imide **2a** (R = CH_3) was completely unaffected by the solvent. Similarly, the mixed sulfonimide **1a** failed to give any detectable reaction with HMPT after 2 weeks at room temperature (five times the duration of reactions in Table I).

Syntheses of chiral acetic acid of high optical purity and high specific radioactivity are currently available.[1,2,15] Schmidt degradation to methylamine and synthesis of the corresponding crystalline *p*-toluenesulfonamide may be carried out in about 80% overall yield. In conclusion, therefore, the ease of generation of the mixed sulfonimide **1a**, an air-stable, highly crystalline compound, combined with its facile reaction with simple carbanions opens the way to use of this reagent for the synthesis of complex substances bearing labeled methyl groups.[25]

Experimental Section

^1H NMR spectra were recorded with a Jeol MH-100 spectrometer and resonances are reported in parts per million downfield from tetramethylsilane as internal standard. Infrared spectra were obtained with a Perkin-Elmer Model 457A spectrometer and are reported in reciprocal centimeters. Ultraviolet spectra were determined with a Beckman Model DB-G instrument. Mass spectra were measured on a Hitachi Perkin-Elmer RMU-6 mass spectrometer. Gas chromatograms were obtained with a Varian-Aerograph Series 1200 gas chromatograph fitted with a 10-ft column of 5% SE-30 on 100–140 Chromosorb G. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were determined in open glass capillaries with a Thomas-Hoover apparatus and are uncorrected. Preparative layer chromatography was carried out with 20 × 20 cm plates, 0.5-mm or 2.0-mm thickness, of Merck silica gel F-254. Column chromatography was conducted with silica gel-60, Merck. Dry HMPT was prepared by distillation at reduced pressure from calcium hydride.

***N*-Methyl(*p*-toluenesulfonyl)trifluoromethanesulfonimide (1a).** A suspension of *p*-toluenesulfonyl chloride (21.2 g, 111 mmol) in 300 mL of water and methylamine hydrochloride (5.0 g, 74 mmol) was rapidly stirred and cooled to 0–5 °C. Aqueous potassium hydroxide (1 N, 148 mL) was then added slowly. After 15 min the ice bath was removed and the solution was stirred at room temperature for 1 h and finally at 60 °C for 2 h. The cooled aqueous solution was acidified (pH <2) and extracted with ether (3 × 500 mL). The combined organic extracts were dried, and the solvent was removed in vacuo to yield 13.7 g of white crystalline solid. The sulfonamide was recrystallized once from hot 2-propanol and used in the next step. *N*-Methyl-*p*-toluenesulfonamide (5.96 g, 32.2 mmol) was added in one portion to a stirred suspension of sodium hydride (50% dispersion, 2.0 g, 41.7 mmol) and 20 mL of dry methylene chloride cooled to −78 °C under an argon atmosphere. When hydrogen evolution was complete (~20 min), trifluoromethanesulfonic anhydride (7.0 mL, 10.9 g, 40 mmol) was added slowly over 15 min. The resulting solution was stirred at −78 °C for 1 h and at room temperature for 2.5 h. Ice water was added and the solution was adjusted to pH 3 with 6 N hydrochloric acid. The aqueous layer was extracted with methylene chloride (3 × 100 mL). The combined organic extracts were dried over anhydrous magnesium sulfate and the solvent was evaporated to give 9.52 g of brown oil. Chromatography of the oily product on 180 g of silica gel and elution with methylene chloride afforded 6.82 g (67%) of **1a** as white needles which were recrystallized from hot 2-propanol: mp 81–82 °C, NMR ($CDCl_3$) δ 2.50 (s, 3 H), 3.49 (s, 3 H, NCH_3), 7.52 (d, J = 8 Hz, 2 H), 8.06 (d, J = 8 Hz, 2 H); IR (CCl_4) 1405, 1380, 1220, 1125 cm^{-1}. Anal. Calcd for $C_9H_{10}F_3NO_4S_2$: C, 34.07; H, 3.18; N, 4.41; S, 20.21; F, 17.96. Found: C, 34.12; H, 3.28; N, 4.37; S, 20.29; F, 17.86.

***N*-Benzyl(*p*-toluenesulfonyl)trifluoromethanesulfonimide (1b).** This mixed sulfonimide was prepared (82%, mp 52.5–53.5 °C) in a fashion analogous to that carried out for **1a** but by using benzylamine: NMR ($CDCl_3$) δ 2.42 (s, 3 H), 5.12 (s, 2 H), 7.2–7.6 (m, 9 H); IR (CCl_4) 1405, 1380, 1220, 1130 cm^{-1}. Anal. Calcd for $C_{15}H_{14}F_3NO_4S_2$: C, 45.80; H, 3.59; S, 16.30. Found: C, 45.78; H, 3.60; S, 16.42.

Reaction of Sulfonimides 1a and 1b with Nucleophiles. A general procedure was developed and adhered to for the reactions shown in Table I. This procedure is illustrated for the alkylation of diethyl benzylmalonate with **1a**: A 10-mL three-neck flask was flamed dry in a stream of argon and charged with potassium hydride (23.6% dispersion, 254 mg, 1.50 mmol). Under an argon atmosphere the hydride was washed several times with cyclohexane and 3 mL of dry HMPT was added. Freshly distilled diethyl benzylmalonate (300 μL, 322 mg, 1.29 mmol) was added cautiously. When hydrogen evolution was complete (~10 min), sulfonimide **1a** (200 mg, 0.63 mmol) was added in one portion. The resulting solution was stirred at room temperature under a positive argon pressure for 72 h. Water (3 mL) was added followed by 8 mL of methylene chloride. The aqueous layer was adjusted to pH 3 with 6 N hydrochloric acid and extracted with methylene chloride (4 × 10 mL). The combined organic extracts were washed with water (2 × 10 mL) and dried over anhydrous magnesium sulfate, and the solvent was removed to yield 473 mg of oil. The products were separated by preparative layer chromatography and the results are shown in Table I. Spectral data and GC and TLC retention times for the products shown in Table I were compared with those obtained from authentic samples.

Registry No. 1a, 73062-44-9; **1b**, 73062-45-0; $CH_2(COOEt)_2K$, 37892-24-3; $CH_2(CN)COOEtK$, 37892-17-4; $PhCH_2CH(COOEt)_2K$, 73062-46-1; PhSHK, 3111-52-2; $CH_3CH(COOEt)_2$, 609-08-5; $(CH_3)_2C(COOEt)_2$, 1619-62-1; $PhCH_2CH(COOEt)_2$, 607-81-8; $PhCH_2CH(CN)COOEt$, 6731-58-4; $(PhCH_2)_2C(CN)COOEt$, 73062-47-2; $PhCH_2(CH_3)C(COOEt)_2$, 55114-30-2; $PhCH_2SPh$, 831-91-4; *p*-toluenesulfonyl chloride, 98-59-9; methylamine hydrochloride, 593-51-1; *N*-methyl-*p*-toluenesulfonamide, 640-61-9; trifluoromethanesulfonic anhydride, 358-23-6; benzylamine, 100-46-9.

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On the Reported Preparation of Diethyl Diacetylmaleate

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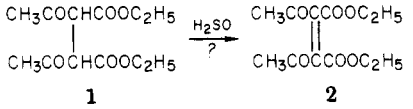
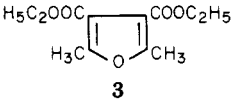
Recently the conversion of diethyl diacetylsuccinate (**1**) to diethyl diacetylmaleate (**2**) by treatment with



1 **2**

H_2SO_4-CCl_4 (but not H_2SO_4–ether or HCl–CCl_4) has been reported.[1] This "unusual acid-catalyzed oxidation" seems most unlikely, especially in view of the authors' own observation that dehydrogenation of **1** with platinum or palladium was unsuccessful.

Evidence for the structure of **2** included IR, Raman, mass, and ^1H NMR spectra and elemental analysis. We have repeated the reaction, obtaining an oil with the same IR and ^1H NMR spectra as described by the authors. However, it is clear from the ^{13}C NMR and mass spectra that the product is the furan **3**[2] rather than the maleate



3

(1) S. C. Airy, C. Martin, and J. M. Sullivan, *J. Org. Chem.*, **44**, 1891 (1979).

2. Thus two *different* olefinic carbon resonances are observed at δ 113.75 (C-3 of furan) and δ 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 ^1H 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 ^1H 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; ^1H and ^{13}C spectra were recorded on a JEOL FX-60 at 59.8 and 15 MHz, respectively, using C_6D_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 δ 201.3, 166.9, 61.9, 57.7, 30.6, and 13.9. After ~2 h additional lines were observed at δ 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 (ε ~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^+·,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_2SO_4 for ~2 min, workup with water, and drying with Na_2SO_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 ^1H NMR spectra identical with those of the previous authors:[1] ^{13}C NMR ($CDCl_3$) δ 13.05, 14.22 (C-2 methyl of furan and OCH_2CH_3), 60.52 (OCH_2CH_3), 113.75 (C-3 of furan), 155.38 (C-2 of furan), 163.50 ($COOC_2H_5$); 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.

(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).
(3) H. P. Kaufmann, *Justus Liebigs Ann. Chem.*, **429**, 247 (1922).
(4) O. Dann, E. Pietschmann, and W. Dimmling, *Arch. Pharm. Ber. Dtsch. Pharm. Ges.*, **292**, 508 (1959).
(5) O. Dann, H. Distler, and H. Merkel, *Chem. Ber.*, **85**, 457 (1952).

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

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

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

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

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_{obsd}, by the concentration of the organic halide was 1.31×10^{-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, $k_0 = k_{obsd}/[KCN]$, 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

(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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