3-Vinyl-2,5-dihydrothiophene 1,1-Dioxide: A Novel, Easily Accessible, High-yielding Precursor to [3]Dendralene, the Simplest Representative of the Diene-transmissive Polyenes

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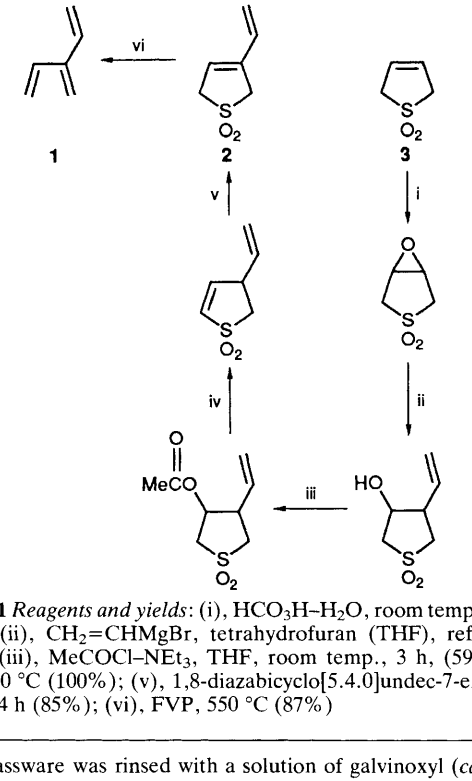
Cheleotropic extrusion of SO_2 from readily prepared 3-vinyl-2,5-dihydrothiophene 1,1-dioxide **2** provides a clean and efficient route to [3]dendralene (3-methylenepenta-1,4-diene **1**), the simplest member of the diene-transmissive polyenes, which contrary to previous reports is a stable, easily handled compound that shows unexpected selectivity in Diels–Alder cycloadditions, thus enhancing its utility as a tandem annelating reagent.

Because of their unusual cross-conjugated properties and emerging synthetic potential, acyclic polyenes of the so-called dendralene-type[1] are beginning to receive steadily increasing attention.[2] Contrary to present[3] and previous reports[4] that the simplest member, [3]dendralene (3-methylenepenta-1,4-diene **1**), is too prone to polymerisation to allow its use in diene-transmissive Diels–Alder reactions, we now show that **1** can be prepared in good yields and a *pure state* as a stable, easily handled compound and also demonstrate its ability to function as a tandem-annelating reagent. Of the few preparations of **1** reported so far, the method of most proven value is that involving pyrolysis of 1,5-diacetoxy-3-acetoxymethylpentane,[5] although extensive losses due to dimerisation are incurred both during pyrolysis and in the subsequent distillation to remove liberated acetic acid.

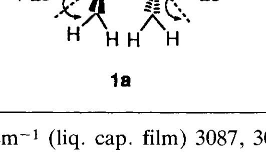
Our preparatively simple route to the triene **1** incorporates, as the crucial step, thermal extrusion of SO_2 from 3-vinyl-2,5-dihydrothiophene 1,1-dioxide **2**, a stable colourless crystalline compound, m.p. 75–76 °C [^{1}H NMR ($CDCl_3$) δ 3.82–3.92 (4H, m), 5.13 (1H, d, J_{trans} 18 Hz), 5.31 (1H, d, J_{cis} 11 Hz), 5.92–5.96 (1H, m), 6.35–6.49 (1H, dd, J 11 Hz, J_{trans} 18 Hz)], which can be obtained in *ca.* 20% overall yield from butadiene sulphone **3** as outlined in Scheme 1. Removal of SO_2 from **2** occurs cleanly and smoothly under flash vacuum pyrolytic (FVP) conditions (550 °C and 0.001 mmHg)† to produce exclusively [3]dendralene **1** as a colourless mobile oil, b.p. 48–50 °C (87%) [^{1}H NMR ($CDCl_3$) δ 5.12–5.18 (2H, m, $J_{4,6}$ 11 Hz), 5.15 (2H, s), 5.35–5.45 (2H, dd, $J_{4,5}$ 18 Hz, $J_{5,6}$ 2 Hz), 6.38–6.52 (1H, dd, $J_{4,5}$ 18 Hz, $J_{4,6}$ 11 Hz); ^{13}C NMR ($CDCl_3$, DEPT) δ 115.38, 115.35, 135.62].



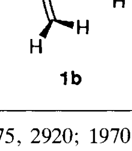
Scheme 1 *Reagents and yields*: (i), HCO_3H–H_2O, room temp., 45 days (49%); (ii), CH_2=CHMgBr, tetrahydrofuran (THF), reflux, 1 h, (83%); (iii), MeCOCl–NEt_3, THF, room temp., 3 h, (59%); (iv), FVP, 650 °C (100%); (v), 1,8-diazabicyclo[5.4.0]undec-7-ene, THF, 40 °C, 24 h (85%); (vi), FVP, 550 °C (87%)

The IR and Raman spectra of **1** allow some conclusions to be drawn about its structure.‡ There is a clear distinction in the Raman effect between polarised and depolarised bands, suggesting a structure with some symmetry; in particular, the region associated with C=C stretches contains a depolarised band at highest frequency, then a polarised band, and finally a weak band (probably polarised) that coincides with a strong IR band. We assign these three bands to the three C=C stretching modes expected, and would argue that the highest and lowest frequency bands are respectively out-of-phase and in-phase combinations of two symmetry-related bond stretches, while the band at intermediate frequency is due to the unique double-substituted bond. There may be some complication involving coupling with the in-phase combination of C–C bond stretches, which is not observed in either the IR or the Raman spectrum; the distinct Raman band just below 1200 cm^{-1} is depolarised, and is therefore likely to be due to the out-of-phase mode.

All these observations are consistent with a structure with a 2-fold axis or mirror plane of symmetry; the 2-fold axis is more likely as it allows the two equivalent CH_2 groups to be nearly co-planar with the unique CH_2 group as well as with each other. Such a structure (see **1a**) is at odds with the twisted conformation **1b**[1] proposed on the basis of the similarity of the UV spectrum (λ_{max} = 224 nm, log ε = 4.4) to that of butadiene (217 nm, 4.32) and also theoretical calculations.[6] In the case of **1a**, simple calculations show that to bring the two conflicting hydrogens 2.0 Å apart (the sum of the van der Waals' radii) requires a twist of about 25° around each 'single' bond; this reduces the conjugation in each *trans*-butadiene unit by a factor of 0.90, which is clearly preferable to the structure **1b** with only one conjugated unit, where the corresponding factor is 0.5.



1a



1b

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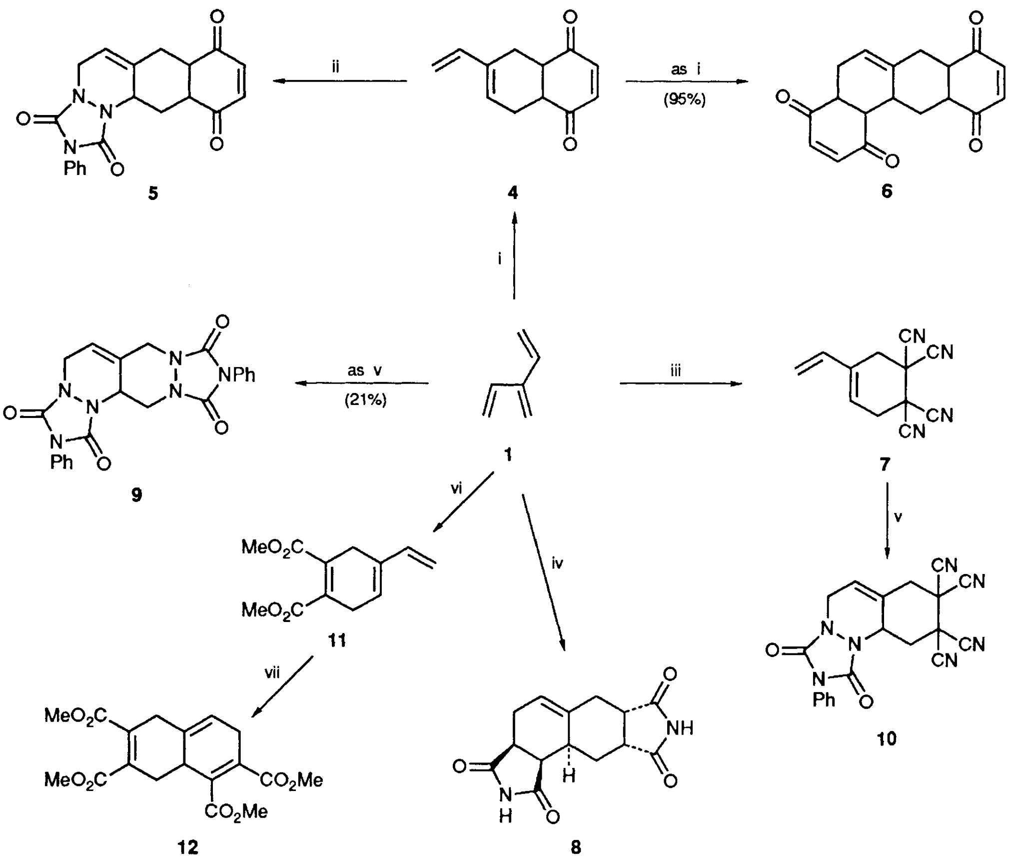
† All glassware was rinsed with a solution of galvinoxyl (*ca.* 5%) in acetone and dried prior to use to safeguard against polymerisation of **1**.

‡ IR: ν/cm^{-1} (liq. cap. film) 3087, 3004, 2975, 2920; 1970, 1825br, 1792, 1715, 1630, 1606, 1585, 1572sh, 1425, 1383, 1292, 1070, 1039, 989, 919–910, 897, 760, 745, 695, 620, 500, 372; (gas) 3085, 3015, 2990, 2920, 1835, 1804, 1631, 1590, 1425, 1380, 1272, 1058, 1039, 988Q, 910, 897, 760, 753, 615, 505, 365 cm^{-1}; ν/cm^{-1} Raman (liq. film) 3085, 3004, 1645, 1630p, 1620p, 1606, 1580p, 1430p, 1418p, 1290p, 1258p, 1185, 1072p, 1045, 990p, 938, 910p, 890p, 810, 780p, 760, 735, 712, 640, 542p, 496, 415, 360, 310, 250 to (bands marked p were polarised, others depolarised).



Scheme 2 *Reagents and yields*: (i), *p*-benzoquinone, toluene, 40 °C, 36 h (90%); (ii), *N*-phenyl-1,2,4-triazoline-3,5-dione, acetone, 40 °C, 2.5 h (63%); (iii), TCNE, CH_2Cl_2, sealed tube, 50 °C, 72 h (92%); (iv), maleimide, THF, sealed tube, 70 °C, 27 h (65%); (v), *N*-phenyl-1,2,4-triazoline-3,5-dione, acetone, sealed tube, 40 °C, 28 h (63%); (vi), DMAD–CH_2Cl_2, sealed tube, 60 °C, 5 h (80%); (vii), large excess of DMAD, sealed tube, 70 °C, 72 h (87%)

Preliminary investigations into the reactivity of **1** as an educt for multiple additions of the Diels–Alder type have yielded some interesting results. By careful regulation of the reaction conditions some selectivity towards mono- and bis-annulation can be achieved as shown in Scheme 2.§ For example, reaction of **1** with an equimolar quantity of *p*-benzoquinone at 40 °C for 36 h affords the mono-adduct **4** (90%), which in turn can undergo a second Diels–Alder cycloaddition with *N*-phenyl-1,2,4-triazoline-3,5-dione to form the 'mixed' adduct **5** (63%). Alternatively, when **4** is treated with a further equivalent of *p*-benzoquinone, the bis-adduct **6**[7] is isolated in almost quantitative yield. Other bis-adducts obtained directly by reaction of **1** with excess of dienophile include **8** (65%) from maleimide on heating in a sealed tube, and **9**, which is formed in 21% yield by tandem annelation with *N*-phenyl-1,2,4-triazoline-3,5-dione in boiling acetone. By comparison, when tetracyanoethylene (TCNE) reacts with **1**, only the mono-adduct **7** (92%) is obtained even in the presence of excess of reagent under forcing conditions; **7** does, however, react with more reactive *N*-phenyl-1,2,4-triazoline-3,5-dione to yield the 'mixed' adduct **10** in 63% yield. On the other hand, dimethyl acetylenedicarboxylate (DMAD) and **1** add selectively to form the mono-adduct **11** in 80% yield. With a large excess of DMAD and prolonged reaction times, **11** undergoes a second addition to give the bis-adduct **12** in good yield (87%).

Full stereochemical assignments of all the adducts awaits further investigation, but in the case of **8**, NOE studies show both maleimide rings to be *anti* to each other and more specifically the bridging hydrogen is *syn* to the ring fusion protons.

Received, 20th June 1990; Com. 0/02776F

References

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5 W. J. Bailey and J. Economy, *J. Am. Chem. Soc.*, 1955, **77**, 1133; other previously reported routes to [3]dendralene include: ester pyrolysis of the corresponding mono- and di-acetates, A. T. Blomquist and J. A. Verdol, *J. Am. Chem. Soc.*, 1955, **77**, 81 and 1806; Hofmann elimination of the corresponding ammonium salt, H. D. Martin, M. Eckert-Maksic and B. Mayer, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 807; and more recently, dimerisation of prop-2-ynyl bromide, H. Priebe and H. Hopf, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 286.
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7 See W. J. Bailey and J. Economy, *J. Am. Chem. Soc.*, 1955, **77**, 1133 for a previous report on the reaction between **1** and *p*-benzoquinone and their isolation of **10** as the sole cycloadduct; other bis-adducts were also obtained by reaction with maleic anhydride and naphthoquinone.

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§ Product yields quoted refer to isolated material; all new compounds had correct analytical and mass spectroscopic characteristics.