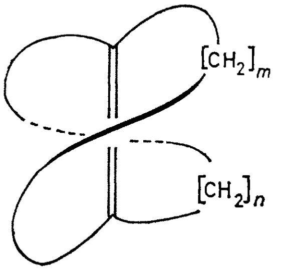
cis- and *trans*-Doubly Bridged Ethylenes *via* Sigmatropic Rearrangements. Synthesis of C_s- and C_1-(±)-15-Thiabicyclo[10.7.0]nonadec-1(12)-ene

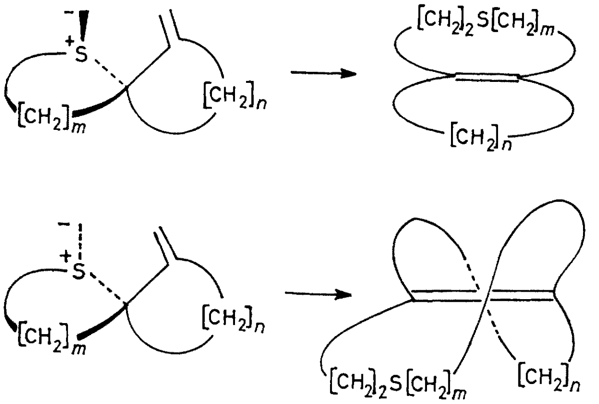
By Vanda Ceré, Claudio Paolucci, Salvatore Pollicino, Edda Sandri,* and Antonino Fava*
(*Istituto di Chimica Organica, Università di Bologna, Viale Risorgimento* 4, 40136 *Bologna, Italy*)

Summary *cis*- and *trans*-Doubly bridged ethylenes result from the stereospecific [2,3]sigmatropic rearrangement of spirocyclic allylic sulphonium ylides.

Bis(*trans*-polymethylene)ethylenes (A),[1] a structural class first recognized by Cahn, Ingold, and Prelog,[2] have recently been synthesized *via* two different approaches.[1,3] This communication describes a novel and effective synthetic strategy to both *cis*- and *trans*-doubly bridged *S*-heterocyclic ethylenes. The crucial step of the new procedure is the shift of a double bond to the required position and geometry by way of a stereospecific [2,3]sigmatropic rearrangement of an allylic sulphonium ylide derived from a thiaspirane (Scheme 1).†

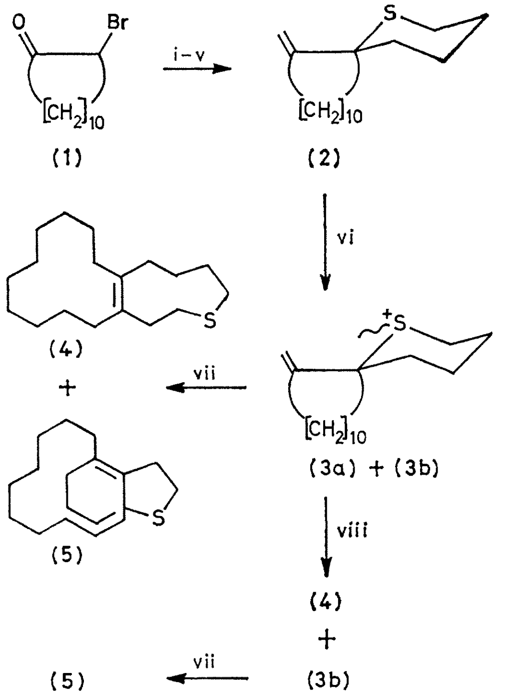


A



Scheme 1

The synthetic sequence leading to the title compounds is displayed in Scheme 2. The spiro-sulphide (**2**) m.p. 56—57 °C, obtained in 14% yield‡ from 2-bromocyclododecanone in 5 steps (i—v), was methylated (vi) to give a 1 : 1 mixture of isomeric sulphonium salts (**3a**) and (**3b**). Although unseparated, the isomers could be unambiguously identified through their SCH_3 n.m.r. shieldings:[4] *cis*-(**3a**), δ 2·70 and *trans*-(**3b**), 3·00. The equimolar mixture of (**3a**) and (**3b**), when treated with 1 equiv. of Bu^{t}OK[5] (vii) gave an equimolar mixture of the isomeric doubly bridged ethylenes (**4**) and (**5**). Monitoring of the reaction (g.l.c., n.m.r.) indicated (**4**) to be formed more rapidly than (**5**), and (**3a**) to be consumed more rapidly than (**3b**). In view of this, the rearrangement was carried out at −70 °C with 0·5 equiv. of the base (viii). The product consisted solely of (**4**), m.p. 48—49 °C, which was separated from the unchanged (**3b**) and the latter rearranged (vii) to essentially pure (**5**) (oil at room temp.). The rearrangement appears to be stereospecific in the present system,§ the *cis*- and *trans*-sulphonium salts (ylides) yielding the *cis*- and *trans*-doubly bridged ethylene, respectively.



Scheme 2. Reagents (yields given in parentheses): i, $HO[CH_2]_4SH$, KOH, EtOH, 10 °C (61·2%); ii, p-$MeC_6H_4SO_2Cl$, pyridine (88%); iii, LiBr, acetone (87%); iv, NaH, 1,2-dimethoxyethane, reflux, 5 h (30%); v, Ph_3PCH_2, Me_2SO, 57 °C, 3 days (82%); vi, CF_3SO_3Me, CH_2Cl_2 (96%); vii, 1 equiv. Bu^{t}OK, tetrahydrofuran–Bu^{t}OH (10/1 v/v), −40 °C (90%); viii, the same as vii except 0·5 equiv. Bu^{t}OK and −70 °C.

---

† The procedure may conceivably be extended to other sigmatropic processes (*e.g.* Cope).

‡ All new compounds gave satisfactory elemental, mass spectral, and n.m.r. data; yields are for isolated products; melting points are uncorrected.

§ Six-membered sulphonium ylides have previously been found to rearrange stereoconvergently, both *cis*- and *trans*-ylides giving the *trans*-olefin (V. Ceré, C. Paolucci, S. Pollicino, E. Sandri, and A. Fava, *J. Org. Chem.*, 1979, **44**, 4128). The apparent discrepancy is probably due to the stringent conformational requirements of the system under investigation here.

The two isomers (**4**) and (**5**) have distinctive ^{13}C n m r spectra In (**4**) the olefinic carbon resonances (δ 135 4 and 133·3 p p m) occur closer together than in (**5**) (δ 135 7 and 131·7 p p m) while the 16 aliphatic carbon resonances fall, as a group, at higher field (δ 32·2—22 2 p p m) than in (**5**) (δ 38·4—24·4 p p m) This is evidence that (**4**) and (**5**) are a *cis–trans* pair of isomeric cyclic olefins [4]

The structures of (**4**) and (**5**) are reflected in their reactivity towards *m*-chloroperbenzoic acid (**4**) gives an epoxide sulphone, (m p 191—192 °C, lowest field ^{13}C resonances at δ 68 8 and 68 2 p p m), while (**5**) resists epoxidation, yielding an unsaturated sulphone (m p 101—102 °C, olefinic ^{13}C resonances at δ 136 5 and 132 0 p p m)

The scope of our synthetic approach would be greatly enlarged by the successful extrusion of the *S*-atom from the heterobridge, which we are attempting

(*Received, 2nd June* 1980, *Com* 594)

---

[1] J A Marshall and M Lewellyn, *J Am Chem Soc* , 1977, **99**, 3508, J A Marshall and K H Chung *ibid* 1979 **101**, 1566

[2] R S Cahn, C Ingold, and V Prelog, *Angew Chem Int Ed Engl* 1966 5 385

[3] M Nakazaki, K Yamamoto, and J Yanagi *J Chem Soc* , *Chem Commun* , 1977, 346 *idem* , *J Am Chem Soc* , 1979, **101**, 147, M Nakazaki, K Yamamoto and M Maeda, *J Chem Soc* , *Chem Commun* , 1980, 294

[4] V Ceré, C Paolucci, S Pollicino, E Sandri, and A Fava, *J Org Chem* , 1978, **43**, 4826

[5] V Ceré, S Pollicino, E Sandri, and A Fava, *J Am Chem Soc* , 1978, **100**, 1516