2. Thus two *different* olefinic carbon resonances are observed at $\delta$ 113.75 (C-3 of furan) and $\delta$ 155.38 (C-2 of furan) and are shown by off-resonance decoupling to be tetrasubstituted. No signal characteristic of a ketonic carbonyl carbon is present. The $^1$H NMR spectrum is obviously in accord with either structure, and the IR and Raman spectra are not decisive. Structure **3** differs from **2** by 16 mass units and in accord with **3**, we find an abundant molecular ion at $m/z$ 240 (30%), loss of ethoxy ($m/z$ 195, 50%) and ethanol ($m/z$ 194, 100%) followed by the loss from these ions of CO ($m/z$ 167, 25%, and $m/z$ 166, 75%). No other ions are present above 10% relative abundance. This pattern resembles that reported previously for the reaction product,[1] but in keeping with structure **3**, it is shifted 16 units lower in mass. The intense but unusual ions reported at $m/z$ 44 and 89[1] are difficult to explain from either structure.

Airy et al. also noted that IR and $^1$H NMR spectra of **1** fail to provide evidence for enolization.[1] However, when **1** is allowed to stand for 2 h in CDCl$_3$ solution in an NMR tube, a second set of $^{13}$C resonances appears, indicating that equilibration between the meso and erythro forms has occurred. Undoubtedly, a small amount of enol is responsible although it cannot be detected in the NMR. Evidence that equilibrium between at least one of the keto forms and one of the enol forms is very rapid is provided by the nearly instantaneous appearance of a UV maximum at 270 nm when a trace of bis(trimethylsilyl)acetamide is added to a 0.49 mM chloroform solution of **1** in a cuvette. This peak represents complete conversion to the bis(trimethylsilyl) derivative of the bis enol of **1** as proved by GC/MS. Indeed, five tautomeric forms of **1** have been characterized in earlier work.[3]

The preparation of diethyl diacetylmaleate remains an elusive goal.

## Experimental Section

IR spectra were recorded on a Perkin-Elmer Model 21, using a thin film pressed between salt plates; $^1$H and $^{13}$C spectra were recorded on a JEOL FX-60 at 59.8 and 15 MHz, respectively, using C$_6$D$_6$ as an internal lock and tetramethylsilane as internal reference. Mass spectra were recorded on an LKB-9000 combined GC/MS instrument using a 2-m packed column coated with 1% OV-17 or an LKB 2091 using a 25-m capillary column coated with SE-30. Ultraviolet spectra were recorded on a Perkin-Elmer Model 552.

**Diethyl diacetylsuccinate** was synthesized in low yield by the previous authors' modification[1] of the procedure of Dann et al.[4] Better results (30% yield) were obtained by the earlier procedure of Dann[5] using acetone as a solvent for the sodioacetoacetic ester and sodium iodide as a catalyst. The product, mp 88 °C, showed the properties recorded by the previous authors. The $^{13}$C spectrum showed lines at $\delta$ 201.3, 166.9, 61.9, 57.7, 30.6, and 13.9. After ~2 h additional lines were observed at $\delta$ 200.9, 58.5, and 30.0, which, on long standing, became approximately 60% as strong as those remaining from the original isomer.

Addition of a small amount of bis(trimethylsilyl)acetamide to an initially transparent 0.49 mM solution caused a peak to appear in the UV at 270 nm ($\epsilon$ ~37 000). Upon GC/MS a single peak, the bis enol ether eluted at 180 °C from a 25-m capillary column coated with SE-30 and showed important ions at $m/z$ (relative intensity) 402 (M$^{+\cdot}$,10), 387 (10), 357 (10), 356 (13), 313 (10), 310 (13), 269 (11), 267 (8), 239 (13), 238 (20), 211 (15), 147 (16), 75 (24), 73 (100), 45 (17), 43 (20), and 29 (9).

**2,5-Dimethyl-3,4-dicarbethoxyfuran (3).** Agitation of a CCl$_4$ solution with cold, concentrated H$_2$SO$_4$ for ~2 min, workup with water, and drying with Na$_2$SO$_4$ as described[1] gave an oil which showed about 30% conversion to **3** by GC/MS at 165 °C on 1% OV-17. No other products besides starting material were observed at this temperature. Complete conversion of **1** to **3** was best realized by omitting the CCl$_4$ entirely. The product (**3**) showed IR and $^1$H NMR spectra identical with those of the previous authors:[1] $^{13}$C NMR (CDCl$_3$) $\delta$ 13.05, 14.22 (C-2 methyl of furan and OCH$_2$CH$_3$), 60.52 (OCH$_2$CH$_3$), 113.75 (C-3 of furan), 155.38 (C-2 of furan), 163.50 (COOC$_2$H$_5$); mass spectrum (see text). Material for combustion analysis was obtained by distillation [bp 95-105 °C (0.1 mm)]. Anal. Calcd for C$_{12}$H$_{16}$O$_5$: C, 59.99; H, 6.71. Found: C, 59.83; H, 6.53.

**Registry No.** 1 (isomer 1), 72952-89-7; 1 (isomer 2), 72952-90-0; 1, bis enol ether, 72952-91-1; 3, 19434-69-6.

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[2] Furan **3** is, in fact, the expected product of sulfuric acid treatment of **1** as discussed many years ago: L. Knorr, *Ber. Dtsch. Chem. Ges.*, **17**, 2866 (1884).

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[4] O. Dann, E. Pietschmann, and W. Dimmling, *Arch. Pharm. Ber. Dtsch. Pharm. Ges.*, **292**, 508 (1959).

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# Evidence for Solid-Liquid Phase-Transfer Catalysis[1]

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The commonly accepted mechanism for crown ether catalyzed solid-liquid biphase displacement reactions is summarized in eq 1-3.[2-4] The key feature in this scheme

$$\mathrm{M^+Nu^-\ (solid) + CE\ (soln) \rightleftharpoons CE{\cdot}M^+Nu^-\ (soln)} \quad (1)$$

$$\mathrm{CE{\cdot}M^+Nu^-\ (soln) + RY\ (soln) \rightarrow CE{\cdot}M^+Y^-\ (soln) + RNu\ (soln)} \quad (2)$$

$$\mathrm{CE{\cdot}M^+Y^-\ (soln) \rightleftharpoons CE\ (soln) + M^+Y^-\ (solid)} \quad (3)$$

is that *nucleophilic displacement occurs in solution and surface reaction is negligible.* Surprisingly, there are no unambiguous data available in the literature which support it. In this note we wish to report kinetic results for cyanide displacement on 1-bromooctane which provide compelling evidence for the solid-liquid phase-transfer mechanism.

Stoichiometric reaction of 18-crown-6·KCN in benzene at 80 °C with a 15-fold excess of 1-bromooctane obeyed pseudo-first-order kinetics. The specific second-order rate constant, $k_0$, obtained by dividing the observed first-order rate constant, $k_{\mathrm{obsd}}$, by the concentration of the organic halide was $1.31 \times 10^{-5}$ L mol$^{-1}$ s$^{-1}$. By use of identical concentrations of reactants and crown ether, a solid-liquid biphase catalytic reaction could be studied by simply adding an excess of solid KCN to the solution and monitoring the disappearance of 1-bromooctane; pseudo-first-order kinetics was maintained. Within experimental error, the second-order rate constant, $k_0 = k_{\mathrm{obsd}}/[\mathrm{KCN}]$, was identical with that found for the stoichiometric reaction. Exactly analogous results were obtained in benzene at 25 °C (Table I). These data firmly establish that the rate-limiting step for the biphase catalytic reaction is nucleophilic displacement in solution.

The situation with acetonitrile as solvent is less certain. Specifically, apparent second-order rate constants for the catalytic reaction at 25 and 80 °C were lower than those for the comparable stoichiometric reactions. While a

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[1] Supported by the National Science Foundation (Grant No. CHE-77-28366).

[2] Weber, W. P.; Gokel, G. W. "Phase-Transfer Catalysis in Organic Synthesis"; Springer-Verlag: Berlin, 1977; p 10.

[3] Starks, C. M.; Liotta, C. L. "Phase-Transfer Catalysis", Academic Press: New York, 1978; p 2.

[4] Vander Zwan, M. C.; Hartner, F. W. *J. Org. Chem.* 1978, *43*, 2655.

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**Table I. Crown Ether Based Cyanide Displacement on 1-Bromooctane[a]**

| TN | temp, °C | solvent | (KCN),[b] $10^3$ M | [$n$-$C_8H_{17}Br$], $10^2$ M | $10^5 k_{obsd}$, $s^{-1}$ | $10^3 k_0$, L $mol^{-1}$ $s^{-1}$ |
|---|---|---|---|---|---|---|
| 0.9 | 80 | benzene | 2.95 | 4.35 | 570 | 131 |
| 11.0 | 80 | benzene | 2.95 | 4.35 | 39[c] | 131 |
| 0.8 | 25 | benzene | 1.19 | 12.5 | 122 | 9.8 |
| 42.0 | 25 | benzene | 1.19 | 12.5 | 1.25[d] | 10.5 |
| 0.9 | 25 | acetonitrile | 9.43 | 9.43 | 61 | 6.5 |
| 7.0 | 25 | acetonitrile | 9.43 | 9.43 | 1.6[e] | 1.7 |
| 0.9 | 80 | acetonitrile | 100 | 10 | | 120[g] |
| 8.0 | 80 | acetonitrile | 9.52 | 9.52 | 16.2[f] | 17 |

[a] Those reactions whose turnover number, TN, is <1.0 represent stoichiometric reactions carried out in the absence of excess of solid KCN; those with TN > 1.0 were solid-liquid biphase reactions (see Experimental Section). For TN < 1.0, $k_0 = k_{obsd}/[n\text{-}C_8H_{17}Br]$; for TN > 1.0, $k_0 = k_{obsd}/[KCN]$. Turnover number is defined as the moles of 1-cyanooctane produced per mole of soluble cyanide ion. [b] In the absence of crown ether, the solubility of KCN in benzene and acetonitrile at 80 °C was $2.2 \times 10^{-4}$ M and $1.2 \times 10^{-3}$ M, respectively. Without added crown ether: [c] $k_{obsd} << 1 \times 10^{-9}$ $s^{-1}$, [d] $k_{obsd} << 1 \times 10^{-9}$ $s^{-1}$, [e] $k_{obsd} = 2.1 \times 10^{-6}$, [f] $k_{obsd} = 3.9 \times 10^{-5}$ $s^{-1}$. [g] Computed directly from a second-order plot.

phase-transfer mechanism is probable, the overall rate appears to contain significant contributions from solubilization (eq 1) and/or precipitation (eq 3).

Finally, it is interesting to note that the reactivity of 18-crown-6·KCN in acetonitrile as judged by the stoichiometric reaction is nearly identical with that found in benzene. It has been suggested that a nonpolar aprotic solvent such as benzene and a dipolar aprotic solvent such as acetonitrile should have weak interaction with "naked" anions.[5] Our data support this view by showing that these solvents have only a minor influence on the nucleophilicity of the cyanide ion.

## Experimental Section

**General Methods.** Unless stated otherwise, all reagents and chemicals were obtained commercially and used without further purification. Benzene was purified by distillation from sodium benzophenone ketyl. Acetonitrile (spectrophotometric grade, Aldrich) was dried by passage through a short column of alumina. The crown ether catalyst (18-crown-6) was purchased from Aldrich and used as obtained. Product mixtures were analyzed by GLC on a Hewlett-Packard Model 5710 A flame-ionization instrument equipped with a Hewlett-Packard 3380 A integrator by using internal standard techniques (6 ft × 0.125 in. OV-17 on Chromosorb Q, column programmed between 90 and 130 °C). Flame-photometry measurements were made with an Instrumentation Laboratory Model 251 spectrophotometer. All kinetic experiments were conducted in 50-mL culture tubes equipped with a Teflon-lined screw cap (Corning No. 9826) and a Teflon-coated magnetic stirring bar. The temperature of the oil bath used for the kinetic experiments was controlled (±0.5 °C) with the aid of a "Therm-O-Watch" Model L6-1000 electronic controller ($I^2R$ Co., Cheltenhan, PA) attached to a thermometer.

**Solubility and Activity Measurements.** The solubility of KCN in benzene and acetonitrile solutions containing 18-crown-6 (0.2 M) at 80 °C was determined by flame photometry, using standard analytical techniques. The activity of resulting solutions for nucleophilic displacement was measured by reacting 2-mL aliquots with a tenfold excess of 1-bromooctane at 80 °C for 6 h. The quantity of reactive cyanide indicated by the yield of 1-cyanooctane (GLC) was, within experimental error, identical with the total amount of cyanide present. Solubilities at 25 °C were determined by chemical reaction. Specific values obtained were the following (solvent, temperature, concentration): $CH_3CN$, 25, 0.17 M; $C_6H_6$, 80, $3.3 \times 10^{-3}$ M; $C_6H_6$, 25, $1.8 \times 10^{-3}$ M; $CH_3CN$, 80, 0.20 M.

**Kinetic Methods.** Procedures similar to the following were used for all stoichiometric reactions [turnover number (TN) < 1.0]. In a typical experiment, 10 mL of a benzene solution containing 18-crown-6 (0.2 M) was stirred vigorously with 4.0 g of ground KCN for 24 h at 80 °C in a sealed 50-mL culture tube. The tube was then opened and a 2-mL aliquot ($6.64 \times 10^{-3}$ mmol of soluble cyanide) was quickly transferred to a second culture tube (located in the 80 °C oil bath) which contained $9.8 \times 10^{-2}$ mmol of 1-bromooctane in 0.25 mL of benzene. The reaction mixture was stirred and the kinetics followed by withdrawing and cooling (room temperature) 0.5-mL samples at different times and monitoring the appearance of 1-cyanooctane. Prior to GLC analysis, samples were filtered through neutral alumina (0.5 g) and combined with 2-mL washings (ethyl ether). This filtration procedure was necessary in order to remove the crown ether so as to simplify the GLC analysis. Kinetics was carried out over 3 half-lives and obeyed pseudo-first-order behavior. Specific second-order rate constants were calculated by dividing the observed first-order rate constant, $k_{obsd}$, by the concentration of 1-bromooctane.

Catalytic reactions (TN > 1.0) were performed by using procedures similar to the above except that 0.5 g of solid KCN was present in the reaction mixture. In this case, the disappearance of 1-bromooctane was followed to 90% completion. The observed first-order rate constant divided by the concentration of soluble cyanide ion yielded the second-order rate constant, which was independent of stirring conditions; mild and vigorous stirring gave identical results.

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**Registry No.** 18-Crown-6·KCN, 42860-64-0; 1-bromooctane, 111-83-1.

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[5] See ref 3, p 81.

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# Simple Syntheses of 1,3-Bis(perfluoroacyl)azulenes and 1,3-Azulenedicarboxylic Acid

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Introduction of a trifluoroacetyl group can be readily carried out on electron-rich aromatic and heteroaromatic compounds. Trifluoroacetic anhydride (TFAA) is sufficiently powerful by itself to acylate *N*-methylpyrrole, thiophene, and furan in the α positions.[2] At least one pyrrole derivative substituted in both α positions has been acylated with neat TFAA on the β carbon.[3] The electron-rich 1 and 3 positions of azulene derivatives also react with TFAA to give the monotrifluoroacetyl compounds.[4]

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