Concurrent Configurational Modification in Conjugated Dienes; a New Pathway in the Isomerization of Alkadienes

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The hexa-2,4-diene derivative (**2**), obtained from 1,6-di(phenylsulphonyl)hexa-2,4-diyne (**1**), is shown to undergo simultaneous isomerization at both double bonds, through an elimination–addition pathway.

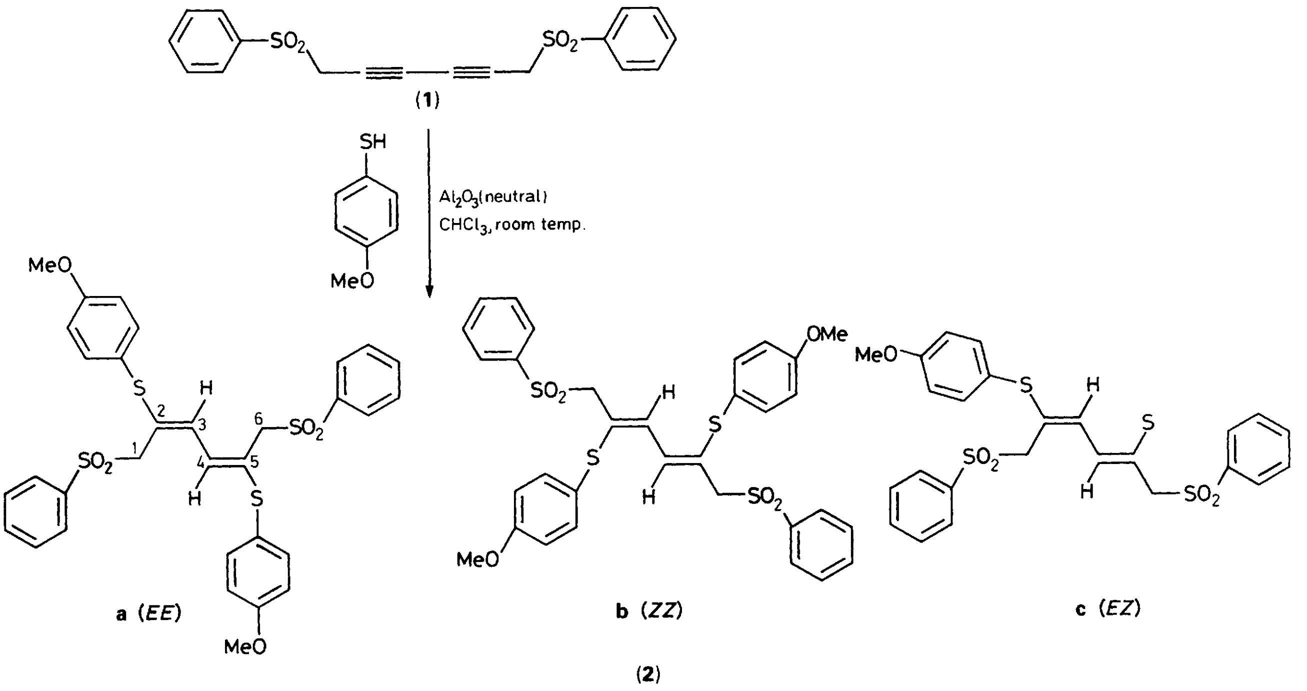
Thiol additions to conjugated alkadiynes have been studied extensively.[1—5] However, few such additions have occurred with total regiospecificity and/or stereospecificity or stereoselectivity. We report the addition of 4-methoxybenzenethiol to 1,6-di(phenylsulphonyl)hexa-2,4-diyne (**1**) with complete regiospecificity and a remarkable degree of stereoselectivity. The addition occurs quantitatively and rapidly (within 5 min) and under very mild conditions (at ambient temperature) requiring no base, in chloroform solution in the presence of neutral alumina. The three isomers (**2a**,**b**,**c**) corresponding to the *E*,*E*, *E*,*Z*, and the *Z*,*Z* geometry were isolated by fractional crystallization (from $CHCl_3$/benzene/MeOH).

Table 1 shows the physical and spectral characteristics of the three isomers. Analysed directly from the reaction mixture, the isomers were formed in a ratio of 52% *E*,*E*:25% *E*,*Z*:23% *Z*,*Z*. Prolonged treatment of the mixture under the the reaction conditions did not alter the composition of the mixture. However, when refluxed in benzene solution, in the presence of 0.5 equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), the composition of the mixture changed to an equilibrium ratio of 18% *E*,*E*:44% *E*,*Z*:38% *Z*,*Z*. Thus, it would appear, under equilibrating conditions, that the *Z*,*Z*- and the *E*,*Z*-isomers predominate, while under kinetic conditions, the *E*,*E*-isomer predominates. When the pure *E*,*E*-isomer, the pure *E*,*Z*-isomer and the *Z*,*Z*-isomer were

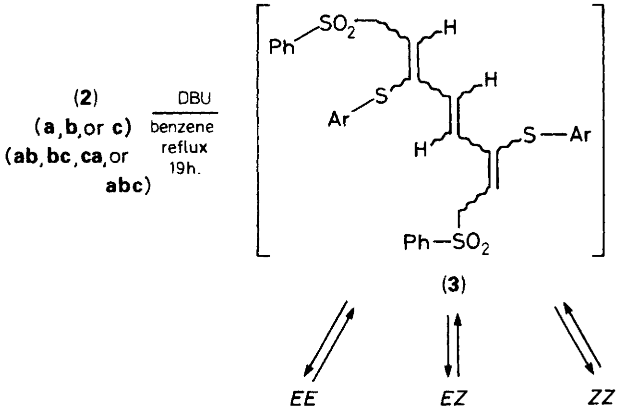
Table 1. The physical and spectral characteristics of isomers (**2a, b, c**).

Isomer[b]	M.p. /°C	UV (MeOH) /nm	IR (KBr) /cm^{-1}	^1H NMR ($CDCl_3$)[a]/δ
E,*E*	244—245	215, 258 ($\lambda_{max.}$) 267, 338	3057, 2966, 2839, 1588, 1385vs, 1149s, 898	7.85—7.55 (m, 10H), 7.21—6.87 (q, 8H), 6.20 (s, 2H), 3.82 (s, 10H)
E,*Z*	127—128	220, 257 ($\lambda_{max.}$) 262, 338	3064, 2964, 2838, 1592, 1385m, 1152s, 1141 s	7.91—7.52 (m, 10H), 7.19—6.79 (m, 8H), 6.76 (d, 1H), 6.34 (d, 1H), 3.88 (s, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 3.79 (s, 4H)
Z,*Z*	247—248	220, 257 ($\lambda_{max.}$) 260, 337	3057, 2972, 2842, 1592, 1385vs, 1140s, 901	7.84—7.53 (m, 10H), 7.15—6.82 (q, 8H), 6.65 (s, 2H), 3.82 (s, 6H), 3.79 (s, 4H)

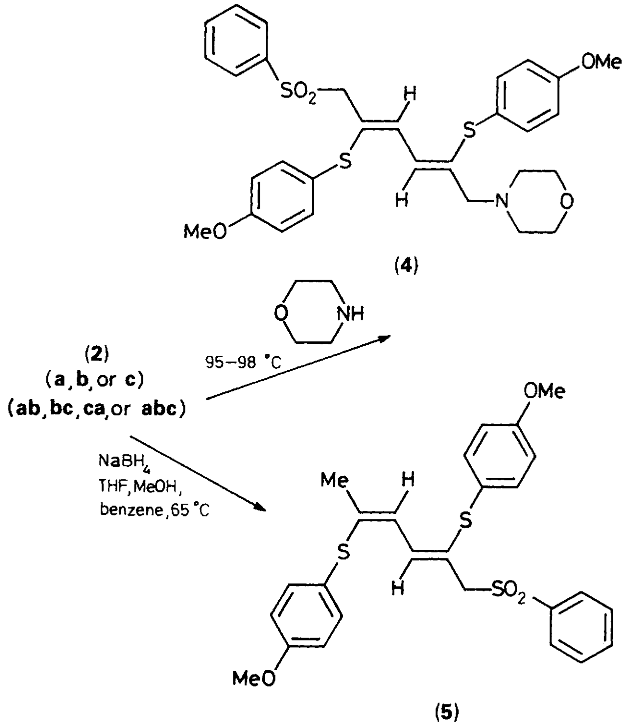
[a] Stereochemical assignments are based upon prior work (ref. 6), vinyl signals are underlined. [b] Satisfactory elemental analyses were obtained.



Scheme 1



Scheme 2



Scheme 3

subjected, individually, to such equilibrating conditions, they yielded the same equilibrium composition as that from a mixture of all the three isomers. The observation of stereomutation at both double bonds suggested the possibility of an elimination-readdition pathway[7] illustrated in Scheme 2.

Such a possibility was confirmed by the provision of other nucleophilic species to capture the 'transient' trienic intermediate (**3**). When the bis-vinyl sulphide (**2**) was reacted with refluxing morpholine, the compound (**4**) was isolated in 70% yield. Similarly, when reacted with $NaBH_4$ in tetrahydrofuran (THF)/MeOH/benzene, the hexadiene derivative (**5**) was obtained in similar yields. In both instances, the product isolated had the *Z*,*Z* geometry as shown in Scheme 3.

While the reversible elimination–addition of the benzene sulphinate results in the equilibrium composition for the geometric isomers (**2a,b,c**), the non-reversible addition of H^- and morpholine yields the *Z*,*Z*-isomer exclusively. To our knowledge, this is the first example of a concurrent modification of configuration in a conjugated diene.†‡ The trienic intermediate (**3**), although unisolable at the moment, offers considerable scope for its exploitation in the synthesis of a

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† This work was presented at the Texas Reaction Mechanism Conference, XIII, Oct 7—8, 1989, in Round Top, Texas.

‡ All new compounds described gave excellent elemental analysis.

variety of other useful hexadiene derivatives. Work is in progress to take advantage of such possibilities. We thank the Robert A. Welch Foundation for their Grant No. AX-1098 which supported this investigation.

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