\text{max}}^{\text{KBr}}$ 3420 (sharp), 1625 (weak), 1606, 1520, and 1470 cm^{-1} ; ultraviolet $\lambda_{\text{max}}^{\text{EtOH}}$ 279 $\text{m}\mu$ (ϵ 16,600), 290 $\text{m}\mu$ shoulder (ϵ 13,200), and 340 $\text{m}\mu$ shoulder (ϵ 1200). *Anal.* Calcd for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.00; H, 5.52; N, 10.34.

***o*-Chlorophenyl(2-methyl-3-indolyl)benzylthiomethane.** Indolenine I ($R_1 = o\text{-Cl}$), 0.155 g, was added to benzyl mercaptan, 0.21 g, in 3 ml of absolute ethanol, and allowed to stand 5 min at 25°. After ether extraction, washing, and crystallization from ethyl acetate-heptane, colorless crystals were obtained in 88% yield, mp 112–115°; infrared $\nu_{\text{max}}^{\text{KBr}}$ 3420, 1625, 1605, 1585, 1560, 1500, and 1460 cm^{-1} ; ultraviolet $\lambda_{\text{max}}^{\text{EtOH}}$ 274 $\text{m}\mu$ (ϵ 9140), 279 $\text{m}\mu$ (ϵ 9250), and 289 $\text{m}\mu$ (ϵ 7750); nmr (CDCl_3) δ 2.05 (singlet, 3 H), 3.48 (singlet, 2 H), 5.45 (singlet, 1 H), 7–8 (multiplet, 14 H). *Anal.* Calcd for $\text{C}_{23}\text{H}_{20}\text{ClNS}$: C, 73.09; H, 5.33. Found: C, 73.07; H, 5.45.

***o*-Chlorophenyl(2-methyl-3-indolyl)carbomethoxymethylthiomethane.** This was prepared similarly to the preceding compound, with substitution of methyl thioglycollate for benzyl mercaptan. After extraction and vain attempts at crystallization, a pale tan oil was obtained in 90% yield: infrared $\nu_{\text{max}}^{\text{neat}}$ 3390, 1735, 1625, 1560, 1460, and 1430 cm^{-1} ; nmr (CDCl_3) δ 2.24 (singlet, 3 H), 3.00 (singlet, 2 H), 3.50 (singlet, 3 H), 5.96 (singlet, 1 H), 7–8 (multiplet, 9 H). *Anal.* Calcd for $\text{C}_{19}\text{H}_{18}\text{ClNO}_2\text{S}$: C, 63.41; H, 5.04. Found: C, 63.15; H, 4.91.

Attempted Condensations with Trifluoroacetaldehyde and Pivalaldehyde. Condensation of trifluoroacetaldehyde ethyl hemiacetal with 2-methylindole in HCl-ethanol or HCl-ethanol-dimethylformamide resulted in a red tar with infrared spectrum suggestive of an indole. Similar attempts with pivalaldehyde gave a mixture of products including a violet solid that did not melt at 350°, and with analysis and molecular weight suggesting a trimer containing three residues each of indole and aldehyde.

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Communications to the Editor

Copper-Catalyzed Decomposition of Benzenesulfonyl Azide in Hydroxylic Media

Sir:

Copper is well known to be an effective catalyst for the decomposition of diazoalkanes and diazocarbonyl compounds. Its role in these reactions has been described¹ as stabilization of a carbene intermediate in a copper-carbene complex. We have now found that copper is an extremely effective catalyst for the decomposition of benzenesulfonyl azide (1). In refluxing methanol containing 1 g of freshly reduced copper powder per 0.1 mole of azide, 1 decomposes smoothly while evolving a stoichiometric quantity of nitrogen.

(1) J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964, pp 118, 125. One may regard the Simmons-Smith reagent as a copper-carbene complex in the sense intended; see E. P. Blanchard and H. E. Simmons, *J. Am. Chem. Soc.*, **86**, 1337 (1964), and earlier references cited therein.

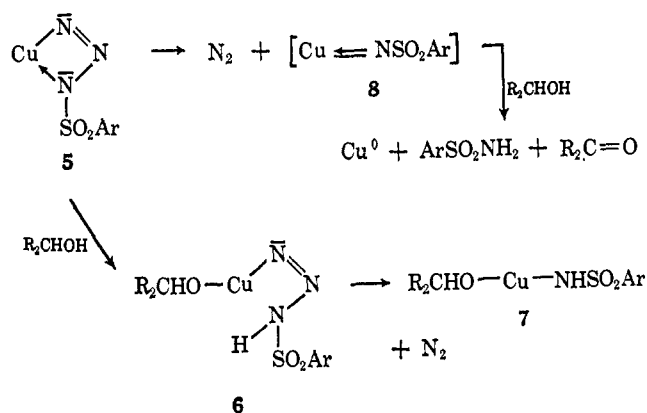
Benzenesulfonamide (2) was isolated in ca. 80% yield, together with methylenebis(benzenesulfonamide) (3) and 1,3,5-tris(benzenesulfonyl)hexahydro-*s*-triazine (4), the minor products apparently resulting from condensation of benzenesulfonamide with formaldehyde formed in major amounts through dehydrogenation of methanol.

In 2-propanol, 2 was again obtained in nearly quantitative yield, and acetone was detected to the extent of approximately 15% of the nitrogen evolved.² Azide decomposition did not occur with copper in dry *t*-butyl alcohol, but on addition of a trace of water to this medium reaction took place at nearly the same rate as in pure methanol, producing complete conversion to the sulfonamide 2. In this case acetone and smaller

(2) The total amount of dehydrogenation product dissolved in a very large amount of the precursor alcohol was estimated by a vpc procedure. It must be assumed that the quantitative result is subject to some gross inaccuracies and therefore is only tentative.

amounts of isobutylene oxide and 2-butanone, characteristic products of the *t*-butoxy radical,³ were identified. In all cases the decomposition of azide was accompanied by the oxidation of a considerable part of the copper and formation of greenish copper-organic complexation with part of the sulfonamide product. In the work-up procedure, the copper ions were sequestered by addition of Versene, thereby releasing the reaction product ligands. Clearly, both copper and alcohol solvent are capable of functioning as reducing agents of the reactive moiety set free by the evolution of nitrogen.

The effect of copper in reducing the activation energy for nitrogen evolution⁴ suggests the occurrence of a complex of copper and azide which may be most simply represented by **5**. Loss of nitrogen in hydroxylic media, as indicated in **6**, could lead to complex **7**, this step corresponding to over-all oxidation of copper. Spontaneous decomposition of **5** could also evolve nitrogen with formation of a transient copper-nitrene complex capable of attacking the solvent in a free-radical reaction not unlike that identified for sulfonyl nitrenes generated photochemically (in alcoholic media⁵) and thermally (in hydrocarbon media⁶⁻⁸). While the exact nature of the product-forming steps cannot be specified, it is noteworthy that reduction to sulfonamide, rather than alkoxylation⁹ or dimerization^{1,10} products, as observed with copper-carbene complexes, predominates in the sulfonyl azide reaction.



On addition of 10 ml of dimethyl sulfoxide (amounting to slightly more than equimolar with azide and less than 1% over-all concentration in solution) to the reaction mixture of 0.1 mole of **1** in methanol containing 1 g of copper, nitrogen evolution was completed in one-fourth the time required in the absence of DMSO. The single product obtained in 97% yield was identified as N-benzenesulfonyldimethyl-

(3) See E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1959, p 623 ff, for a discussion of this subject.

(4) For recent references to such catalysis in the decomposition of diazo substrates, see P. Yates and R. J. Crawford, *J. Am. Chem. Soc.*, **88**, 1562 (1966).

(5) M. Reagen and A. Nickon, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 13, 1965, Abstracts p 11S.

(6) J. P. Heacock and M. T. Edmison, *J. Am. Chem. Soc.*, **82**, 3460 (1960).

(7) M. F. Sloan, W. B. Renfrow, and D. S. Breslow, *Tetrahedron Letters*, **14**, 2905 (1964).

(8) M. F. Sloan, T. J. Prosser, N. R. Newburg, and D. S. Breslow, *ibid.*, **14**, 2945 (1964).

(9) P. Yates, *J. Am. Chem. Soc.*, **74**, 5376 (1952).

(10) A. Losse, *J. Prakt. Chem.*, (2) **79**, 509 (1909).

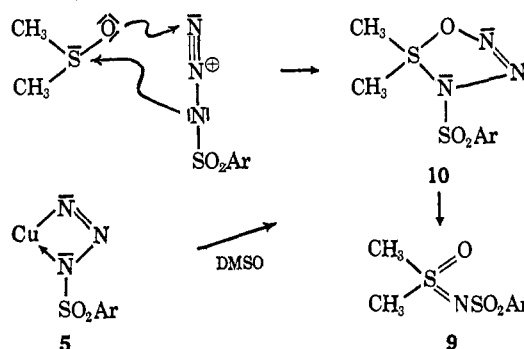
Table I. Rates of Nitrogen Evolution during Copper-Catalyzed Decomposition of Benzenesulfonyl Azide in 2 Mole% Solution at $61 \pm 0.5^\circ$

Solvent medium (ml)	Copper ^a		$k, \text{min}^{-1} \times 10^2$		No additive
	0.50 g	1.00 g	Cu_2Cl_2 0.50 g	Cu_2O 0.50 g	
CH_3OH (100)	0.49	1.52	1.67	0.00 ^c	0.00 ^c
	0.47	1.51	1.66		
CH_3OH (100) + CH_3COOH (1)	1.26				0.00 ^c
CH_3OH (100) + H_2O (1)	1.02				0.00 ^c
	0.85				
	0.86				
CH_3OH (100) + DMSO (1)	1.72				0.1-0.2 ^b
	1.73				
$(\text{CH}_3)_2\text{CHOH}$ (100)	0.45	1.40		0.00 ^c	0.00 ^c
	0.44	1.42			

^a Fisher electrolytic copper dust, washed with ether and reduced in an autoclave under hydrogen, was used. ^b A rough approximation. ^c Signifies no measurable decomposition.

sulfoximine (**9**), previously isolated in 25-35% yield from the photolysis of **1** in pure DMSO. We have also found that DMSO and azide **1**, even in the absence of copper, undergo a slow reaction at the temperature of refluxing methanol, such that in about ten times the period required for complete reaction in the presence of copper less than 40% of the sulfoximine (**9**) is produced.

Since DMSO increases the rate of decomposition of **1** in forming **9**, it must have in some fashion participated in the decomposition mechanism. The most attractive explanation is to assume that the DMSO is an excellent dipolarophile, capable of complexing the sulfonyl azide which is a relatively sluggish 1,3-dipolar reagent. Formation of the sulfoximine could then proceed by way of the oxathiazoline **10**. The marked acceleration of the copper-catalyzed reaction by DMSO with quantitative conversion to **9** may be attributed to the interaction of DMSO with the complex **5**, leading again to **10**, and thence to **9** (see Table I).



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Copper-Catalyzed Decomposition of Benzenesulfonyl Azide in Cyclohexene Solution

Sir:

Further manifestations of a copper-azide complex¹ have been encountered in the decomposition of benzenesulfonyl azide (**1**) in cyclohexene solution. No

(1) H. Kwart and A. A. Khan, *J. Am. Chem. Soc.*, **89**, 1950 (1967).