yielded a yellow-orange solid, which was shown by ^{1}H NMR to be a ca. 1:1 mixture of the thioether **6** and the thioester **7** (vide infra). Recrystallization from methanol yielded white needles of **7** (0.2 g, 14%): mp 102–104 °C; ^{1}H NMR ($CDCl_3$) δ 2.35 (3 H, s, Me), 7.25 (4 H, br s, Ar), 8.2 (4 H, q, $J = 7$ Hz, Ar). Anal. Calcd for $C_{14}H_{11}NO_3S$: C, 61.54; H, 4.03; N, 5.12. Found: C, 61.44; H, 4.16; N, 5.45.

The methanol filtrate, when allowed to stand for a few hours (with concomittant concentration of dissolved material), followed by cooling, deposited 0.1 g (6%) of white crystals, mp 178–180 °C, which are identical by mmp, IR, and ^{1}H NMR with the *Z* thioether **6** obtained previously from the reaction of **5** with sodium *p*-toluenethiolate.[11]

Hydrolysis of 3 with $H_2{}^{18}O/Na^{18}OH$. ^{18}O-enriched water (22.51%) (0.25 mL, 13 mmol) was added to 8 mL of dry THF. Sodium (11.6 mg, 0.5 mmol) was added, and after its dissolution, **3** (200 mg, 0.5 mmol) in dry THF (2 mL) was added. After the mixture was warmed to 35–40 °C for a few min, the characteristic yellow color of **1** began to develop. The mixture was stirred at room temperature for 21 h, the solvent was then removed under reduced pressure, and the resulting yellow powder was dried at 70 °C over P_2O_5 at 1 mmHg. The dried material was dissolved in anhydrous methanol and cooled to 0 °C, and one drop of concentrated sulfuric acid was added. The small amount of white solid formed (mainly **2**) was filtered, and the filtrate was slowly concentrated to yield two types of readily separable crystals: plates, mp 235–237 °C, of *p*-nitrobenzoic acid (identified by mass spectra and mmp) and needles, mp 156–157 °C, of enol **2**. The mass spectrum of this enol shows a parent peak at *m/e* 248 with M + 1 and M + 2 peaks with intensities predicted by the ^{13}C natural abundance but with no appreciable ^{18}O incorporation. The complete spectrum is identical with that of **2** previously prepared from *p*-nitrobenzoyl chloride and methyl cyanoacetate.[11] The *p*-nitrobenzoic acid isolated by this procedure shows a *m/e* 169 (M^+ for ^{18}O acid) with an intensity of ca. 20% of that of the peak at *m/e* 167 (M^+ for the ^{16}O acid), indicating that incorporation of ^{18}O into the acid from the 22.5% ^{18}O-enriched water is complete within the accuracy of determination of relative peak intensities.

Hydrolysis of 4 with $H_2{}^{18}O/Na^{18}OH$. This reaction was run in a fashion similar to that for the hydrolysis of **3**, except that the cooled solution of **1** in methanol was acidified with dry HCl gas instead of concentrated sulfuric acid. The enol **2** that precipitated from this acid treatment was filtered off, and its mass spectrum showed only M^+ at 248, with no ^{18}O enrichment.

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Registry No. (*Z*)-**3**, 83291-80-9; (*Z*)-**4**, 83291-81-0; (*Z*)-**6**, 80641-26-5; **7**, 28122-84-1; p-$O_2NC_6H_4COCl$, 122-04-3; $CH_2(CN)CO_2Me$, 105-34-0; sodium *p*-toluenethiolate, 10486-08-5.

Neutral Regioselective Copper-Catalyzed Hydration of Some Nitriles to Amides[†]

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A variety of methods exist for the hydration of nitriles to amides.[1] While acidic and basic catalysts have long been employed, the importance of catalytic hydration especially under neutral conditions is being increasingly recognized.[2,3] The hydration of nitriles like acrylonitrile to give acrylamide,[4–6] an important industrial chemical, dictates regioselectivity as a further criterion in the hydration reaction.

Table I. Conversion of Nitriles to Amides[a]

nitrile	amide	crude yield %[b]	mp, °C found[c]	mp, °C reported
acetonitrile	acetamide	50	81	82.3[d]
acrylonitrile	acrylamide	89	83.6	84–85[d]
2-chloro-acrylonitrile	2-chloro-acrylamide	65	91.2	94[e]
benzonitrile	benzamide	83	129	132.5–133.5[d]
phenyl-acetonitrile	phenyl-acetamide	76	159.3	156–160[f]
malononitrile	2-cyano-acetamide[g,h]	96	112	121

[a] All amides gave satisfactory NMR (^{1}H and ^{13}C) and IR data; ^{13}C chemical shift data (δ) when not available in literature are mentioned here. 2-Chloroacrylamide (solvent D_2O): 167.65 ($CONH_2$), 133.42 (=CCl), 125.42 (=CH_2). Malonamide (solvent D_2O): 173.06 ($CONH_2$), 43.17 (CH_2). 2-Cyanoacetamide (solvent Me_2SO): 164.59 ($CONH_2$), 116.24 (C≡N), 25.29 (CH_2). [b] Yields are not necessarily optimized. Crude products were spectroscopically pure. [c] Melting pints of crude products. [d] Weast, R. C., Ed. "Handbook of Chemistry and Physics", 52nd ed.; CRC Press: Cleveland, OH, 1971–1972. [e] Ivanov, S. S.; Koton, M M. *Zh. Obshch. Khim.* **1958**, *28*, 139; *Chem. Abstr.* **1958**, *52*, 12757*d*. [f] "The Condensed Chemical Dictionary", 8th ed.; Van Nostrand-Reinhold: New York, 1971; p 678. [g] Contains ~10% of the diamide. [h] A product mixture containing monoamide and diamide in the ratio of 1:3 was obtained when the time of reaction was 4 h and the substrate catalyst ratio was 0.5.

Considerable patent literature[7] exists on the use of "reduced copper" for the hydration of acrylonitrile to acrylamide, but there is a paucity of published information on the generality of the reaction, experimental conditions, yield data, properties of the catalyst, etc. We have examined in detail the use of copper(0) as a catalyst for the hydration of various nitriles to the corresponding amides (eq 1).

$$\mathrm{RCN} \xrightarrow[\mathrm{H_2O}]{\mathrm{Cu(0)}} \mathrm{RC(O)NH_2} \qquad (1)$$

The catalyst was prepared by reducing copper(II) sulfate with sodium borohydride. The resulting black powder, essentially copper(0) (X-ray) had a surface area of ~8 m^2/g (BET). This catalyst was very effective in the re-

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gioselective hydration of acrylonitrile to acrylamide in 89% yield. Absence of byproducts such as ethylene cyanohydrin and β,β'-dicyanodiethyl ether testified to the remarkable regioselectivity of the reaction. Another sensitive substrate, 2-chloroacrylonitrile, was hydrated regioselectively to 2-chloroacrylamide in good yield.

The sparingly water soluble nitriles such as benzonitrile and phenylacetonitrile also underwent facile hydration to the respective amides. No cosolvents were needed to bring about hydration. With malonitrile, a mixture of mono- and diamides was obtained, the composition being dependent on the amount of catalyst and reaction time (Table I).

The reusability of the recovered catalyst was demonstrated by using phenylacetonitrile as the test case. No regression in the activity of the recovered catalyst was noticed.

Experimental Section

Melting points (uncorrected) were determined on a Mettler FP 5 instrument. Infrared spectra were recorded on a Perkin-Elmer 567 instrument, and ^{1}H and ^{13}C NMR spectra were taken on a JEOL FX-100 NMR spectrometer. X-ray diffractograms were obtained by using a Phillips Model PW (1140) X-ray generator with Cu Kα radiation. The BET surface area measurements were made on a Sorptomatic Model 1810 (Carlo Erba Strumentazione, Italy).

Preparation of the Copper Catalyst. In a 2-L three-necked flask equipped with a magnetic stirring bar, an addition funnel, and a nitrogen inlet were placed copper sulfate pentahydrate (31.2 g, 0.125 mol) and deaerated water (150 mL, 8.33 mol). An alkaline solution of sodium borohydride was prepared by dissolving sodium borohydride (5.28 g, 0.14 mol) in NaOH (5.2 g of NaOH in 250 mL of water). The sodium borohydride solution was transferred to the addition funnel and added dropwise to the cooled copper sulfate solution (5 °C) with stirring during a period of 2 h. A steady flow of N$_2$ was maintained throughout the addition. The stirring was continued for another 1 h. The flask was then transferred to a glovebox, the supernatant liquid was decanted off, and the catalyst was repeatedly washed with water until the washings were neutral. The wet catalyst, stored in an atmosphere of nitrogen, was used for the hydration reaction.

General Method for the Hydration of Nitriles. A 1-L Parr shaker bottle was charged with the copper catalyst (8 g, 0.125 mol), acrylonitrile (14 g, 0.263 mol), and water (220 mL, 12.2 mol). Hydroquinone (0.2 g) was added as the polymerization inhibitor. The flask was then flushed with N$_2$ and securely stoppered. All these operations were carried out inside the glovebox under an N$_2$ atmosphere. The reaction flask was then heated to 90 °C and maintained at that temperature for 2 h with vigorous shaking. The contents of the flask were cooled to room temperature, and the catalyst was filtered off. The filtrate was then evaporated to dryness under reduced pressure (15–20 mmHg) at 40–45 °C. The residue was collected and dried. The crude yield of acrylamide was 16.6 g (89%); mp 83.6 °C. A similar procedure was followed for the hydration of acetonitrile, 2-chloroacrylonitrile, and malononitrile (see Table I).

In the case of cold water insoluble amides (benzamide, phenylacetamide), the pressure was carefully released at the end of the reaction and the catalyst was filtered off while the solution was hot. The amide crystallized out from the solution on cooling. It was then filtered and dried.

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Registry No. Acetonitrile, 75-05-8; acrylonitrile, 107-13-1; 2-chloroacrylonitrile, 920-37-6; benzonitrile, 100-47-0; phenylacetonitrile, 140-29-4; malononitrile, 109-77-3; acetamide, 60-35-5; acrylamide, 79-06-1; 2-chloroacrylamide, 16490-68-9; benzamide, 55-21-0; phenylacetamide, 103-81-1; 2-cyanoacetamide, 107-91-5; copper, 7440-50-8; copper sulfate, 7758-98-7.

Communications

Donor-Atom Effects on Relative E2 Rate Constants for Reactions of Anions with Cyclohexyl Bromide

Summary: 2-Naphthoxide oxanions (2-NpO$^-$) and carbazole nitranions (Cb$^-$) react with cyclohexyl bromide in Me$_2$SO solution to give cyclohexene, whereas 9-methylfluorene carbanions (9-MeFl$^-$) give substitution and benzenethiolate thianions give both elimination and substitution. The relative order of E2 rate constants for anions of the same basicity is ArS$^-$ > 2-NpO$^-$ > Cb$^-$ > 9-MeFl$^-$.

Sir: In 1956 the observation was made independently in three laboratories that weakly basic, highly nucleophilic anions are surprisingly effective at promoting elimination reactions. In EtOH, PhS$^-$ ions were shown to rival EtO$^-$ ions in their ability to promote E2 reactions with t-BuCl[1] or cyclohexyl tosylate (c-C$_6$H$_{11}$OTs),[2] and in acetone Cl$^-$ ions were shown to be effective in promoting elimination from c-C$_6$H$_{11}$OTs.[3] These results were later confirmed and extended by additional investigations of E2 reactions of (a) ArS$^-$ ions with c-C$_6$H$_{11}$Br and c-C$_6$H$_{11}$OTs in EtOH,[4] (b) EtS$^-$ and MeO$^-$ with PhCH$_2$C(X)Me$_2$ in MeOH,[5a] (c) Cl$^-$, Br$^-$, I$^-$, with RC(Br)Me$_2$ in acetone,[5b] and (d) Cl$^-$, Br$^-$, I$^-$, AcO$^-$, CN$^-$, N$_3^-$, PhO$^-$, and PhS$^-$ with c-C$_6$H$_{11}$X in acetone and other dipolar nonhydroxylic ("aprotic") solvents such as dimethylformamide (DMF) and Me$_2$SO.[6] In the latter study, the observation that the relative E2 rate constants appeared to correlate well with anion nucleophilicities, as defined by S$_N$2 rate constants in hydroxylic solvents, and not at all with anion basicities, as defined by pK_a values in DMF solvent, led to the conclusion that the anion is bonded to carbon, as well as to hydrogen, in the E2 transition state.[6] Eck and Bunnett have argued, however, that the interaction of the anion with carbon cannot be significant because it fails to respond to S$_N$2-type steric effects.[5b] A counter argument has been presented,[7] and Saunders and Cockerill conclude that "there is no

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