Synthesis and Some Thermal Reactions of Conjugated *meso*-Diallenes

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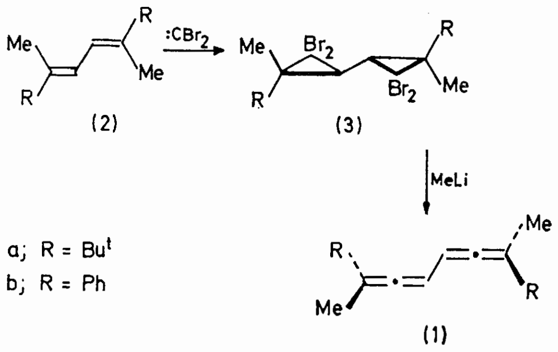
Summary The conjugated *meso*-diallenes (**1a**) and (**1b**), prepared from the corresponding *trans,trans*-dienes by a two-step procedure, added sulphur dioxide to give 2,5-dimethylenesulpholen derivatives (**5**) by a disrotatory mode.

WHEN suitably substituted, a diallene can exist in a *meso*-configuration and as a racemic modification. Here we describe a stereospecific synthesis of the *meso*-diallenes (**1a**) and (**1b**) and some of their thermal conversions. Coupling of the appropriate vinyl-lithium or vinylic Grignard deri-



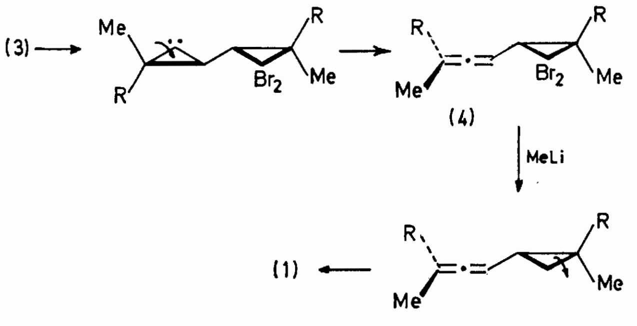
SCHEME 1[1]

vatives, with cuprous chloride as catalyst,[2] afforded pure (**2a**) and (**2b**).[3] Reactions of these dienes with an excess of bromoform and potassium t-butoxide yielded the adducts (**3a**) and (**3b**) (27 and 44% respectively) (Scheme 1). The adducts were homogeneous as indicated by t.l.c., and the structural assignments were based on spectroscopic evidence; furthermore, crystallographic space-group determinations demand that both molecules have a centre of symmetry,† a requirement which is only satisfied by the *meso*-configuration.

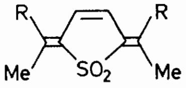
Treatment of the adducts with methyl-lithium afforded the diallenes (**1a**) and (**1b**) (90 and 91% respectively). The spectroscopic and crystallographic data† were consistent with the *meso*-configuration in both cases.

The conversion of *trans*-substituted cyclopropylidenes into allenes occurs with a high degree of stereospecificity.[4,5] Applying this preferred mode of ring-opening to the conversion of the diadduct (**3**) first into the allene (**4**) and then into the diallene (**1**) provides an explanation for the observed stereospecificity (Scheme 2). The specificity can only be significant if the size of group R is considerably larger than that of a methyl group.

Reactions of diallenes (**1a**) and (**1b**) with sulphur dioxide at room temperature gave in high yields the 2,5-dimethylenesulpholen derivatives (**5a**) and (**5b**), respectively; the process is *disrotatory* which is in accordance with the orbital-symmetry requirement for a concerted cheletropic [4 + 2] cycloaddition.[6] A solution of diallene (**1b**) slowly underwent a thermal reaction at 150°; however, in refluxing tetrahydrofuran and in the presence of cuprous chloride the diallene rearranged rapidly and quantitatively into the 3,4-dimethylenecyclobutene derivative (**6b**);[7] the stereochemistry shows that the overall reaction is *conrotatory* which is expected for a concerted process. Diallene (**1a**) was unreactive under these conditions. The effect of cuprous chloride on this reaction is under investigation.



SCHEME 2



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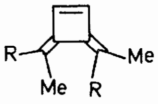

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