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# 2-Carbomethoxy-1,3-butadiene: A Convenient Synthesis of a Stable Precursor and a Survey of Its Diels–Alder Reactions[1]

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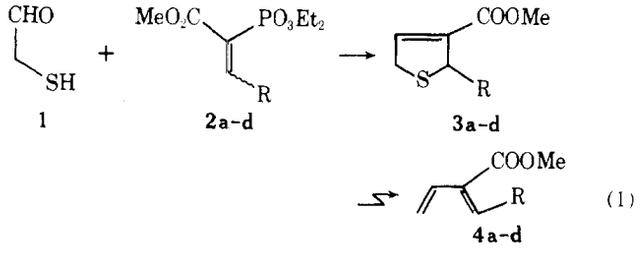
A facile synthesis of 3-carbomethoxy-2,5-dihydrothiophene sulfone (**3a**) and some 2-substituted derivatives is reported. The materials decompose thermally into sulfur dioxide and conjugated dienes. The Diels–Alder reactions of 2-carbomethoxy-1,3-butadiene appear to proceed well only with electron-deficient dienophiles, but $^{13}C$ NMR indicates that in most cases the products are a mixture of regioisomers.

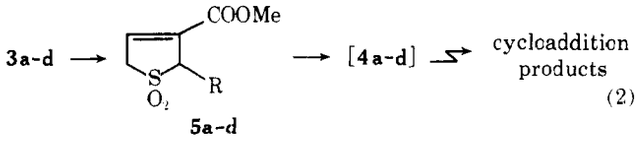
We have recently reported[2] a procedure which allows the rapid assembly of 3-carboxylated 2,5-dihydrothiophenes in high yield and have shown that these are excellent precursors to substituted 1,3-butadienes which carry an ester function at the interior position of the diene system. Notable omissions from the compounds described[2] were those derived from $\alpha$-mercaptoacetaldehyde (1) and in particular the parent compound **3a** (eq 1). Using the previously described conditions




(1)

**a**, R = H
**b**, R = Ph
**c**, R = c-$C_6H_{11}$
**d**, R = *n*-$C_4H_7$

(refluxing pyridine, triethylamine solution), 1 consistently refused to provide dihydrothiophenes in acceptable yields. This omission was especially unfortunate as diene **4a** is reported[3] to be very unstable and the possibility of storing **4a** as the sulfone **5a** which would undergo chelatropic sulfur dioxide elimination (eq 2) under the conditions required for




(2)

Diels–Alder cycloaddition was a distinctly attractive possibility. Goldberg and Dreiding[4] have recently reported the synthesis of **4a** by another method, but we report here the simple solution to the synthesis of **3a** and the reaction of **4a** with some representative dienophiles.

## Results and Discussion

**A. Dihydrothiophene Synthesis and Oxidation.** Prior work on the condensation of vinylphosphonates[2] and vinylphosphonium salts[5] with $\alpha$-mercaptocarbonyl compounds had utilized pyridine as solvent to provide the required base and to facilitate dissolution of the reactants. Other related reactions have employed phase-transfer conditions.[6] Neither of these procedures produced acceptable amounts of products when **1** was employed. After extensive experimentation, it was found that the simple expedient of using dichloromethane containing triethyl amine as the reaction medium afforded excellent yields of **3**. The reaction mixture is initially heterogeneous but becomes homogeneous as the reaction proceeds. The same method works well for other $\alpha$-mercaptoaldehydes, but not ketones. In some cases, using homologues of **1**, the yields using the present procedure were marginally lower than when pyridine was used, but the products required substantially less purification. The compounds prepared using **1** are shown in Table I.

The oxidation of **3** to sulfones **5** was carried out by the previously reported method.[7] Decomposition of these on a gas chromatograph afforded sulfur dioxide and diene as the only volatile products.

**B. Diels–Alder Reactions of 2-Carbomethoxy-1,3-butadiene (4a).** Sulfone **5a** is a stable crystalline compound. When it is heated in refluxing toluene, a moderately rapid evolution of sulfur dioxide occurs. In the absence of added dienophile a high yield of dimethyl 4-vinylcyclohexene-1,4-dioate (**6**)[8] is formed. No sign of isomeric materials could be

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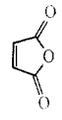
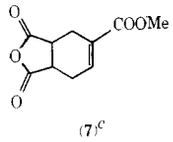
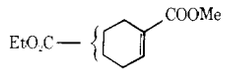
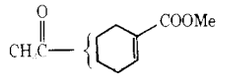
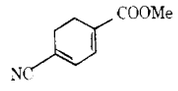
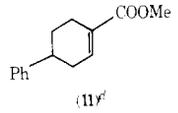
**Table I. Yields and NMR Spectra of 3 and 5 Derived from 1a**

| compd no.[a] | registry no. | R | yield, % | mp, °C | proton magnetic resonance[b] |
|---|---|---|---|---|---|
| **3a** | 67488-46-4 | H | 68 | 27–28[c] | 6.72 (bs, 1), 3.82 (s, 4), 3.68 (s, 3) |
| **3b** | 67488-47-5 | Ph | 91 | 66–68 | 7.19 (s, 5), 6.97 (m, 1), 5.45 (m, 1), 4.00 (m, 2), 3.57 (s, 3) |
| **3c** | 67488-48-6 | $c$-$C_6H_{11}$ | 88 | 34–35 | 6.95 (m, 1), 4.60–4.35 (bm, 1), 3.78 (s, 5), 2.3–0.9 (bm, 11) |
| **3d** | 67488-49-7 | $n$-$C_3H_7$ | 75 | *d* | 6.85 (m, 1), 4.6–4.2 (m, 1), 3.77 (bs, 5), 2.08–1.13 (m, 4), 0.92 (t, 3, $J$ = 7 Hz) |
| **5a** | 67488-50-0 | H | 90 | 57–58 | 7.00 (m, 1), 3.98 (bs, 4), 3.80 (s, 3) |
| **5b** | 67488-51-1 | Ph | 50 | 170–71 dec | 7.40[e] (m, 6), 5.46 (s, 1), 4.33 (d, 2, $J$ = 4 Hz), 3.90 (s, 3) |
| **5c** | 67488-52-2 | $c$-$C_6H_{11}$ | 87 | 96–98 | 7.11 (t, 1, $J$ = 3 Hz), 3.82 (s, 6), 2.4–0.9 (bm, 11) |
| **5d** | 67488-53-3 | $n$-$C_3H_7$ | 86 | 42–43 | 7.02 (t, 1, $J$ = 3 Hz), 4.02–3.70 (m, 3), 3.82 (s, 3), 2.20–1.20 (bm, 4), 0.93 (t, 3, $J$ = 7 Hz) |

[a] All new compounds gave acceptable elemental analyses. [b] Run in $CDCl_3$ solution unless otherwise stated; tabulation follows the order chemical shift ($\delta$), multiplicity, number of protons, coupling constant. [c] bp 108–110 (15 mm). [d] Noncrystalline. [e] In $CF_3CO_2D$ solution.

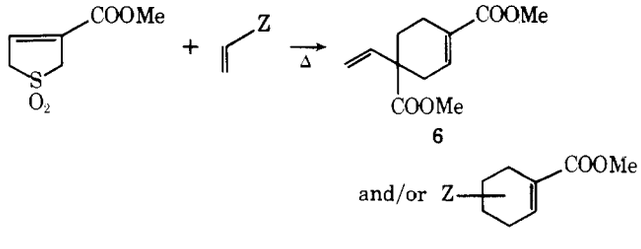
**Table II. Diels–Alder Reactions of 2-Carbomethoxy-1,3-butadiene (4a)**

| run no. | dienophile | registry no. | product (no.) | registry no. | yield, % | ref | proton magnetic resonance[a] |
|---|---|---|---|---|---|---|---|
| 1 | none | | (6)[b] | 58683-55-9 | >80 | 8 | 6.80 (m, 1), 6.0–4.8 (ABX m, 3), 3.65 (s, 3), 2.75–1.65 (m, 6) |
| 2 |  | 108-31-6 |  (7)[c] | 67488-54-4 | 73 | | 7.10 (m, 1), 3.73 (s, 3), 3.51 (m, 2), 3.00–2.45 (m, 4) |
| 3 |  | 140-88-5 |  (8) | 67488-44-2 | 90 | 8 | 6.85 (bs, 1), 4.10 (q, 2, $J$ = 7 Hz), 3.68 (s, 3), 2.6–2.1 (m, 7), 1.26 (t, 3, $J$ = 7 Hz) |
| 4 |  | 78-94-4 |  (9) | 67488-45-3 | 69 | 12 | 6.98 (m, 1), 3.70 (s, 3), 2.85–1.80 (m, 7), 2.18 (s, 3) |
| 5 |  | 920-37-6 |  (10) + (6) | 67488-55-5 | 43 | | 6.90 (AB quart, 1, $J$ = 5 Hz), 3.80 (s, 3), 2.58 (bs, 4) |
| 6 |  | 100-42-5 |  (11)[d] | 22787-67-3 | 49 | 13 | 7.27 (s, 5), 7.10 (m, 1), 3.73 (s, 3), 3.05–1.65 (m, 7) |
| 7 | 2-octene | 111-67-1 | (6) | | 70 | | |
| 8 |  | 108-22-5 | (6) | | 68 | | |
| 9 |  | 110-87-2 | (6) | | 98 | | |

[a] In $CDCl_3$ solution. [b] bp 88–90 °C (0.2 mm) [lit.[8] bp 110–113 °C (0.8 mm)]. [c] mp 110–111 °C. [d] mp 34–37 °C.

detected by gas chromatography or by proton or carbon NMR.

Incorporation of a dienophile into the reaction mixture led to one of three results (Table II). In some cases, only the dimer **6** was formed, while in others the expected product was formed. In one case, the reaction led to a mixture of **6** and the expected product. In general, it appears that diene **4a** reacts well with electron-deficient dienophiles (runs 1–5) and styrene (run 6) but with simple olefins and more electron-rich mate-



rials (runs 7–9) the desired condensation cannot compete with dimerization. This is in contrast to the recently reported[9] reactions of 2,3-dicyanobutadiene which reacts well with both electron-rich and electron-deficient dienophiles. In the present case, apparently there is insufficient electron deficiency to allow **4a** to function in an "inverse electron demand" sense. As indicated, the product isolated upon the reaction of 2-chloroacrylonitrile was diene **10.** Whether the dehydrochlorination of the initial adduct occurred during the reaction or in the subsequent work-up is unknown. However, a large amount of decomposition occurred during the reaction which may well be caused by the liberation of hydrogen chloride. The low yield of **10** is likely due to this decomposition of the dienophile.

The regioselectivity of the Diels–Alder reactions of **4a** appears to be variable. Although we were unable to confirm the presence of two regioisomers in any case by either proton NMR or gas chromatography, $^{13}C$ NMR of **8** and **9** clearly show the presence of more than two vinyl and three ring methylene carbon atoms. Since stereoisomerism is absent, these results can only be accommodated by the formation of regioisomers. Although the assignment of the NMR absorptions is ambiguous, in each case the ratio of isomers appears to be approximately 3:1. Similar investigation of **6** and **11** revealed no sign of extra absorptions and thus they appear to be homogeneous.

Clearly, the inability to effect condensation with electron-rich dienophiles and the formation of regioisomers limits the synthetic application of diene **4a.** We hope that the application of Lewis acid catalysis[10] will improve this situation and are planning to investigate this in the near future. Nevertheless, the ability of **3** to function as dienophiles[11] and synthons for thiophenes and hydrocarbons makes them of potential synthetic value.

## Experimental Section

Proton magnetic resonance spectra were run on a JEOL C60HL spectrometer and carbon spectra were run on a Bruker CXP 100 spectrometer at 22.64 MHz using a flip angle of 36°. Spectra were recorded in deuteriochloroform unless otherwise noted and are reported in parts per million downfield from $Me_4Si$ as internal standard. Gas chromatographic analyses were performed on an F and M Model 720 instrument, utilizing a 10 ft × 0.25 in. column packed with 10% Dexsil 300 on Chromosorb W.

**Materials.** Phosphonates **2** were prepared as previously described.[2] Mercaptoacetaldehyde (in the form of its dimer *p*-dithiane-2,5-diol) and all dienophiles were commercially available.

**3-Carbomethoxy-2,5-dihydrothiophene (3a).** A suspension of 0.9 g (0.012 mol) of mercaptan **1** in 75 mL of methylene chloride containing 1.3 g (0.013 mol) of triethylamine was heated to reflux under a nitrogen atmosphere. A solution of phosphonate **2a** (0.01 mol) in 10 mL of methylene chloride was added dropwise to the refluxing solution. After 4 h, the solution was cooled, diluted with 175 mL of methylene chloride, washed with 5% hydrochloric acid (2 × 150 mL), and dried over sodium sulfate and the solvent was evaporated. The residual material was filtered through a short column of neutral alumina, using 1:1 ether–methylene chloride as eluant. Removal of solvent at reduced pressure gave **3a** (1.17 g = 68%), which crystallized on standing (mp 27–28 °C): $^1H$ NMR (see Table I); $^{13}C$ NMR 37.2, 39.0, 51.8, 135.6, 140.8, 164.2; IR ($CHCl_3$) 1720 $cm^{-1}$.

The reaction can easily be scaled up to 20 times this size. Purification is then best effected by distillation bp 108–110 °C (15 mm). An analytical sample was collected from GLC.

Dihydrothiophenes **3b, 3c,** and **3d** were prepared in an exactly analogous fashion.

**Oxidation of 3a to 5a.** To a cooled solution of **3a** (0.02 mol) in methylene chloride (25 mL) was added, dropwise with stirring, a solution of 0.04 mol of *m*-chloroperbenzoic acid in 100 mL of the same solvent. The mixture was stirred for 3 h at 0–10 °C and overnight at ambient temperature. The filtered solution was washed with 50 mL of saturated aqueous sodium carbonate solution, dried, and concentrated to give **5a** as a white crystalline material which was washed with a small amount of cold ether. The yield was 3.15 g (90%) of material: mp 57–58 °C; $^1H$ NMR, see Table I; $^{13}C$ NMR, $\delta$ 52.4, 55.0, 57.8, 129.7, 134.0, 162.7.

Sulfones **5b, 5c,** and **5d** were prepared in an exactly analogous manner.

**General Procedure for the Diels–Alder Reactions of 4a.** To a solution of 0.01 mol of sulfone **5a** and a small amount of hydroquinone in 35 mL of toluene was added 0.10 mol of the appropriate dienophile (in the case of run no. 2, only 0.01 mol of dienophile was used) and the solution was heated at reflux overnight. The solvent and excess dienophile were evaporated at reduced pressure and the residue chromatographed over neutral alumina using ether to afford the products shown in Table II. Analytical samples were obtained by crystallization or collection from GLC.

The presence of regioisomers in **8** and **9** was inferred from the $^{13}C$ NMR spectra. Compound **9** showed absorption at $\delta$ 209.6, 167.1, 138.8, 137.7, and 129.9 and six absorptions between 20 and 30 among others. Compound **8** exhibited absorptions at $\delta$ 176.2, 175.1, 167.5, 138.9, 137.6, and 130.2 and five absorptions between 20 and 30 among others. Such complexities can only be due to the presence of regioisomers. Other products showed the following absorptions:

**6:** 174.6, 167.2, 139.6, 136.8, 129.6, 115.1, 52.2, 51.4, 47.4, 32.4, 29.7, 21.8.

**7:** 173.4, 173.1, 165.4, 137.8, 131.3, 52.1, 39.6, 38.8, 24.4, 22.7.

**11:** 167.6, 146.0, 139.0, 130.3, 128.6, 126.8, 126.3, 51.4, 39.2, 33.8, 29.6, 24.9.

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**Registry No.**—**1,** 4124-63-4; **2a,** 993-88-4; **2b,** 67227-92-3; **2c,** 67488-56-6; **2d,** 66982-68-1; **4a,** 44641-19-2; **7** diacid, 67488-57-7.

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