

Figure 1. Rate of Diels-Alder reaction vs. catalyst concentration.

nm. Attempts to use quinone, or copper(II) fluoroborate and quinone, to catalyze the Diels-Alder reactions failed. Tetrakis(acetonitrile)copper(I) fluoroborate was prepared<sup>15</sup> and was found to catalyze the Diels-Alder reaction with furan. Preliminary kinetic measurements were obtained by NMR spectroscopy under pseudo-first-order conditions (furan in 5-fold excess). A plot of rate constants vs. the mole percent of  $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$  (based on the dienophile concentration) is shown in Figure 1 for acrylonitrile and chloroacrylonitrile. The experimental evidence indicates that copper(I) is the catalytic species.

### Experimental Section

**General Methods.** Infrared spectra were obtained with a Perkin-Elmer Model 298 infrared spectrophotometer. Nuclear magnetic resonance (NMR) spectra were measured with a Varian T-60A spectrophotometer at 60 MHz. Fourier transform nuclear magnetic resonance spectra were obtained with a Hitachi Perkin-Elmer R-600 high-resolution NMR spectrophotometer at 60 MHz. <sup>13</sup>C and 200-MHz proton nuclear magnetic resonance spectra were obtained with a Varian XL-200 spectrophotometer. Spectra were obtained in chloroform-*d* with either tetramethylsilane or hexamethyldisiloxane as an internal standard.

**Representative Example: 2-Carbomethoxy-7-oxabicyclo[2.2.1]hept-5-ene.** Methyl acrylate (9.0 mL, 100 mmol), furan (15 mL), cupric fluoroborate (1.0 g, 4.2 mol%, based on methyl acrylate), and hydroquinone (0.10 g, 0.91 mol%) were placed in a 50-mL round-bottomed flask. The flask was flushed with nitrogen and stirred for 2 weeks at room temperature. The mixture was poured into 25 mL of aqueous EDTA and extracted with diethyl ether (3 × 50 mL). The ether extracts were dried over magnesium sulfate, and removal of the solvent gave crude ester as a brown liquid, 5.08 g (33%). Vacuum distillation afforded pure ester as a colorless liquid: bp 66–69 °C (0.2 torr) [lit.<sup>8</sup> bp 60 °C (0.15 torr)]; 4.00 g (26% isolated). Spectra data are completely in accord with literature values for the compounds prepared in this work (Table I).

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**Registry No.**  $\text{Cu}(\text{I})(\text{CH}_3\text{CN})_4\text{BF}_4$ , 15418-29-8; 2-carbomethoxy-7-oxabicyclo[2.2.1]hept-5-ene, 21987-33-7; 7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid, 24363-23-3; 2-carboethoxy-7-oxabicyclo[2.2.1]hept-5-ene, 84752-03-4; 7-oxabicyclo[2.2.1]hept-5-ene-2-carbonitrile, 53750-68-8; 2-chloro-7-oxabicyclo[2.2.1]hept-5-ene-2-carbonitrile, 84752-04-5; 7-oxabicyclo[2.2.1]hept-5-ene-2-carboxyl chloride, 84752-05-6; 2-nitro-7-oxabicyclo[2.2.1]hept-5-ene, 84752-06-7; methyl acrylate, 96-33-3; acrylic acid, 79-10-7; ethyl acrylate, 140-88-5; acrylonitrile, 107-13-1; 2-chloroacrylonitrile, 920-37-6; acryloyl chloride, 814-68-6; nitroethene, 3638-64-0; cupric fluoroborate, 38465-60-0; hydroquinone, 123-31-9; furan, 110-00-9.

### A Convenient Synthesis for 3-Alkyl- and 3-Alkenylfurans, Including Perillene

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Furans substituted at the 3-position with alkyl or alkenyl groups are of interest because of their pronounced toxicity<sup>1</sup> and because they form the basis for the structures of several natural products.<sup>2,3</sup> Although a reasonably efficient synthesis for 3-methylfuran has been reported,<sup>4</sup> procedures described in the literature for synthesis of 3-alkylfurans are lengthy, or they require highly specialized reagents.<sup>5-7</sup> We now report an efficient synthesis of two alkylfurans by alkylation of dialkylcuprates with methyl 3-furantiosylate.

It has been reported<sup>2</sup> that 3-furanmethanol reacts with methanesulfonyl chloride to produce an unstable mesylate that in turn reacts with enolates such as the sodium salt of diethyl malonate. We confirmed this finding but were unable to produce the required alkylfurans by modifying the side chain. We also found that by using NaOH instead of pyridine as the basic catalyst,<sup>8</sup> a tosylate could be produced by reaction of 3-furanmethanol with *p*-toluenesulfonyl chloride, which appeared more stable than the mesylate, although it could not be isolated. Thus, we were able to generate the tosylate and allow it to react in situ with lithium dimethylcuprate and lithium dibutylcuprate to afford the required 3-ethyl- and 3-pentylfurans, respectively, in good yield.

The natural product perillene (4) has been of recent synthetic interest,<sup>9-13</sup> and it was also necessary to obtain other 3-alkenylfurans for toxicity testing. It was therefore of interest to determine whether the new procedure could

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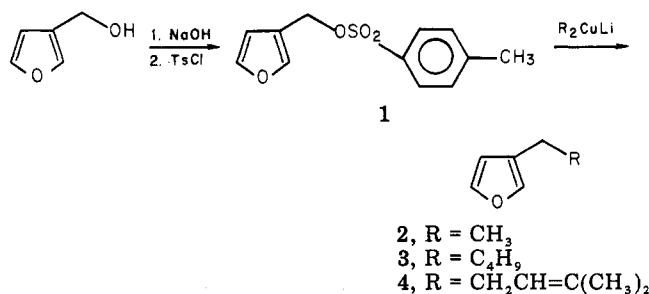
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be used to prepare 3-alkenylfurans, in which the procedures for generating the required cuprate reagents are more complex. The alkenyllithium compounds necessary to produce the required cuprates were obtained via the corresponding alkenyltriphenyltin compounds.<sup>14-16</sup> After a model study with lithium diallylcuprate proved the feasibility of the approach [3-(1-butenyl)furan showed  $m/e$  122 ( $M^+$ ),  $^1H$  NMR  $\delta$  7.15 (m, 1 H), 7.0 (m, 1 H), 6.1 (m, 1 H), 5.5-5.65 (br m, 1 H), 4.78 (d, 1 H,  $J = 16$  Hz), 4.75 (d, 1 H,  $J = 11$  Hz), 2.2-2.5 (m, 4 H)], perillene was obtained in modest yield, using the previously unreported lithium bis(3-methyl-2-butenyl)cuprate.

### Experimental Section

Melting points were obtained on a Thomas-Hoover apparatus and are uncorrected. NMR spectra ( $CDCl_3$ ) were obtained on Varian T-60 and FT-80 spectrometers. Microanalyses were performed on a Hewlett-Packard CHN microanalyzer at the University of Kansas. Electron-impact mass spectrometry was carried out at 70 eV on a Nermag R-10-10 quadrupole mass spectrometer.

**3-Ethylfuran (2).** 3-Furanmethanol (4.9 g, 0.05 mol) and *p*-toluenesulfonyl chloride (10.45 g, 0.055 mol) were dissolved in 125 mL of ether, and the solution was cooled to  $-20$  °C. Freshly powdered sodium hydroxide (7.5 g, 0.1875 mol) was added portionwise to the solution over a 2-h period. The mixture was then stirred for 1 h and poured into ice-water. The ether layer was separated and washed twice more with cold water. The ether solution was then dried ( $Na_2SO_4$ ) and filtered in the cold. Lithium dimethylcuprate was prepared by the method of Johnson<sup>17</sup> from 27.5 g (0.14 mol) of CuI and 200 mL of a 1.5 M solution of methyllithium. After addition of the methyllithium was complete, the mixture was stirred at  $-20$  °C for 30 min, the ether solution of the 3-[[*p*-tolylsulfonyl]oxy]methyl]furan (1) added dropwise, and the mixture stirred for 6 h at  $-20$  °C. Saturated aqueous ammonium chloride (200 mL) was then added below 0 °C and the mixture stirred for 10 min. The ether solution was washed with saturated NaCl ( $2 \times 100$  mL). The ether was removed by distillation through a 6-in. Vigreux column. The crude product was distilled (25 mm, room temperature) in a Kugelrohr apparatus to yield 3.0 g of colorless liquid that contained 5% ether (60% yield). Pure 3-ethylfuran (1.87 g) was obtained by distillation in a spinning-band column, bp 92 °C. The compound was shown to be homogeneous by GLC (1% OV-17 column), NMR, and mass spectroscopy. 2: mass spectrum,  $m/e$  96 ( $M^+$ ), 81 ( $M^+ - CH_3$ ), 67 ( $M^+ - C_2H_5$ ), 54 ( $M^+ - C_2H_5O$ );  $^1H$  NMR  $\delta$  7.2 (m, 1 H), 7.1 (m, 1 H), 6.2 (m, 1 H), 2.4 (q, 2 H), 1.2 (t, 3 H,  $J = 8$  Hz). Anal. Calcd for  $C_6H_8O$ : C, 74.97; H, 8.39. Found: C, 74.75; H, 8.12.

**3-Pentylfuran (3).** This was prepared as shown above, except that the addition of the cuprate was carried out at  $-50$  °C, and the mixture was stirred for 4 h. Spinning-band distillation yielded first the coupling product octane (bp 125 °C) and then 3.1 g (45%) of 3-pentylfuran: bp 160 °C (lit.<sup>18</sup> bp 160 °C); mass spectrum,

$m/e$  138 ( $M^+$ ), 95 ( $M^+ - C_3H_7$ ), 82 ( $M^+ - C_4H_9$ ), 81 ( $M^+ - C_4H_9$ );  $^1H$  NMR  $\delta$  7.2 (m, 1 H), 7.1 (m, 1 H), 6.2 (m, 1 H), 2.3 (t, 2 H,  $J = 6$  Hz), 1.8-1.2 (m, 6 H), 0.9 (t, 3 H,  $J = 6$  Hz). Anal. Calcd for  $C_9H_{14}O$ : C, 78.21; H, 10.21. Found: C, 78.30; H, 10.40.

**(3-Methyl-2-butenyl)triphenyltin.** A small amount of 1-bromo-3-methyl-2-butene<sup>19</sup> and iodomethane was added to a suspension of Mg (10 g, 0.42 mol) in ether (120 mL). After reaction was initiated, the mixture was heated to reflux and a solution of the remainder of 29.8 g (0.2 mol) 1-bromo-3-methyl-2-butene and triphenyltin chloride (50 g, 0.13 mol) in tetrahydrofuran (120 mL) was added over 4 h, the temperature being allowed to rise to 50 °C. Benzene (120 mL) was then added and the mixture heated under reflux overnight. The cooled mixture was then treated with saturated aqueous ammonium chloride (100 mL), the liquid was decanted, and the salts were washed twice with ether. The combined organic solutions were dried ( $Na_2SO_4$ ) and the solvents evaporated in vacuo to yield the solid product. This was recrystallized from petroleum ether to afford colorless crystals (39.7 g, 73%): mp 73-74 °C;  $^1H$  NMR  $\delta$  7.3 (m, 15 H), 5.3 (t, 1 H), 2.3 (d, 2 H,  $J = 8$  Hz), 1.6 (s, 3 H), 1.4 (s, 3 H). Anal. Calcd for  $C_{25}H_{24}Sn$ : C, 65.91; H, 5.77. Found: C, 66.08; H, 5.61.

**3-(4-Methyl-3-pentenyl)furan (Perillene, 4).** (3-Methyl-2-butenyl)triphenyltin (25.1 g, 0.06 mol) was dissolved in ether (100 mL). Phenyllithium (42 mL of 1.6 M solution, 0.067 mol) was added slowly with stirring. After 1 h of stirring at 25 °C, the white precipitate was removed by centrifugation and the supernatant used for further reaction. This was slowly added at  $-78$  °C to a suspension of cuprous iodide (2.66 g, 0.014 mol) in ether. This red mixture was stirred for 30 min, after which a solution of 3-[[*p*-tolylsulfonyl]oxy]methyl]furan, prepared from 0.98 g of 3-furanmethanol as described under 3-ethylfuran above, was slowly added at  $-78$  °C, and the mixture was stirred for 4 h at  $-78$  °C. The mixture was treated with saturated aqueous ammonium chloride (50 mL) at 0 °C, washed with saturated NaCl ( $2 \times 25$  mL), and dried ( $Na_2SO_4$ ), and the solvents were evaporated. This material was purified by column chromatography on silica gel followed by medium-pressure chromatography, using hexane as eluant. A colorless liquid, 0.23 g (15%), was obtained: mass spectrum,  $m/e$  150 ( $M^+$ ), 135 ( $M^+ - CH_3$ ), 81 ( $M^+ - C_5H_9$ ), 69 ( $M^+ - C_5H_9O$ );  $^1H$  NMR  $\delta$  7.2 (m, 1 H), 7.1 (m, 1 H), 6.2 (m, 1 H), 5.1 (t, 1 H), 2.5-2.0 (m, 4 H), 1.8 (s, 3 H), 1.6 (s, 3 H). Anal. Calcd for  $C_{10}H_{14}O$ : C, 79.96; H, 9.39. Found: C, 79.68; H, 9.19.

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**Registry No.** 1, 84802-88-0; 2, 67363-95-5; 3, 6177-84-0; 4, 539-52-6;  $(CH_3)_2CuLi$ , 15681-48-8;  $(C_4H_9)_2CuLi$ , 24406-16-4;  $(C-C_4H_9)_2C=CHCH_2_2CuLi$ , 84809-72-3; 3-furanmethanol, 4412-91-3; 1-bromo-3-methyl-2-butene, 870-63-3; (3-methyl-2-butenyl)triphenyltin, 65733-49-5.

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### Denitrogenation. Novel High-Temperature Reactions of *N,N*-Dimethylaniline

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### Introduction

Nitrogen removal studies are important for denitrogenation in petroleum and coal conversion technologies. *N,N*-Dimethylaniline was selected as an appropriate model for denitrogenation of aniline, pentylamine, indole, and carbazole moieties present in coal and petroleum because it contains two distinct C-N bond types. Heterocyclic

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