Journal of

The Chemical Society,

Chemical Communications

NUMBER 13/1972 **5 JULY**

A New Synthesis of Unsaturated Aldehydes

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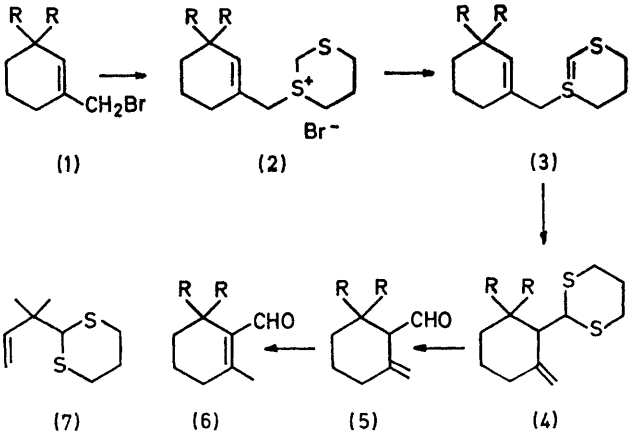
Summary Primary allylic bromides A–Br and 1,3-dithian react to give sulphonium bromides; these form ylides which undergo [2,3]-sigmatropic rearrangement to 2-substituted 1,3-dithians; hydrolysis then gives the $\beta\gamma$-unsaturated aldehydes A'–CHO. (A' = rearranged allylic system corresponding to A).

By means of the Claisen rearrangement an allylic alcohol A–OH can be converted[1] into the $\gamma\delta$-unsaturated aldehyde A'-CH_2·CHO; a valuable feature is that in this way the group –CH_2·CHO can be introduced efficiently into a sterically congested environment.[2] We now describe a related reaction sequence which allows the similar introduction of the aldehyde group itself, and provides a convenient method of converting an allylic bromide A–Br into the $\beta\gamma$-unsaturated aldehyde A'–CHO.

The allylic bromide (**1**; R = H) when treated with 1,3-dithian at 20° gave compound (**2**; R=H), m.p. 123—124°, in high yield. Treatment of (**2**; R = H) at −78° in tetrahydrofuran with n-butyl-lithium gave (**3**; R = H), which was expected, by analogy,[3] to rearrange to the 2-substituted 1,3-dithian (**4**; R = H). On warming to 20° and normal work-up (**4**) was obtained in over 80% yield as a homogeneous oil and was characterised by accurate mass and other spectral data [τ ($CDCl_3$) 5·20 (2H, s) and 5·67 (1H, d, J 9·5 Hz)]. We have similarly prepared the related 1,3-dithians (**4**; R = Me) and (**7**). Since good methods are available[4] for the hydrolysis of 1,3-dithians, a new route is thus opened to $\beta\gamma$-unsaturated aldehydes. Moreover, when the initial allylic bromide contains a hydrogen atom at the γ-carbon atom, the aldehyde first formed can be converted by prototropic isomerisation into an $\alpha\beta$-unsaturated aldehyde. We have, for example, obtained γ-cyclocitral[5] (**5**; R = Me) by the new method, and have demonstrated by spectroscopic methods its conversion into β-cyclocitral (**6**; R = Me).



Baldwin[6] has recently used a carbene rearrangement sequence in order to convert $\gamma\gamma$-dimethylallyl bromide into 2,2-dimethylbut-3-enoic acid (*i.e.* A–Br $\longrightarrow$ A'–CO_2H), an overall result similar to that achieved by the present method. Baldwin's method should be applicable to secondary allylic bromides, whereas ours may be restricted to primary representatives. Our immediate products, the 2 substituted 1,3-dithians, are valuable not only as the precursors of aldehydes, but also because they are readily transformed[4,7] into ketones, hydroxy-ketones, and diketones.

We thank the S.R.C. for a Studentship (to E.H.).

(*Received*, 6*th April* 1972; *Com.* 585.)

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