riod, the pressure rose to about 200 mm. The argon was carefully bled off to maintain the pressure at about 150 mm. A 0.25-mole run could be completed in 12–16 hr. When all of the silver salt had turned a bright yellow and bromine vapor was visible in the Pyrex wool plug and in the space above it, the system was evacuated very slowly (about 5 mm. per minute). When the pressure in the vacuum system had dropped to less than 100μ, the center tube in B was raised a bit at a time until clear of the mercury; the systen was then evacuated to a hard vacuum ($< 1\ \mu$ pressure). If bromine was apparent in trap A, its contents were repeatedly passed through the mercury bubbler from trap A to reservoir D and back until all color had been removed. The center tube of B was raised to allow free passage on the A to D portion of the cycle and lowered on the D to A portion. The stopcock on the sidearm of trap A was closed and the contents of the trap distilled through two U-traps at −96° and at −130°, respectively. Any material passing through the −130° trap (mostly CO_2) was discarded. The methyl-d_3 bromide in the −130° trap was measured gasometrically and transferred to a storage bulb. The material in the −96° trap (presumably acetic-d_3 acid-d and acetyl-d_3 bromide) amounted to about 50 mg./g. of silver salt and had a density of 1.1 g./ml. and a vapor pressure of 20 mm. at 0°. It was not investigated further. The average yield of methyl-d_3 bromide was 78%. Its vapor pressure at −41° and at 0° was 81 mm. and 680 mm., respectively (Nolin and Leitch[6] give 681.5 mm. at 0°).

1,2-Dimethoxy-d₆-ethane-d₄ and 2-methoxy-d₃-ethan-d₄-ol. A reaction tube of about 200-ml. capacity, fitted with a breakseal and a neck constricted for sealing under vacuum, was loaded in a dry box with 2.30 g. (0.10 mole) of sodium. The reaction tube was then attached to a Dry Ice condenser having a side arm for the introduction of other reactants and protected from moisture with an ascarite filled drying tube. Approximately 50 ml. of sodium-dried liquid ammonia was distilled into the reaction tube from a flask attached by means of an adapter to the side arm of the condenser. The flask and adapter were then removed, and the side arm was capped with a rubber syringe stopper through which 6.61 g. (0.10 mole) of ethylene-d_4 glycol was slowly introduced by means of a hypodermic syringe and long needle. The reaction tube was maintained at −35° to −40° during the addition. When the addition of the glycol was complete the syringe was washed three times with 10-ml. portions of sodium-dried ether. If much unreacted sodium remained caked on the walls of the tube, the syringe was replaced by a stainless-steel wire and the solids chipped off the glass. The apparatus was then allowed to warm slowly to room temperature overnight to allow the ammonia and some of the ether to evaporate. The last traces of ammonia and ether and about 0.1 g. of unreacted glycol were removed by baking the reaction tube at 100° under hard vacuum ($< 1\ \mu$ pressure) for about 4 hr. Methyl-d_3 bromide (0.10 mole, measured gasometrically) was distilled into the tube which was then sealed off at the constriction. After 10 days at room temperature, the reaction tube was attached *via* its breakseal to a series of traps on a vacuum line, and the volatile components of its contents were distilled into the first trap. The last traces were removed from the reaction vessel by heating it at 100° for 4 hr. A small amount of noncondensible material was pumped off. Approximately 1–2 millimoles of volatile material was removed from the material in the trap by distilling it through a −96° trap. The liquid residues from two such experiments were combined and fractionated through a 15-in. heated Vigreux column to yield 0.93 g. of forerun, b.p. 78–81.5°, $d_{20.5}$ 0.978, $n_D^{25.2}$ 1.37644; 5.05 g. of 1,2-dimethoxy-d_6-ethane-d_4, b.p. 83–84°; 0.49 g. of an intermediate cut, b.p. 115–121°, $d_{20.5}$ 0.993, $n_D^{25.5}$ 1.38572; 4.38 g. of 2-methoxy-d_3-ethan-d_4-ol, b.p. 122–124°, $d_{20.5}$ 1.042, $n_D^{25.5}$ 1.39701 and 6.57 g. of residual ethylene-d_4 glycol. The 1,2-dimethoxy-d_6-ethane-d_4 was dried over freshly cut sodium and distilled on a vacuum line, $d_{22.2}$ 0.944, $n_D^{25.2}$ 1.37447. It had the following vapor pressures at the temperatures indicated: 67 mm. at 24.4°, 65 mm. at 23.9°, 64 mm. at 23.4°, 34 mm. at 12°, 18 mm. at 0°, 3 mm. at −23°, and about 1 mm. at −41°.

1,2-Dimethoxy-d₆-ethane-d₄ from 2-methoxy-d₃-ethan-d₄-ol. 2-Methoxy-d_3-ethan-d_4-ol (1.44 g., 0.017 mole) was treated with 0.40 g. (0.017 mole) of sodium and 17.4 millimoles of methyl-d_3 bromide using the procedure described above. There was obtained 0.9 millimole of material volatile at −96°. The material from the −96° trap was dried over sodium and distilled on the vacuum line to yield 1.46 g. (85%) of 1,2-dimethoxy-d_6-ethane-d_4.

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Preparation of α-Morpholinoacrylonitrile

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In connection with a study of vinyl monomers containing a basic substituent it became desirable to synthesize the title compound. The literature[1] reveals but one preparation of α-(substituted amino)-acrylonitriles; this procedure involves the use of liquid HCN and more than two moles of secondary amine.

$$ClCH_2CHO + HCN \longrightarrow ClCH_2CH(OH)CN \xrightarrow{2\ R_2NH} CH_2{=}C(NR_2)CN + R_2NH{\cdot}HCl \quad (I)$$

We have found that the previously unreported I, ($R_2 = C_4H_8O$), can be prepared in fair yields by an improved procedure which (*a*) avoids the use of liquid HCN, (*b*) substitutes caustic for an excess of the more expensive amine, and (*c*) permits the whole operation to be performed in one flask without the isolation of intermediates. Dimethyl chloroacetal is hydrolyzed with dilute mineral acid to the free aldehyde. To the resultant solution is added an aqueous solution of the amine hydrochoride and, after cooling, sodium cyanide to form the β-chloroaminonitrile. Dehydrochlorination, to give the title compound, is accomplished by addition of one equivalent of sodium hydroxide. The technique is applicable to other secondary amines.

The product was unstable and decomposed on standing at room temperature even in the dark.

EXPERIMENTAL[2]

To 63 g. (0.5 mole) of dimethyl chloroacetal (Carbide and Carbon Chemical Co.) was added 80 ml. of 0.75*N* hydro-

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[1] O. Nicodemus, H. Lange, and H. Kranz, U.S. Patent 2,211,152 (to General Aniline and Film Corp.), August 13, 1941.

[2] Melting points are uncorrected.

chloric acid and the mixture warmed (80°) and stirred under reflux until a clear solution resulted (about 15 min.). A solution of morpholine hydrochloride (0.60 mole) in 160 ml. of water was then added and the flask contents cooled to below 10°. Then 30 g. of 95% sodium cyanide (0.60 mole) in 100 ml. of water was slowly introduced below the surface of the cooled, stirred solution. The flask was immersed in the cooling bath so that the liquid level was well below the surface of the bath. After 2 hr. in the cold, a solution of 24 g. (0.60 mole) of sodium hydroxide in 60 ml. of water was added. The mixture was stirred in the cold for an additional hour and then filtered. The white solid was collected, washed with cold water several times, and air dried. The yield of α-morpholinoacrylonitrile, m.p. 62.5–63.5° after recrystallization from 30–60° petroleum ether, was 40 g. (58%).

Anal. Calcd. for $C_7H_{10}N_2O$: C, 60.85; H, 7.30; N, 20.28. Found: C, 61.50; H, 7.15; N, 20.09.

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A New Method for the Preparation of Formamidine

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The formation of formamidine as an intermediate was first reported by Odo and Sugino by the electrolytic reduction of cyanamide in 8% $(NH_4)_2SO_4$ catholyte at a tin cathode.[1]

$$NH_2CN + 2H \longrightarrow NH_2{\cdot}CH{=}NH$$

Further study on the mechanism of this electrode reaction showed that the first step in the reduction of cyanamide to formamidine seems to be favored by carrying it out catalytically over palladium rather than electrochemically. The yield is almost quantitative. It was surprising to us that this simple method had not been previously reported.

EXPERIMENTAL[2]

Twenty grams of palladium-charcoal catalyst[3] (containing 1.4% Pd) in 200 cc. water was placed in a reduction bottle provided with two separatory funnels and with a stream of hydrogen flowing through it to exclude air. The bottle was first shaken to reduce the catalyst completely. To it, there was added 100 cc. of 12% H_2SO_4 (or 100 cc. of 9% HCl) from one funnel. Then, from the other funnel, an aqueous solution of 11 g. of freshly prepared cyanamide (purity 97% as silver cyanamide) in 100 cc. water was added portion-wise (1.5 cc. at intervals of 3 min.) for 3 hr. with shaking at room temperature, while the hydrogen continued to be taken up. The reduction was complete about 10 min. after the last portion had been added at which time 5.8 l. (0.25 mole, 100% of theoretical) of hydrogen had been absorbed.

After the reduction, the mixture was filtered and the filtrate was combined with catalyst washings. The resulting solution was adjusted to *p*H 4.8–5.0 by adding a small amount of Amberlite 1R4B and was evaporated to dryness below 60° under diminished pressure. The crystals of formamidine sulfate (or hydrochloride) separated. After recrystallization from methanol, 22.5 g. of pure formamidine sulfate (or 18.8 g. hydrochloride) was obtained, m.p. 156–158° (hydrochloride, 76–78°), yield 95% (hydrochloride, 92%).

Anal. of the sulfate. Calcd. for $CH_4N_2\cdot{}^1/_2H_2SO_4$: N, 30.11. Found: N, 29.82.

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[1] K. Odo, K. Sugino, *J. Electrochem. Soc.*, **104**, 160 (1957).

[2] All melting points are uncorrected.

[3] This catalyst consisted of activated charcoal with absorbed Pd, prepared according to the procedure of Wieland, *Ber.*, **45**, 484 (1912).

Metalation of Aryl Fluorides in Tetrahydrofuran

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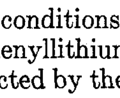
The metalation of fluorobenzene with phenyllithium at 0° in diethyl ether by Wittig and coworkers gave products which indicated that *o*-fluorophenyllithium was one of the intermediates.[1-3] Under the conditions that were employed, however, *o*-fluorophenyllithium was too reactive to be successfully detected by the formation of derivatives as such.

Later work demonstrated that the *o*-fluorophenyllithium gave rise to the more reactive "benzyne" intermediate which was indirectly responsible for products that were obtained such as triphenylene.[4-7]

More recent work in this laboratory has shown that *o*-fluorophenyllithium can be obtained in excellent yields from *o*-fluorobromobenzene and *n*-butyllithium at -60° by means of the halogen-metal interconversion reaction.[6] Evidence was also obtained for the formation of the "benzyne" intermediate by the isolation of 1,4-dihydronaphthalene-1,4-endoxide (I) when the *o*-fluorophenyllithium was permitted to warm to room temperature in the



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[1] G. Wittig, G. Pieper, and G. Fuhrmann, *Ber.*, **73** 1193 (1940).

[2] G. Wittig and W. Merkel, *Ber.*, **75**, 1491 (1942).

[3] G. Wittig, *Naturwiss.*, **30**, 696 (1942).

[4] G. Wittig and L. Pohmer, *Angew. Chem.*, **67**, 348 (1955).

[5] G. Wittig and L. Pohmer, *Chem. Ber.*, **89**, 1334 (1956).

[6] H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **78**, 2217 (1956).

[7] H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **79**, 2625 (1957).