Thermal 'Ene' Addition of Monothiobenzil to 2-Methylpent-2-(and -1-)-ene

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Summary The α-acyl thione, monothiobenzil, undergoes thermal 'ene' additions at 80—100° to 2-methylpent-2-(and -1-)ene in an inverse orientation mode to yield desyl alkenyl sulphides.

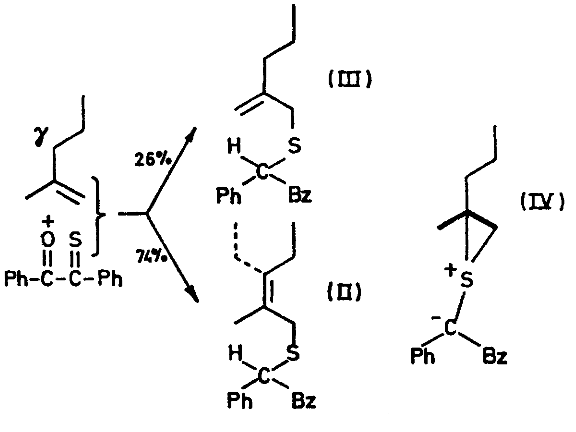
Whilst Arnold[1] has shown that α-dicarbonyl compounds undergo 'ene' additions to allylic olefins to provide homoallylic alcohols, the corresponding reactivity of α-acylthiones has not heretofore been studied.

When a solution of monothiobenzil (0·06M) in degassed 2-methylpent-2-ene [prepared by dissolution of the dissociable green polymer[2] of PhC(:S)C(:O)Ph in the olefin] was heated *in vacuo* for 2 h at 100°, the blue colour due to the free thiocarbonyl group[2] disappeared rapidly ($t_{\frac{1}{2}}$, 1st order, *ca.* 20 min at 80°). Removal of the olefin, found to be compositionally unchanged, gave a pale yellow residue which was resolved by t.l.c. into benzil (15% w/w), a minor unidentified component, and a sulphurated material (75%) which, on the basis of satisfactory elemental, i.r., and ^{1}H n.m.r. analyses, coupled with chemical functional group tests, is concluded to consist solely of the diastereomeric *threo-* and *erythro-*forms (2:1) of desyl 1-ethyl-2-methylallyl sulphide (I) [desyl = PhCO·CH(Ph)-].

Likewise, the reaction of 2-methylpent-1-ene with monothiobenzil, which appeared to proceed somewhat more easily at the same temperature, afforded a mixture of desyl 2-methylpent-2-enyl sulphide [(II) *cis–trans*-ratio not known; 74%] and desyl 2-propylallyl sulphide (III) (26%).

This evidence shows that the additions proceed *via* inverse 'ene' modes (illustrated in the Scheme for 2-methylpent-1-ene), and, through the absence of products of insertion of the thiocarbonyl group into C_γ–H bonds of the olefin, that alternative free-radical allylic substitution mechanisms can be discounted. Cyclohexene was very unreactive towards monothiobenzil, and no sulphides could be isolated.

Our results may be compared with the known 'ene' additions (at −78°) of hexafluorothioacetone to allylic olefins,[3] and our knowledge[4] that thiobenzophenone does not react appreciably with such olefins during 24 h at 140°, to reveal the profound influence of the substituents carried by the thiocarbonyl group on enophilic reactivity.



Scheme

To investigate the possibility that the monothiobenzil additions could be proceeding *via* two-step mechanisms involving the intermediacy of rearrangeable zwitterionic intermediates [*e.g.* (IV)] we also performed the additions in the presence, separately, of methanol and acetic acid (in equal volume with the olefins). It can be argued that these protic additives would cause an intermediate such as (IV) to yield desyl methoxyalkyl and desyl acetoxyalkyl sulphides *via* solvolysis of the episulphonium bridge. However, experimentally no diversion from the normal 'ene' adducts was evident, and we therefore provisionally regard the fundamental 'ene' additions of this discovery as concerted processes.

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[3] J. W. Middleton, *J. Org. Chem.*, 1965, **30**, 1395.

[4] G. T. Knight and B. Saville, unpublished observations.