note that *p*-bromoacetophenone is converted into acetophenone in only 13% yield using tri-*n*-butyltin hydride,[10] while *m*-bromoacetophenone is converted into acetophenone in 94% yield electrochemically, without appreciable base-catalyzed aldolization. The electrochemical method is, however, more difficult to scale up for large-scale preparations. For the occasional highly base-sensitive system, one may, furthermore, take advantage of the pH independence of the electrochemical reduction of alkyl halides[11] by purposely adding an acid (phenol or even mineral acid[12]) to the mixture to protonate the carbanion as formed.

Experimental Section

Apparatus and Chemicals.—Dimethylformamide was refluxed over calcium hydride [70° (0.1 mm)] for 1 hr, followed by distillation *in vacuo* through a 10 × 300 mm glass helix packed column. Tetraethylammonium bromide was recrystallized from an ethanol ether mixture and dried *in vacuo*. Controlled-potential electrolyses were carried out with the aid of a potentiostat based upon a Kepco KS-120-2.5 programmable power supply.[13]

Electrolyses.—A modified polarographic H cell was used for small-scale electrolyses; the dme was replaced by a mercury pool, for which electrical contact was maintained *via* a platinum contact piercing the cell wall. A mechanical stirrer and Cd(Hg)–$CdCl_2$ reference[14] (isolated by a methyl cellulose plug[15]) were positioned close to the mercury surface. One side of the cell contained the catholyte [5 ml of a solution of the organic substrate (10^{-2} *M*) and Et_4NBr (10^{-1} *M*) in DMF, and the other side of the cell contained a silver anode in a solution of 10^{-1} *M* Et_4NBr in DMF. A methyl cellulose plug[15] separated the two sides of the cell. Electrochemical reductions were carried out upon samples freshly purified by preparative glpc. After electrolysis, the contents of the cell were analyzed directly by vpc (Varian Aerograph Model 1740). Preparative electrolysis of *p*-iodobromobenzene was carried out in 90% ethanol containing 0.1 *M* tetraethylammonium bromide in a large crystallizing dish containing a platinum anode, mercury pool cathode, Cd(Hg)–$CdCl_2$ reference electrode, and mechanical stirrer. Hydrazine hydrate was added as the anodic depolarizer; its oxidation to nitrogen at the anode also generates protons to prevent the solution from becoming basic. From 28.3 g (0.1 mol) of *p*-iodobromobenzene was isolated, after dilution with water, extraction with pentane, and distillation of the solvent, 14.7 g (94%) of bromobenzene, homogeneous by vpc.

***p*-Bromo-2-chloroethylbenzene.**—*p*-Bromo-2-phenylethanol[16] was prepared through lithium aluminum hydride reduction of *p*-bromophenylacetic acid. A solution of 20.0 g each of the alcohol and thionyl chloride was refluxed overnight. Thionyl chloride was then removed with warming at the rotary evaporator. Distillation afforded *p*-bromo-2-chloroethylbenzene: yield 15 g (65%); bp 70° (0.15 mm); nmr (CCl_4) τ 2.73 and 3.07 (AB pattern, $J = 8.5$ Hz, area 4), 6.50 (t, $J = 6.5$ Hz, area 2), and 7.07 (t, $J = 6.5$ Hz, area 2).

Anal. Calcd for C_8H_8ClBr: C, 43.88; H, 3.62. Found: C, 43.61; H, 3.51.

Registry No.—*p*-Bromo-2-chloroethylbenzene, 23386-17-6.

Acknowledgment.—Financial support was provided by the National Science Foundation and the Petroleum Research Fund of the American Chemical Society.

(11) See footnote *a*, Table I.

(12) A. J. Fry and R. H. Moore, *J. Org. Chem.*, **33**, 1283 (1968).

(13) P. Birman, "Power Supply Handbook," Kepco Inc., Flushing, N. Y., 1965, p 129.

(14) L. W. Marple, *Anal. Chem.*, **39**, 844 (1967). This electrode is *ca.* −0.9 V relative to sce.

(15) G. Dryhurst and P. J. Elving, *ibid.*, **39**, 607 (1967).

(16) D. Sontag, *Ann. Chim.* (Paris), **1** (11), 359 (1934).

Base-Catalyzed Reactions of α-Cyano-β-furylacrylic Esters

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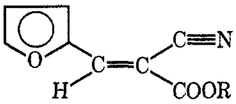
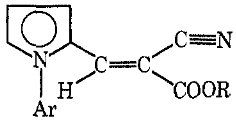
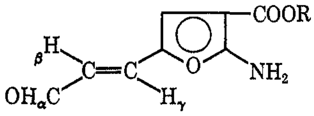
The ring-opening reactions of the furan derivatives with ammonia and amines have been extensively investigated by a number of authors.[2] Leditschke[3] reported that the reaction of α-cyano-β-furylacrylic esters (**1**) with primary arylamines afforded α-cyano-1-aryl-2-pyrroleacrylic esters (**2**). However, we have found that **1**, when treated with morpholine instead of the primary arylamines, gives rise to an unexpected colored product. We have shown this product to have the structure γ-(4-alkoxycarbonyl-5-aminofuryl)-acrolein (**3**).



1



2



3a, R = C_2H_5
b, R = $PhCH_2$

The product **3a** obtained from ethyl α-cyano-β-furylacrylate (**1**, R = C_2H_5) and morpholine, was recrystallized from chloroform as yellowish green needles, mp 174–175°, having a molecular ion peak at *m/e* 209, and a molecular formula of $C_{10}H_{11}NO_4$. When treated with 2,4-dinitrophenylhydrazine and semicarbazide, **3a** gave the corresponding hydrazone **4** and semicarbazone **5**, respectively, and when treated with fuchsin reagents, showed a positive test for aldehyde. All attempts to acetylate **3a** were unsuccessful, and catalytic hydrogenation led to a colorless polymer.

The ir spectrum of **3a** ($CHCl_3$) revealed the disappearance of the cyano group. The NH_2 and ester C=O stretching frequencies appeared at 3508 and 3382 and at 1672 cm^{-1}, respectively, comparable with those of ethyl 5,7-dimethyl-2-amino-3-benzofuroate (3480 and 3346, and 1679 cm^{-1}).[4] The aldehydic CH stretching bands are clearly observed at 2818 and 2730 cm^{-1}.

The nmr spectrum (deuterated DMSO) showed that morpholine used in the reaction is not entering into the reaction product. The presence of the CH=CHCHO system is supported by the fact that the two olefinic protons and aldehydic proton constitute the three spin AMX pattern. A rather large coupling constant between the two olefinic protons suggests the *trans* configuration about the C=C bond. The mass spec-

(1) Chemical Laboratory, Department of Education, University of Utsunomiya, Japan.

(2) P. Bosshard and C. H. Eugster, *Advan. Heterocycl. Chem.*, **7**, 378 (1966).

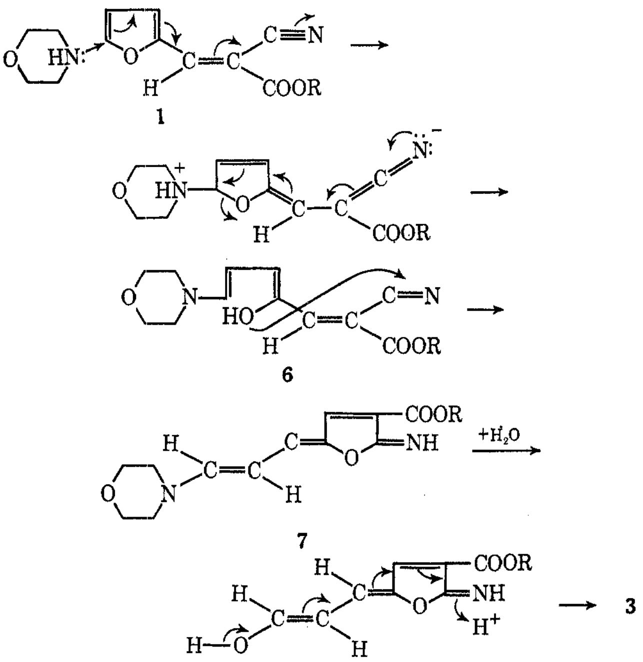
(3) H. Leditschke, *Chem. Ber.*, **85**, 483 (1952).

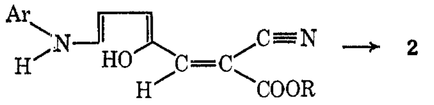
(4) J. Derkosch and I. Specht, *Monatsh. Chem.*, **92**, 542 (1961).

trum showed a fragment ion peak at m/e 163, which is considered to be generated by loss of C_2H_5OH from the parent ion peak by McLafferty rearrangement.[5]

A plausible reaction mechanism is postulated in Scheme I. It seems reasonable to assume that initially the base may attack the 5-position of the furan ring in **3**. Cyclization of the intermediate **6** may occur between the OH and CN groups to give the intermediate **7**, which then yields, when treated with water, the product **3**. When the primary arylamines are used as a base in the reaction, the resulting intermediate **8** similar to **6** would cyclize between the OH and NH groups to give the product **2**.

SCHEME I





8

Experimental Section

Nmr spectra were obtained on a JNM-C-60 high-resolution nmr spectrometer at a temperature of 19–20°. Tetramethylsilane (δ, 0) was used as an internal reference standard. Ir spectra were determined in the chloroform solution using a Perkin-Elmer 521 spectrophotometer. Mass spectra were measured with JMS-O1S instrument operating at 75 eV.

Reaction of Ethyl α-Cyano-β-furylacrylate(1a) with Morpholine.—A mixture of 10 g (0.052 mol) of the ester and 40 ml of morpholine was stirred at room temperature for 30 min. The reaction was exothermic, and the solution immediately turned orange, then reddish brown, and finally dark red. After being allowed to stand overnight, the viscous solution was poured into 1.0 l. of water under vigorous stirring. The resulting solid matrial was recrystallized from chloroform to give 5.9 g (54% yield) of **3a** as yellowish green needles: mp 174–175°; uv max ($CHCl_3$) 284 mμ (ϵ 5200), 374 (34,000); (99.5% EtOH) 228 (10,100), 284 (7200), 387 (36,500); ir ($CHCl_3$) 3508, 3382 (NH_2), 2818, 2730 (aldehyde CH), 1685 (aldehyde C=O), 1672 (ester C=O), 1636 (C=C), 1612, 1378, 1312, and 985 cm^{-1} (furan ring); nmr (d_6-DMSO) δ 1.27, 4.23 ($COOCH_2CH_3$), 6.06 (quartet, H_β, $J_{\beta\gamma}$ = 15.0 Hz, $J_{\alpha\beta}$ = 7.8 Hz, $J_{\alpha\gamma}$ = *ca.* 0), 7.30 (d, H_γ, $J_{\beta\gamma}$ = 15.0 Hz), 9.78 (d, H_α, $J_{\alpha\beta}$, = 7.8 Hz), 7.14 (s, furan ring H), 7.82 (broad, NH_2).

Anal. Calcd for $C_{10}H_{11}NO_4$: C, 57.42; H, 5.26; N, 6.70. Found: C, 57.49; H, 5.17; N, 6.77.

The 2,4-dinitrophenylhydrazone (**4**) occurred as dark brown needles (from pyridine–methanol), mp over 250°.

Anal. Calcd for $C_{16}H_{15}N_5O_7$: N, 17.99. Found: N, 18.05.

The semicarbazone 5 occurred as yellow needles (from methanol), mp 203–204°.

Anal. Calcd for $C_{11}H_{14}N_4O_4$: N, 21.05. Found: N, 20.98.

Reaction of Benzyl α-Cyano-β-furylacrylate (1b) with Morpholine.—The reaction procedure was the same as described above. Recrystallizations of solid **3b** from chloroform and from glyme–ethanol gave brown needles: mp 188–189°; uv max ($CHCl_3$) 287 mμ (ϵ 5,100), 375 (30,600); (99.5% v/v EtOH) 227 (9400), 285 (7000), 385 (33,200); ir ($CHCl_3$) 3495, 3380 (NH_2), 2800, 2720 (aldehyde CH), 1685 (aldehyde C=O), 1672 (ester C=O), 1630 (C=C), 1613, 1382, 1303 cm^{-1} (furan ring); nmr (d_6-DMSO) δ 5.23 (s, $COOCH_2Ph$), 6.04 (quartet, H_β, $J_{\beta\gamma}$ = 15.0 Hz, $J_{\alpha\beta}$ = 7.8 Hz), 7.20 (s, furan ring H), 7.30 (d, H_γ, $J_{\beta\gamma}$ = 15.0), 7.99 (broad, NH_2), 9.45 (d, H_α, $J_{\alpha\beta}$ = 7.8); mass spectrum (75 eV) m/e 271 (molecular ion peak).

Anal. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.82; H, 4.74; N, 5.04.

Registry No.—**3a**, 23386-18-7; **3b**, 23386-19-8; **4**, 23386-20-1; **5**, 23386-21-2.

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[5] G. Spiteller, *Monatsh. Chem.*, **92**, 1142 (1961).

Chromous Sulfate Reduction of 2-Methyl-3-hexyne-2,5-diol

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The reduction of nonterminal acetylenes by chromous sulfate[2] has been reported[3] to lead stereoselectively to *trans* olefins in high yields. Sterically hindered alkylacetylenes are found to react slowly or to be inert to chromous sulfate. Conversely, the presence of hydroxyl or carboxyl substituents near the acetylenic bond enhances reduction.

We have found that the reduction of 2-methyl-3-hexyne-2,5-diol with aqueous chromous sulfate, while proceeding readily at room temperature, does not produce the expected *trans*-2-methyl-3-hexene-2,5-diol. Rather the reaction leads to three isomeric reduction products (Scheme I) in which the hydroxyl group rather than the triple bond is reduced. The overall yield of products is 70%, the balance being recovered starting material.

The hydrogenolysis of a hydroxyl group under such mild conditions is unusual and seems to have been previously observed only in reductions with lithium aluminum hydride.[4,5]

The reduction products (**1**, **2**, and **3**) were isolated in pure form by preparative gas chromatography (glpc) (see Experimental Section).

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[2] For a review of the reactions of Cr(II), see J. R. Hanson and E. Premuzic, *Angew. Chem.*, **80**, 271(1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 247 (1968).

[3] C. E. Castro and R. D. Stephens, *J. Amer. Chem. Soc.*, **86**, 4358 (1964).

[4] W. Oroshnik, A. D. Mebane, and G. Karmas, *ibid.*, **75**, 1050 (1953).

[5] J. Meinwald and L. Hendry, *Tetrahedron Lett.*, 1657 (1969).