

ANOMALOUS PRODUCTS FROM COPE REARRANGEMENTS IN IMINE SYSTEMS

R.K. Bramley, J. Caldwell and R. Grigg.\*

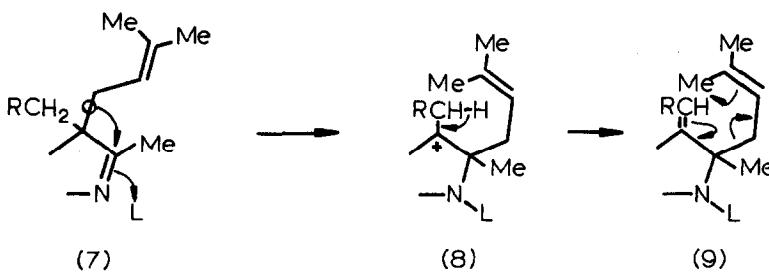
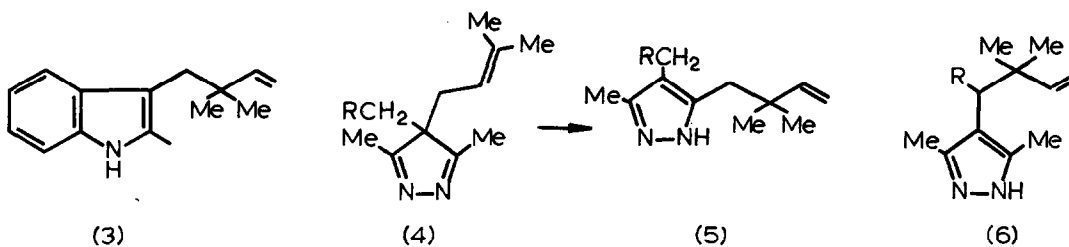
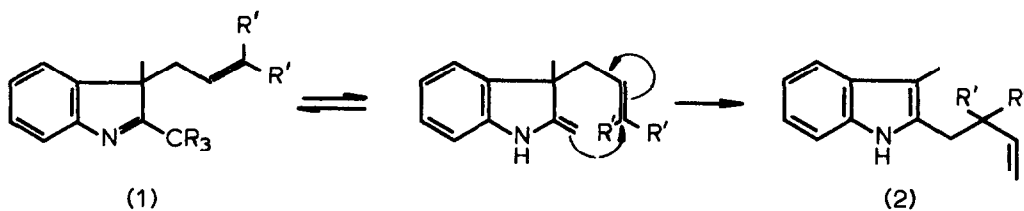
Department of Chemistry, Nottingham University, Nottingham NG7 2RD.

(Received in UK 27 June 1973; accepted for publication 13 July 1973)

Thermal rearrangement of 3-allylindolenines and 4-allylisopyrazoles results in imine-enamine prototropy followed by a Cope rearrangement (e.g. 1→2; R=R<sup>1</sup>=H)<sup>1</sup>. However, thermal rearrangement of the indolenine (1;R=H,R<sup>1</sup>=Me), produced in addition to the expected Cope product (2;R<sup>1</sup>=Me), another indole with a terminal allyl group and only one indolic methyl group (n.m.r.). Rearrangement of the trideuteriomethylindolenine (1;R=D, R<sup>1</sup>=Me) showed that the "anomalous" product had the C(3) methyl group functionalised, and enabled structure (3) to be assigned to this minor (10%) product. Similarly the isopyrazoles (4;R=H or Me) gave, in addition to the expected Cope products (5;R=H or Me; 30% and 35% respectively), the "anomalous" products (6;R=H or Me; 40% and 44% respectively). The Cope products (5;R=H or Me) were solids whilst (6;R=H or Me) were oils and their n.m.r. spectra enabled them to be readily distinguished e.g. (5;R=H) τ(CDCl<sub>3</sub>) 7.5 (S,2H, nuclear-CH<sub>2</sub>-), 7.85 and 8.13 (both S, 6H, 2 x nuclear Me); (6;R=H) τ(CDCl<sub>3</sub>) 7.85 (S,6H, 2 x nuclear Me) and 8.13 (S,2H, nuclear-CH<sub>2</sub>-) The n.m.r. spectrum (CCl<sub>4</sub>) of (6;R=Me) showed evidence of restricted rotation (50:50 conformer population), in that the methyl substituent on the chiral carbon atom appeared as a pair of doublets at τ8.94 and 9.06 (restricted rotation is evident from a study of Dreiding models).

The "anomalous" products (3) and (6) are thought to arise by a Plancher-Brunner type [1,2]-shift<sup>2</sup> catalysed by traces of Lewis acids, followed by deprotonation and Cope rearrangement (7-9; partial formulae). The dimethylallyl group is known to have a much greater migratory aptitude than the allyl group in Plancher-Brunner rearrangements<sup>3</sup> and thus competes

with Cope rearrangement (1→2) in the dimethylallyl case but not in the allyl case.



#### References

1. R.K. Bramley and R. Grigg, Chem. Comm., 1969, 99; R.K. Bramley, J. Caldwell and R. Grigg, J. Chem. Soc., (Perk I), in press.
2. Heterocyclic Compounds, 1952, Vol. 3., 80, Ed. by R.C. Elderfield, Pub. Wiley; Y. Kanaoka, K. Miyashita and O. Yonemitsu, Chem. Comm., 1969, 1365; G. Casnati and A. Pochini, Chem. Comm., 1970, 1328.
3. G. Casnati, A. Dossena and A. Pochini, Tetrahedron Letters, 1972, 5277.