Methoxythallation of Acyclic Allenes

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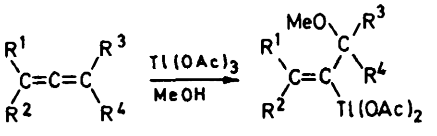
Summary Treatment of allenes with thallium(III) acetate in methanol gave stable methoxythallation products.

It was shown earlier that oxymercuration[1] of allenes proceeds with predominant formation of substituted 1-

alkenyl organomercury compounds and in view of the broad similarity of oxythallation to oxymercuration,[2] it was expected that similar oxythallation products would be obtained from allenes. Solvolytic dethallation of these products by C–Tl bond heterolysis, which in the case of adducts from olefins appears to occur quite readily,[3] would, in the present instance, involve a transition state resembling a vinyl cation—a process which is usually rather slow.[4] Oxythallation products from allenes therefore should be stable enough to be isolated.



(1) (2)

a; $R^1 = R^2 = R^3 = R^4 = Me$
b; $R^1 = R^3 = Me, R^2 = R^4 = H$
c; $R^1 = R^4 = H, R^2 = R^3 = Me$
d; $R^1 = R^2 = R^4 = H, R^3 = Et$

We now report that allenes react with thallium(III) acetate in methanol to give fairly stable products. 2,4-Dimethylpenta-2,3-diene (**1a**) gave the pentene (**2a**), m.p. 137—138 °C, in almost quantitative yield.† The structure was assigned on the basis of its n.m.r. spectrum [δ 1·45 (d, J_{Tl-H} 80 Hz, aliph. Me), 2·03 (d, J_{Tl-H} 187 Hz, *cis*-Me at sp^2 C), 1·94 (d, J_{Tl-H} 107 Hz, *trans*-Me) 3·34 (d, J_{Tl-H} 4 Hz, OMe), and 2·00 (sharp s, OAc) p.p.m.]

Similarly, penta-2,3-diene (**1b**) gave a mixture (94% yield) of the *cis*- (**2b**) and *trans*- (**2c**) pentenes, and penta-1,2-diene (**1d**) gave (**2d**), (50%), m.p. 135 °C. Structures (**2b**—**d**) were also assigned on the basis of their n.m.r. spectra.

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† All new compounds gave satisfactory analytical data.

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[3] H. J. Kabbe, *Annalen*, 1962, **656**, 204; R. J. Ouellette, G. Kordosky, C. Levin, and S. Williams, *J. Org. Chem.*, 1969, **34**, 4104; E. C. Taylor and A. McKillop, *Accounts Chem. Res.*, 1970, **3**, 338.

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