

the phenyl<sup>11</sup> and vinyl<sup>11,12</sup> substituted methylenecyclopropanes give products bearing the substituents preferably to exclusively on the exocyclic methylene carbon—in contrast to the results reported herein.

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**Registry No.** 1, 56407-82-0; 2, 82823-83-4; 3a (isomer 1), 94110-97-1; 3a (isomer 2), 94160-61-9; 3b (isomer 1), 94110-98-2; 3b (isomer 2), 94160-62-0; 4, 94110-99-3; 5a, 94111-00-9; 5b, 94111-01-0; 7, 94111-02-1; 10, 6626-84-2; 11, 94111-03-2; 12, 94111-04-3; 13, 94111-05-4; 14a, 94111-06-5; 14b, 94111-07-6; 14c, 94111-08-7; *cis*-14d, 94111-09-8; *trans*-14d, 94111-10-1; 16, 94111-11-2; (Ph<sub>3</sub>P)<sub>4</sub>Pd, 14221-01-3; TMSCN, 7677-24-9; C<sub>2</sub>H<sub>5</sub>CH(SCH<sub>3</sub>)<sub>2</sub>, 57093-94-4; coumarin, 91-64-5; 2-cyclopenten-1-one, 930-30-3; triisopropyl phosphite, 116-17-6; palladium acetate, 3375-31-3.

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## Dewar Thiophene: Its Generation and Trapping with Furan

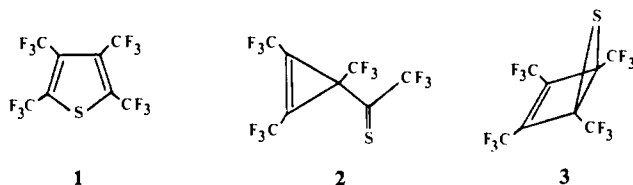
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The Dewar structure has received considerable attention since its proposal as an alternative to the Kekulé formulation of benzene;<sup>1</sup> however, it was not until comparatively recently that van Tamelen and Pappas isolated the first substituted Dewar benzene<sup>2a</sup> and shortly after the parent compound.<sup>2b</sup> In heteroaromatic systems, extensive efforts have been made to obtain Dewar isomers. Substituted Dewar pyrroles<sup>3</sup> and pyridines<sup>4</sup> have been obtained by photolysis, and the first substituted Dewar furan was recently synthesized.<sup>5</sup> Except for Dewar pyridine<sup>6</sup> no parent Dewar isomers of the heteroaromatics have been reported.

The first isolation of a thiophene valence bond isomer was reported by Heicklen et al.<sup>7a</sup> who investigated the photolysis of 2,3,4,5-tetrakis(trifluoromethyl)thiophene (**1**). The product was



initially thought to be the cyclopropenylthio ketone **2**;<sup>7</sup> however, the Dewar structure, **3** was later assigned<sup>8</sup> on the basis of the <sup>19</sup>F NMR spectrum.

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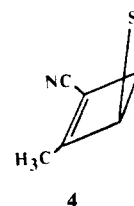
**Table I.** 400-MHz <sup>1</sup>H and 100-MHz <sup>13</sup>C NMR Data for Thiophene/Furan Diels-Alder Adducts

adduct	chem shifts, ppm <sup>a</sup>		assignment <sup>b</sup>
	δ <sub>H</sub>	δ <sub>C</sub>	
<b>5</b>	6.31	134.9	a,a'
	4.93	79.4	b,b'
	3.37	36.9	d,d'
	2.32	51.0	c,c'
<b>6</b>	6.60	134.8	a,a'
	4.97	78.8	b,b'
	3.06	38.6	d,d'
	2.93	50.0	c,c'

<sup>a</sup> Chemical shifts in CDCl<sub>3</sub> relative to Me<sub>4</sub>Si. <sup>b</sup> The prime notation is introduced to account for the magnetic nonequivalence within each set of chemically equivalent atoms.

Kobayashi et al.<sup>9</sup> generated **3** by direct photolysis of **1** in the gas phase and confirmed its structure by <sup>19</sup>F and <sup>13</sup>C NMR spectroscopy. **3** reverts thermally to **1** with a half-life of 5.1 h in benzene at 160 °C<sup>9,10</sup> and undergoes Diels-Alder cycloaddition with a variety of dienes.<sup>9-11</sup> More recently their studies of Dewar thiophenes have been extended to include bis- and tris(trifluoromethyl)thiophenes.<sup>12</sup>

Day et al.<sup>13</sup> have reported the formation of a Dewar thiophene while investigating the photorearrangement of cyanothiophenes. It was trapped in the form of its Diels-Alder adducts with furan. Direct proof of the adducts' structures was not provided but their NMR spectra were said to be similar to those for comparable adducts of a substituted Dewar pyrrole already isolated in the same laboratory.<sup>3b</sup> With either 3-cyano-2-methyl- or 3-cyano-4-methylthiophene the same Dewar isomer, **4**, was directly isolated



and identified by <sup>1</sup>H NMR. **4** undergoes formation of Diels-Alder adducts with furan and 2,5-diphenyl-3,4-benzofuran.<sup>14</sup> Despite extensive studies of the photolysis of thiophenes<sup>15</sup> the formation and isolation of their Dewar isomers is limited to the cases just described.

We now wish to present the first report on the generation and trapping of the parent Dewar thiophene. This was accomplished by irradiating (229 nm) a solution of thiophene in furan (mole ratio ~1/10) at ca. 25 °C. Capillary GC/MS analysis (OV-101, 0.3 mm × 50 m, T<sub>1</sub> = 115 °C, rate 2 °C/min) indicated the presence of two 1:1 thiophene and furan adducts, **5** and **6**, in a 5/3 ratio. Compounds **5** and **6** were separated by preparative GC (15% SE-30, ~6 mm × 2 m, 130 °C) and each assigned the structure of a furan Diels-Alder adduct with Dewar thiophene based on MS and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

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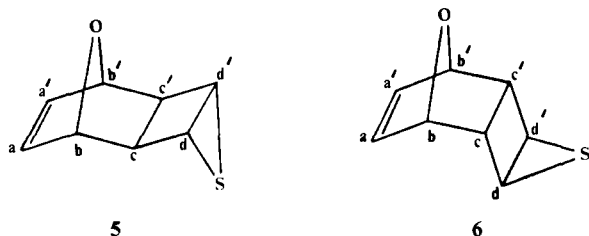
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Exact mass measurement by MS gave an  $M^+$  corresponding to  $C_8H_8OS$  and indicated the formation of  $C_4H_4S$  and  $C_4H_4O$  as a major fragmentation process (**5**,  $m/e$  152 (90%), 123 (78%), 107 (63%), 84 (100%), 68 (84%); **6**,  $m/e$  152 (51%), 123 (77%), 107 (43%), 84 (100%), 68 (66%)). In each case the  $^1H$  NMR showed four sets of two chemically equivalent protons and the  $^{13}C$  NMR four sets of two identical carbon atoms in agreement with the  $C_2$  symmetry of the structures. The complete NMR data are summarized in Table I. The NMR chemical shifts are entirely consistent with the assigned structures, **5** and **6**. Selective  $^1H$  decoupling in the  $^{13}C$  NMR experimentally verified the carbon and hydrogen associations for the assignments of Table I.

Although the symmetry of the molecules gives rise to magnetically nonequivalent protons and renders their  $^1H$  NMR spectra higher than first order, selective decouplings in the  $^1H$  NMR spectra of **5** and **6** permit their stereochemistry to be determined. An exo configuration of the four-membered ring, as in structure **5**, produces a dihedral angle of nearly  $90^\circ$  between protons  $H_b$  and  $H_c$  and consequently a very small  $J_{b-c}$  coupling constant would be expected. In the alternative endo configuration of the four-membered ring, as in structure **6**, the corresponding dihedral angle is much smaller and therefore the coupling constant should be closer to a normal value. Selective proton-decoupling experiments revealed that the adduct assigned structure **5** had no discernible coupling between its  $H_b$  and  $H_c$  protons, while in the other adduct a significant  $J_{b-c}$  coupling was observed.

For the stereochemistry of the thiirane ring segment there are in each case two possibilities, thereby generating the complete set of four possible stereoisomers that might conceivably be obtained from the Diels-Alder addition between furan and Dewar thiophene. In two stereoisomers, protons  $H_c$  and  $H_d$  are cis, while in the other two, these protons must be trans. Within each pair of cis or trans isomers the dihedral angle between the  $H_c$  and  $H_d$  protons is the same; however, the dihedral angle in the trans isomers is much larger as compared with the cis isomers. Examining the  $H_c$ - $H_d$  coupling patterns helps in assigning the actual stereochemistry in **5** and **6**. In the two adducts these couplings are very similar, suggesting that protons  $H_c$  and  $H_d$  bear the same relationship in the two compounds. The adducts where these protons are trans should clearly be, for steric reasons, the favored Diels-Alder products in relation to their counterparts with the opposite stereochemistry at the thiirane ring. On this basis, the isolated adducts were assigned structures **5** and **6**.

In order to ascertain that the trapped species was indeed an intermediate and not a short-lived excited state of thiophene, the photolysis of thiophene was repeated at  $-170^\circ C$  in a glassy matrix (10% thiophene in diethyl ether v/v). At the conclusion of irradiation (8 h, Cd resonance lamp), furan was distilled under vacuum and deposited on top of the glass. The mixture was allowed to warm up to  $-78^\circ C$  and stirred overnight while slowly warming up to  $25^\circ C$ . The formation of the two adducts **5** and **6** was established on the basis of capillary GC retention time, coinjection with samples from the liquid phase photolysis, and capillary GC/MS. The ratio of products, **5/6**, was the same as in the liquid-phase photolysis, suggesting that the nature of the intermediate trapped was the same in the two cases.

The combined chemical yield of **5** and **6** in the liquid-phase photolysis was 1.2% of thiophene consumed.<sup>16</sup> The relatively low yield can be explained in terms of the operativeness of primary

steps other than isomerization to the Dewar form, the incomplete trapping of the Dewar thiophene by furan and the destruction of the adducts by free radical attacks and secondary photolysis. That secondary photolysis of **5** and **6** occurs was shown in an auxiliary experiment using the vycor (4 mm) filtered radiation of a Cd resonance lamp  $\lambda \geq 235$  nm. Under this condition the effective  $\lambda$  from a Cd resonance lamp is the 326-nm  $Cd(^3P_1)$  resonance line. At this wavelength, thiophene does not absorb light, but **5** and **6** do ( $\lambda_{max} \approx 287$  nm, onset of absorption is  $\lambda \approx 350$  nm). Correcting for secondary photolysis increases the combined primary yield of **5** and **6** to ca. 2.5-3.0%.

In addition to the Dewar thiophene products we have also observed the formation of several furan dimers.<sup>17</sup>

Further studies are in progress.

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**Registry No.** **5**, 93806-46-3; **6**, 93920-71-9; thiophene, 110-02-1; furan, 110-00-9.

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### Systematic Substitution on the Cubane Nucleus. Amide Activation for Metalation of "Saturated" Systems

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Cubane has the highest strain energy (166 kcal/mol) of any stable organic compound available in multigram amounts. The 1,4-dicarboxylic acid from which cubane is made can be prepared easily,<sup>1</sup> and from it various 1,4-disubstituted and monosubstituted cubanes have been synthesized by standard functional group manipulations.<sup>1,2</sup> Otherwise, and in very much more limited amounts, only 1,3-disubstituted cubanes<sup>1b,3</sup> and the fully substituted octa(trifluoromethyl)cubane,<sup>4</sup> octaphenylcubane,<sup>5</sup> and hexabromo-1,4-dicarboxycubane<sup>20</sup> have been reported. The degree of substitution and substitution pattern have always been incident to the synthesis of the skeleton. As we are now interested in differently substituted cubanes for themselves and as precursors for dehydrocubane (cubene), 1,1':3,3'-biscyclobutane, cross-linked cubane polymers, etc., we have developed, and report here, the first method for direct and systematic substitution on the cubane nucleus.

The geometry of cubane requires substantial rehybridization of the component carbons from normal  $sp^3$  bonding (25% s). The 155-Hz  $^{13}C$ -H nuclear coupling constant in cubane translates into 31% s character in that bond and an expectation of enhanced acidity.<sup>6</sup> Stock and Luh have reported that isotope exchange, H for D, occurs fairly readily from cubane- $d_1$  using lithium cyclohexylamide in cyclohexylamine at  $50^\circ C$ .<sup>7</sup> However, the

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