

## Selective Functionalisation of 1,3-Dienes via Organosulphur Intermediates

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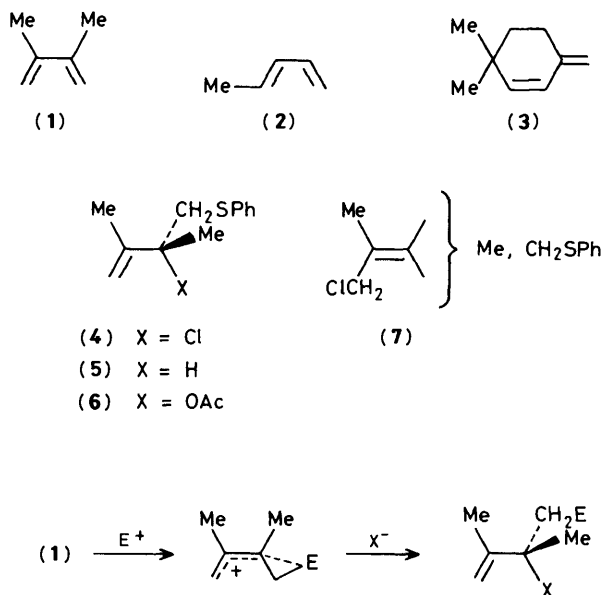
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The 1,2-adducts from 1,3-dienes and sulphenyl chlorides are shown to be useful intermediates by their conversions into a variety of functionalised alkenes.

In connection with studies of the sesquiterpenes called turmerones,<sup>1</sup> we required methods for the oxidative functionalisation of 1,3-dienes, selectively at the terminal position. The synthetic applications of 1,3-dienes would be enhanced if just one of their double bonds could be transformed. We report methodology for achieving such transformations, derived from the addition of a sulphenyl chloride to the 1,3-diene.

Using the representative substrates 2,3-dimethylbuta-1,3-diene (**1**), penta-1,3-diene (**2**), and 3,3-dimethyl-6-

methylenecyclohexene (**3**) we found that hydroboration<sup>2</sup> (borane, di-isopentylborane, or 9-BBN, 9-borabicyclo[3.3.1]nonane; all in tetrahydrofuran, THF), epoxidation [using a peracid (peracetic, *m*-chloroperbenzoic, or *p*-nitroperbenzoic acid), Payne's reagent<sup>3</sup> (hydrogen peroxide + either acetonitrile or benzonitrile), or hypochlorous acid<sup>4</sup>] and hydrometallation [metallo-component = dicyclopentadienylzirconium<sup>5</sup> or (pyridine)cobaloxime<sup>6</sup>] were not efficient for the selective modification of 1,3-dienes. For example, diene (**3**) gave no reaction in dichloromethane with *m*-chloroper-

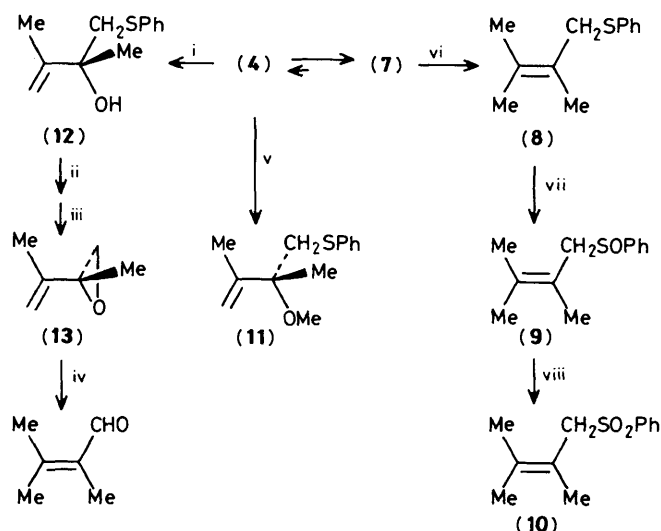


Scheme 1.  $E^+$  = electrophilic species,  $X^-$  = nucleophilic counterion.

benzoic acid, was rearranged by peracetic acid (with or without sodium carbonate), or was over-oxidised by 9-BBN in THF, followed by alkaline hydrogen peroxide.

Obviously, where a mono-adduct was formed in these reactions, it underwent further reaction at the remaining double bond at a rate comparable to or faster than the initial reaction. A selective monofunctionalisation can be achieved by a reagent that generates a transition state that profits from allylic stabilisation of positive charge *en route* to adduct (*cf.* Scheme 1). Thus, it is known that benzenesulphenyl chloride reacts with 1,3-dienes to give 1,2-adducts under kinetic control, which readily rearrange to the thermodynamically more stable 1,4-adducts.<sup>7,8</sup> However, these observations have hardly been developed for synthetic purposes (but see ref. 9).

We report reactions of both the 1,2- and 1,4-adducts of PhSCl with 1,3-dienes, which make these adducts attractive synthetic intermediates. The chemistry is well exemplified by the behaviour of the diene (1). This reacts with PhSCl (1 mol. equiv. in  $CH_2Cl_2$ , rapid reaction at  $-78^\circ C$ ) to give 2-chloro-2,3-dimethyl-1-phenylthiobut-3-ene (4), quantitatively. The reaction procedure and work-up are essentially those described<sup>10</sup> for mono-enes reacting with PhSCl. Compound (4) is a kinetic product because on distillation (Kugelrohr, oven temp.  $140^\circ C$ ,  $10^{-3}$  mmHg), or on storage at room temperature for several weeks in the liquid state or for a few days in acetonitrile, it rearranges in high yield to give 1-chloro-2,3-dimethyl-4-phenylthiobut-2-ene (7, mixture of *E* and *Z* isomers). Compounds (4) and (7) are versatile starting materials for the preparation of a variety of useful sulphur compounds (*cf.* Scheme 2). As expected, adduct (4) was not reduced by lithium triethylborohydride<sup>11</sup> in tetrahydrofuran (THF) (4 days at room temp.), whereas (7) was smoothly converted into 2,3-dimethyl-1-phenylthiobut-2-ene (8) (87%) by 1 M  $LiEt_3BH$  (1.1 mol equiv.) in THF (3 h at room temp.). Oxidation of compound (8) with sodium periodate in aqueous ethanol gave the sulphoxide (9) (73%); longer reaction times and excess of  $NaIO_4$  resulted in the sulphone (10). The thiranium ion from ionisation of the adduct (4) could be selectively trapped with oxygen nucleophiles ( $HO^-$ ,  $MeO^-$ , or  $AcO^-$ ) giving products (12), (11), and (6), respectively in



Scheme 2. Reagents: i, aq. NaOH-dioxane or wet  $Ag_2O$ ; ii,  $Me_3O^+BF_4^-$  in  $CH_2Cl_2$ ; iii,  $NaH-CH_2Cl_2$ ; iv, cat.  $CF_3CO_2H$  in  $CH_2Cl_2$ ; v, NaOMe in MeOH; vi,  $LiEt_3BH$  in THF; vii, aq.  $NaIO_4-EtOH$ ; viii, excess of reagent vii.

*N.B.* All compounds shown here as chiral were obtained as racemic mixtures.

good yields. With borohydride ( $NaBH_4$  in dimethylformamide,  $80^\circ C$ ) as trapping agent<sup>12</sup> the adduct (4) gave a 1:1 mixture of compound (8) and 2,3-dimethyl-4-phenylthiobut-1-ene (5). The adduct (12) was converted into 1-methyl-1-prop-2-enyloxirane (13) by sequential treatment with trimethyl-oxonium fluoroborate and sodium hydride in dichloromethane. The epoxide was identified both spectroscopically and by acid-catalysed conversion into 2,3-dimethylbutanal (isolated as its 2,4-dinitrophenylhydrazone which was compared with an authentic specimen). Analogous chemistry to that described has been accomplished with dienes (2) and (3), and with methanesulphenyl chloride instead of PhSCl.

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