Highly Substituted Dienes from Butyne-1,4-diol. A One-flask Synthesis and the Mechanism of Formation of 3-(*N*,*N*-Diethylamino)-2-phenylsulphinylbutadiene

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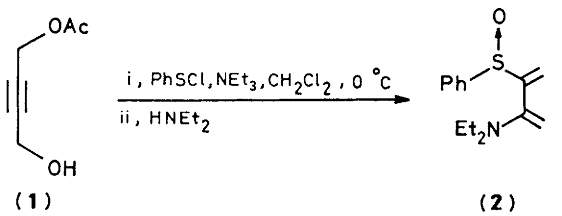
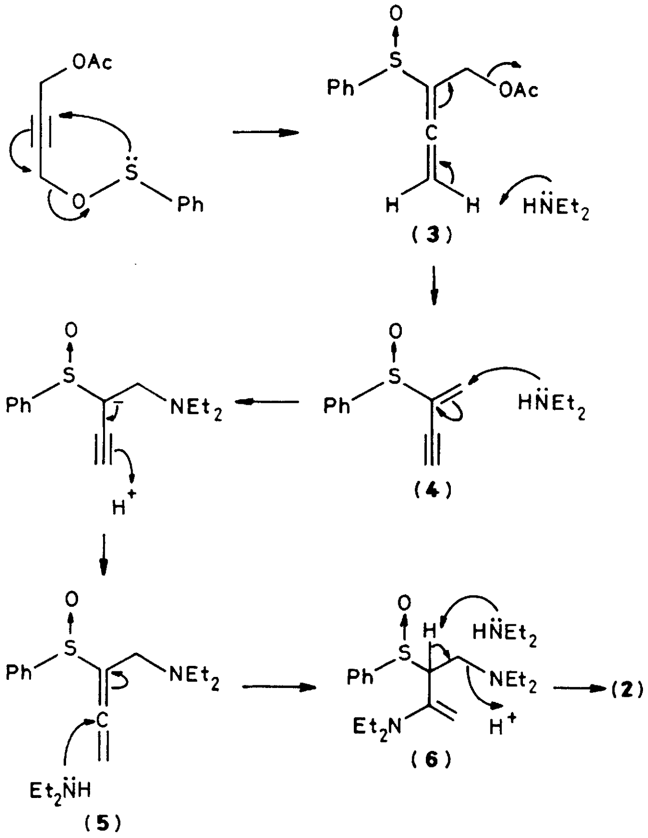
When 4-acetoxybut-2-yn-1-ol is treated with benzenesulphenyl chloride and triethylamine, followed by diethylamine, 3-(*N*,*N*-diethylamino)-2-phenylsulphinylbutadiene is produced, in a multistep process, in 90% overall yield.

There has been considerable recent interest in the synthesis and Diels–Alder reactions of polysubstituted butadienes.[1–3] Whilst investigating the utility of butyne-1,4-diol and its derivatives as potential precursors for butadienes, 4-acetoxybut-2-yn-1-ol[4] (**1**), in CH_2Cl_2 at 0 °C was treated sequentially with triethylamine, benzene sulphenyl chloride[5] and two equiv. of diethylamine. Both of the latter additions led to rapid, exothermic, reactions. After an aqueous workup and removal of the solvent under reduced pressure, 3-(*N*,*N*-diethylamino)-2-phenylsulphinylbutadiene (**2**) was isolated as a light-yellow oil in 93% yield.

Diene (**2**) is an oil, which decomposes rapidly upon





attempted distillation or chromatography. It has a half-life (neat) of *ca.* 4 days at −20 °C. Its structure was assigned unequivocally by the following spectroscopic data. The proton n.m.r. spectrum shows δ 7.3—7.7 (5H, m), 6.12, 5.90, 3.94, and 3.78 (each 1H, s), 2.91 (4H, quart., J 7 Hz), and 0.91 (6H, t, J 7 Hz). The ^{13}C spectrum has resonances at δ 143.3, 131.1, 128.7, and 125.6 (arom.), 155.9, 147.3, 115.8 and 92.8 (vinylic),[1] and 42.8 and 11.2 p.p.m. (diethylamino). In the off-resonance spectrum the peaks at δ 155.9 and 147.3 remained singlets whereas those at 115.8 and 92.8 became triplets. The i.r. spectrum included bands at 1590, 1050, and 930 cm^{-1}.

When alcohol (**1**) was treated with benzenesulphenyl chloride and di-isopropylethylamine, in CH$_2$Cl$_2$ at 0 °C, 2-phenylsulphinylbuta-2,3-dien-1-yl acetate (**3**)† was isolated in 70% yield. Allene (**3**) reacts rapidly and exothermically with two equiv. of diethylamine in CH$_2$Cl$_2$ or CDCl$_3$ to form diene (**2**) quantitatively. Although no intermediates have been detected in this reaction, which appears to be a simple S_N2' reaction, further experiments demonstrate that at least some of the product is being formed by a more complicated pathway. Treatment of allene (**3**) with two equiv. of triethylamine in CH$_2$Cl$_2$ for 1 h at 20 °C leads, in 74% yield, to 3-phenylsulphinylbut-3-en-1-yne‡ (**4**), the product of a 1,4-elimination of acetic acid from (**3**). Enyne (**4**) is the sole observable product when allene (**3**) is treated with NaI, NaCN, or NaOAc, all in hexamethylphosphoramide, conditions which might be expected to favour S_N2' reactions.

Di-isopropylamine in CDCl$_3$ also reacts with allene (**3**) to form enyne (**4**). Upon addition of diethylamine to this reaction mixture, or purified enyne (**4**), a strongly exothermic reaction occurs and new n.m.r. resonances [δ 5.20 (t, J 2.5 Hz), 3.33 and 3.07 (AB quart. of t, J_{AB} 15 Hz, J_t 2.5 Hz), 2.46 (quart., J 7 Hz), and 0.88 (t, J 7 Hz)] appeared immediately, followed by a slow conversion into diene (**2**). These resonances were assigned to 1-diethylamino-2-phenylsulphinylbuta-2,3-diene (**5**), the 2.5 Hz coupling constant being typical for 1,6-couplings in buta-2,3-dienyl systems, and the AB quartet being due to diastereotopicity induced in the C-1 methylene by the sulphoxide.§ This product is readily explained by a Michael addition to the vinyl sulphoxide moiety of (**4**), followed by protonation of the propargyl anion to form the more stable allenic sulphoxide.[8]

There are several possible mechanisms for the formation of diene (**2**) from allene (**5**). Since the reaction is accelerated by addition of excess of diethylamine and is slowed down by the presence of protonated amines, we do not believe that either a concerted or an acid-catalysed process is taking place. This leaves an S_N2' reaction or an addition–elimination sequence. We favour the latter because an S_N2' reaction would presumably occur only on allene (**5**) when protonated, to avoid diethylamide ion as a leaving group. In fact the conversion of (**5**) into diene (**2**) is much slower in the presence of dialkylammonium ions, a convenient proton source, than in their absence. Michael additions to allenic sulphoxides are highly favoured,[6,7] and the fact that diene (**2**) shows no tendency to undergo Michael addition of diethylamine to its vinyl sulphoxide moiety, would suggest that the presumed intermediate (**6**) is highly unstable with respect to elimination to form diene (**2**). This is not surprising as the allene-conjugated diene rearrangement must be exothermic by at least 40 kJ/mol.

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the Am. Chem. Soc., and to Research Corporation for partial support of this research.

Received, 16th February 1982; Com. 172

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† Fully identified by proton and ^{13}C n.m.r. and i.r. spectroscopy.

‡ 3-Phenylsulphinylbut-3-en-1-yne (**4**): m.p. 56—57 °C; δ(^{1}H) (CDCl$_3$) 7.3—7.9 (5H, m), 6.50 (1H, s), 6.15 (1H, s), and 3.31 (1H, s), δ(^{13}C) (CDCl$_3$) 142.62, 138.16, 131.81, 129.14, 125.44, 124.68, 87.35, and 75.36 p.p.m.; ν 3280, 2090, 1590, 1575, 1470, 1055, 930, 750, and 690 cm^{-1}.

§ 2-Phenylsulphinylbuta-2,3-dien-1-ol also shows an AB quartet for the C-1 methylene protons although its acetate, allene (**3**) does not.