sultone in 40 ml of dry methanol. The mixture, which turned dark blue, was stirred at room temperature for 15 min. Upon acidification with hydrogen chloride the solution turned red. After removal of the solvent by rotary evaporation, the residue was chromatographed with ethyl acetate on Chrom AR-1000. A fraction moving with the solvent front was recovered as a dark red solid that had melting point, ir, and nmr identical with those of the red photoproduct (**4**) described above. A small second fraction which was difficult to elute was not characterized.

Reaction of 1,2-Dibromoacenaphthylene-5,6-sultone and Pyrrolidine.—A solution of 75.8 mg (0.195 mmol) of 1,2-dibromoacenaphthylene-5,6-sultone in 100 ml of dry ether was treated with 70 mg (0.975 mmol) of pyrrolidine at room temperature and the solution immediately turned a dark purple. The ether was removed from the solution by rotary evaporation. The residue was heated at 85° *in vacuo* for 4 hr and the solid chromatographed on Chrom AR-1000 using benzene to elute the bright red product: yield 72.4 mg (0.158 mmol) (81%); mp 180–181°; ir (KBr) 3190 (OH) (m), 2920 (CH) (w), 1620 (C=C) (m), 1140 (SO_2–N) (s), 1175 (ArH) (w), 1095 (w), 1060 (w), 1025 (w), 835 cm^{-1} (w); nmr δ ($CDCl_3$) 1.77 (m, 4, CH_2), 3.25 (m, 4, NCH_2), 6.98 (d, 1, J = 7.4 Hz), 7.52 (d, 1, J = 7.4), 7.65 (d, 1, J = 7.4), 8.21 (d, 1, J = 7.4), 10.73 ppm (s, 1, O–H); uv (C_6H_{12}) 470 nm (ε 1320), 377 (7390), 359 (9040), 335 (9280), 289 (5910), 248 (22,400), 208 (21,400). *Anal.* Calcd for $C_{16}H_{13}NBr_2O_3S$: C, 41.85; H, 2.85; N, 3.05; Br, 34.81; S, 6.98. Found: C, 42.00; H, 2.99; N, 2.93; Br, 34.80; S, 6.73.

Photolysis of 1,2-Dibromoacenaphthylene-5,6-sultone in Acrylonitrile.—A solution of 20.0 mg (51.5 μmol) of 1,2-dibromoacenaphthylene-5,6-sultone in 5 ml of freshly distilled acrylonitrile was irradiated in a Pyrex container for 8 hr, employing a Hanovia 450-W medium-pressure mercury lamp. A small amount of solid precipitated during the irradiation. Upon removal of the remaining acrylonitrile, a red crystalline material was recovered which had infrared absorptions identical with 1,2-dibromoacenaphthylene-5,6-sultone. A small amount of a dark oil was also obtained whose structure was not identified.

Control Reaction. Acenaphthene-5,6-sultone and Pyrrolidine in Ether.—To a solution of 20.0 mg (0.086 mmol) of acenaphthene-5,6-sultone in 100 ml of dry ether was added 0.5 ml (0.43 g, 5.98 mmol) of pyrrolidine. Monitoring of the solution by tlc indicated that no reaction occurred during a period of 1 hr.

Registry No.—**1**, 26988-41-0; sodium acenaphthene-5-sulfonate, 26988-42-1; sodium 6-nitroacenaphthene-5-sulfonate, 26988-43-2; 6-aminoacenaphthene-5-sulfonic acid, 26988-44-3; 1,2-dibromoacenaphthylene-5,6-sultone with methanol, 26988-49-8; 1,2-dibromoacenaphthylene-5,6-sultone with pyrrolidine, 26988-50-1.

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Reaction of Nitroprusside with Amines[1]

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In the course of our studies of pentacyanoferrates ($Fe(CN)_5X^{3-}$), we came across a report which described the preparation of aminepentacyanoferrates ($Fe(CN)_5NH_2R^{3-}$) by reaction of nitroprusside ($Fe(CN)_5NO^{2-}$) with primary amines.[2] The reaction of nitroprusside with ammonia and amines was, in fact, first studied by Hofmann and Manchot who also noticed that a gas (presumably nitrogen) was evolved.[3] However, although 2 mol of amine is consumed for each mole of complex produced, no reports have appeared on the *organic* products of this reaction.

$$2RNH_2 + Fe(CH)_5NO^{2-} \longrightarrow Fe(CN)_5NH_2R^{3-} + N_2 + \text{organic products}$$

We have found that the organic products (Table I) are substances derived from *N*-nitrosamines, which indicates that nitroprusside functions as a nitrosating agent. Moreover, nitroprusside is unique in being a nitrosating (and deaminating) agent which is stable in *alkaline aqueous solution. Thus, the deamination of benzylamine can be carried out at an initial pH as high as 12.7.* At higher pH's, nitroprusside is destroyed, according to[4]

TABLE I

PRODUCTS OF REACTION OF NITROPRUSSIDE WITH AMINES

Amine	Products (yield, %)[a]	Additional products (yield, %) (in air)[b,c]
Benzylamine	Benzyl alcohol (120)	Benzonitrile (20), benzaldehyde (trace)
Allylamine	Allyl alcohol (38)	Acrylonitrile (trace)
Cyclohexylamine	Cyclohexanol (120), cyclohexene (9)	Cyclohexanone (3)
2-Octylamine	2-Octanol (70), 1- and 2-octene (16)	2-Octanone (10)
1-Butylamine	1-Butanol (42), 2-butanol (8)	. . .[d]
Diethylamine	*N*,*N*-Diethyl-*N*-nitrosamine (44)	

[a] Yields are based on a stoichiometry of 2 amine: 1 nitroprusside; formation of some $Fe(CN)_5OH_2^{3-}$ in place of $Fe(CN)_5NH_2R^{3-}$, however, may also occur; *cf.* yields for benzylamine and cyclohexylamine. [b] Yields of oxidized products varied with pH and with concentration of nitroprusside; average yields are reported. Yields of nitrosation products (in air) were *ca.* 10% lower than under nitrogen. [c] Infrared spectra of all product mixtures showed weak absorptions at *ca.* 1640 cm^{-1} (>C=N–). [d] The expected oxidation product, *n*-butyraldehyde, reacts with nitroprusside; see ref 10.

$$Fe(CN)_5NO^{2-} + 2OH^- \longrightarrow Fe(CN)_5NO_2^{4-} + H_2O$$

Primary amines give deaminated products (alcohols and olefins), while a secondary amine gives the *N*-nitrosamine. Tertiary and aromatic amines are largely inert. The deaminations are of interest since they probably involve generation of diazonium and carbonium ions in *alkaline solution.*

Moss[5] recently studied the reactions of diazonium ions (prepared from hydrolysis of diazotates) in alkaline solution. He found that the diazotates prepared from primary carbinamines gave predominantly diazoalkanes on hydrolysis, *e.g.*

$$C_4H_9N{=}N{-}O^- \xrightarrow{H_2O} C_4H_9N{\equiv}N^+OH^- \longrightarrow C_3H_7CHN_2 + H_2O$$

We have not observed diazoalkanes with nitroprusside, probably because the hydroxide ion concentration is

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[1] Taken from the M.S. Theses of M. A. G. and M. C. N., Boston College, 1970.

(2) D. J. Kenney, J. P. Flynn, and J. B. Gallini, *J. Inorg. Nucl. Chem.*, **20**, 75 (1961).

(3) (a) K. A. Hofmann, *Justus Liebigs Ann. Chem.*, **3 2**, 1 (1900); (b) W. Manchot and P. Woringer, *Ber.*, **46**, 3514 (1913).

(4) J. H. Swinehart and P. A. Rock, *Inorg. Chem.*, **5**, 573 (1966).

(5) R. A. Moss, *J. Org. Chem.*, **31**, 1082 (1966).

still too low for proton abstraction from the diazonium ion.[6]

On the other hand, there is a qualitative parallel between the products of nitrous acid and nitroprusside deaminations. Thus, with nitrous acid, cyclohexylamine gave 68% cyclohexanol and 20% cyclohexene,[7] and 2-octylamine gave 20% 1- and 2-octene and 27% 2-octanol.[8] There are differences in product *ratios*, however, which indicate that hydroxide ion is involved in the nitroprusside deamination. The higher ratio of 1- to 2-butanol with nitroprusside (5:1 *vs.* 2:1[9]) is evidence for an SN2 attack of hydroxide ion on the 1-butyldiazonium ion. Alternatively, the possibility exists that all the products are formed directly from an amine–nitroprusside complex.

The first step in these nitrosations almost certainly involves addition of the amine to the coordinated nitric oxide.[10]

$$\mathrm{RNH_2 + Fe(CN)_5NO^{2-} \rightleftharpoons RNH_2NOFe(CN)_5{}^{2-}}$$

The lower basicity of aromatic amines is consistent with their inertness to nitroprusside.

The resulting complex might react directly with a molecule of amine, with displacement of the *N*-nitrosamine.

$$\underset{\mathbf{1}}{\mathrm{RNH_2NOFe(CN)_5{}^{2-}}} + \mathrm{RNH_2} \longrightarrow \mathrm{RNHNO + H^+ + RNH_2Fe(CN)_5{}^{3-}}$$

$$\mathrm{RNHNO \longrightarrow RN{\equiv}N^+{:}OH^- \longrightarrow R^+ \longrightarrow products}$$

Another possibility involves loss of water from **1**, leading to a diazonium ion complex which would then react with a molecule of amine.

$$\underset{\mathbf{1}}{\mathrm{RNH_2NOFe(CN)_5{}^{2-}}} \xrightarrow{-\mathrm{H_2O}} \mathrm{RN{\equiv}N{-}Fe(CN)_5{}^{2-}} \xrightarrow{\mathrm{RNH_2}} \mathrm{RNH_2Fe(CN)_5{}^{3-} + RN{\equiv}N^+ \longrightarrow R^+ \longrightarrow products}$$

The intermediates apparently are too short-lived to be detected by conventional spectrophotometry.

When nitroprusside is allowed to react with amines in presence of air, small amounts of oxidized products are formed, together with the compounds listed above. These materials (Table I) are produced only in the presence of *both* nitroprusside and air, and their yields increase when the reactions are carried out under pure oxygen. Control experiments show that they are *not* produced by reaction of the corresponding alcohols with nitroprusside. Autoxidation of an intermediate nitroprusside–amine complex seems to be a reasonable pathway for these oxidative deaminations.

Experimental Section[11]

Materials.—Allylamine, benzylamine, 1-butylamine, cyclohexylamine, diethylamine, and 2-octylamine were obtained from the usual commercial sources and were distilled prior to use. Sodium nitroprusside dihydrate (Fisher) was used without further purification.

Reaction of Nitroprusside with Amines.—The reaction of cyclohexylamine (under nitrogen) and benzylamine (under oxygen) with nitroprusside will be described in detail. Procedure and product identification were similar in all other cases.

A solution of sodium nitroprusside dihydrate (24.0 g, 0.084 mol) in 90 ml of water was flushed with nitrogen and was added dropwise, under nitrogen, to a deaerated solution of cyclohexylamine (1.4 g, 0.014 mol) and sodium carbonate (0.75 g, 0.007 mol) in 30 ml of water. An immediate, but slow, evolution of gas occurred. The reaction mixture was stirred for *ca.* 10 hr, during which a small amount of brown solid gradually precipitated. Potassium carbonate (*ca.* 20 g) was then added (to salt out organic materials) and the mixture extracted with five 40-ml portions of ether. The ethereal extract was dried (magnesium sulfate) and the ether taken off. There remained 0.9 g of a pale yellow oil, the infrared spectrum of which was identical with that of cyclohexanol. When the oil was submitted to vpc (135°, 6 ft × 0.25 in., 20% Carbowax 20M on 80–100 Chromosorb P column, He pressure 18 psi), two peaks were observed. Retention times corresponded to cyclohexene (9%) and cyclohexanol (120%), respectively.

A solution of sodium nitroprusside dihydrate (25.5 g, 0.086 mol) in 100 ml of water was added dropwise to a solution of benzylamine (1.5 g, 0.014 mol) and sodium carbonate (1.5 g, 0.014 mol) in 45 ml of water. The solution was stirred under oxygen for *ca.* 24 hr. Potassium carbonate (*ca.* 20 g) was then added and the mixture extracted with five 20-ml portions of ether. The ethereal extract was dried (magnesium sulfate) and the ether stripped off. There remained 1.1 g of an orange oil. When the oil was submitted to preparative vpc (125°, 20 ft × 0.375 in., 30% SE-30 on 60–80 Chromosorb W column, He pressure 20 psi), two peaks were observed, the retention times and infrared spectra of which corresponded to benzonitrile (40%) and benzyl alcohol (116%), respectively.

Registry No.—Nitroprusside, 1784-20-9; benzylamine, 100-46-9; allylamine, 107-11-9; cyclohexylamine, 108-91-8; 2-octylamine, 693-16-3; 1-butylamine, 109-73-9; diethylamine, 109-89-7.

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[6] No carbon-deuterated benzyl alcohol was obtained from reaction of benzylamine with nitroprusside in D_2O, indicating that phenyldiazomethane is not an intermediate in the deamination.

[7] H. Söll in Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, XI/2, G. Thieme Verlag, Stuttgart, 1958, p 133 ff.

[8] R. A. Moss and S. M. Lane, *J. Amer. Chem. Soc.*, **89**, 5655 (1967).

[9] F. C. Whitmore and D. P. Langlois, *ibid.*, **54**, 3441 (1932).

[10] C-Nitrosations of ketones with nitroprusside have been observed; *cf.* J. H. Swinehart, *Coord. Chem. Rev.*, **2**, 387 (1967).

[11] Infrared spectra were determined with a Beckman IR-10 instrument. Vpc determinations were performed on a Varian Aerograph 1700 instrument; vpc peak areas were calibrated with standards.

Reaction of Perfluoroalkyl Halides with Grignard Reagents

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The reactions of perfluorocarbon halides (Cl, Br, or I) with Grignard reagents reported in the literature[2-6] were mainly for the syntheses of fluorocarbon Grignard reagents. These alkyl or aryl exchange reactions were carried out at low temperatures (0 to −70°), because of the thermal instability of the fluorocarbon Grignard reagents. The present investigation was a study of this reaction at higher temperatures (>25°).

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[4] R. J. DePasquale and C. Tamborski, *J. Organometal. Chem.*, **13**, 273 (1968).

[5] W. L. Respress and C. Tamborski, *ibid.*, **11**, 619 (1968).

[6] R. J. DePasquale, *ibid.*, **15**, 233 (1968).