# 1,3-Dipolar Cycloadditions to an Isoquinolinium Imine Obtained by Thermally Disallowed Valence Tautomerism of a 6-Cyclohexylimino-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-*b*]azirine

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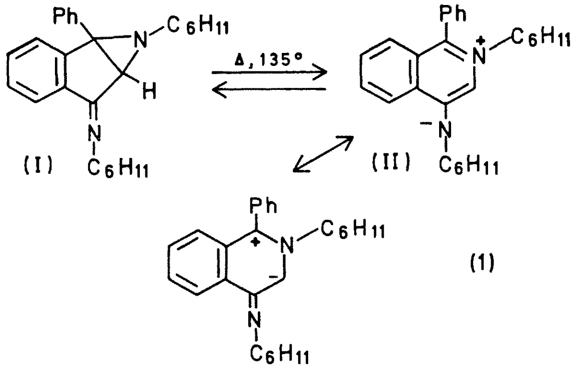
*Summary* 1-Cyclohexyl-6-(cyclohexylimino)-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-*b*]azirine at 135° in toluene undergoes a formally disallowed valence tautomerism to an isoquinolinium imine which may be trapped as an azomethine ylide in a series of 1,3-dipolar cycloadditions.

HUISGEN and his co-workers[1] have convincingly demonstrated the thermal conrotatory 2–3-bond cleavage of substituted aziridines to azomethine ylides predicted by application of the Woodward–Hoffmann rules to the isoelectronic analogue, the cyclopropyl anion.[2] Subsequent 1,3-dipolar cycloadditions of the azomethine ylide intermediate to a variety of homomultiple and heteromultiple bonds are firmly established.[3] When the aziridine ring is constrained in a bicyclic structure at the 2–3 bond, thermal conrotatory ring opening is not possible for steric reasons. We report the thermally disallowed valence tautomerism of 1-cyclohexyl-6-(cyclohexylimino)1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-*b*]azirine[4] (I) to the isoquinolinium imine (II) (Equation 1) and subsequent trapping of the latter as an

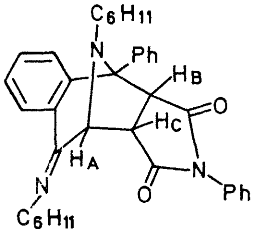


azomethine ylide in a series of 1,3-dipolar cycloadditions. Heating of a degassed solution of (I) with an equimolar quantity of *N*-phenylmaleimide in toluene at 135° for 12 hr or refluxing in *p*-xylene under $N_2$ gave the crystalline adduct (III)† (82%) m.p. 235—237°, $\nu_{max}$ ($CHCl_3$): 1775, 1713 (C=O), 1649 $cm^{-1}$ (C=N); $M^+$ 557·3048, calc. 557·3042 $\delta$ ($CDCl_3$,$Me_4Si$ as standard) 0·5—2·2 (m, 20H, $C_6H_{11}$), 2·2—2·9 (m, 1H, C*H*N), 3·5—4·1 (m, 1H, C=NCH), 3·87 (t, 1H, $J$ = 9 Hz, $H_C$), 4·32 (d, 1H, $J$ = 9 Hz, $H_B$ proton), 5·14 (d, 1H, $J$ = 9 Hz, $H_A$), 6·0—8·3 p.p.m. (m, 14H, ArH). Compound (III) was assigned the *endo*-structure shown on the basis of the n.m.r. spectrum, which showed 9 Hz coupling to the bridgehead proton consonant with a dihedral angle of 20°,[5] predicted from an examination of molecular models and by comparison with adduct (IV) described below.

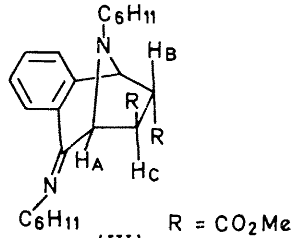
The colourless indeno[1,2-*b*]azirine could be recovered from the purple toluene solution of (II) obtained by heating to 130°: this demonstrates the reversibility of the valence tautomerism.

Reaction of (I) with either an equimolar quantity of dimethyl fumarate or dimethyl maleate in degassed toluene at 135° for 48 h gave the adduct (IV)† (68% and 54%) m.p. 156—157° $\nu_{max}$ ($CHCl_3$): 1731 (C=O), 1642 $cm^{-1}$ (C=N); $M^+$ 528·2995, calc. 528·2988; $\delta$ ($CDCl_3$,$Me_4Si$ as standard) 0·5—2·2 (m, 20H, $C_6H_{11}$), 3·23 (s, 3H, $CO_2CH_3$), 3·37 (q, 1H, $J_{BC}$ = 7·3 Hz, $J_{AC}$ = 1·8 Hz, $H_C$), 3·65 (s, 3H, $CO_2CH_3$) 4·30 (d, 1H, $J$ = 7·3 Hz, $H_B$), 5·01 (d, 1H, $J_{AC}$ = 1·8 Hz, $H_A$‡), 6·4—8·3 (m, 9H, ArH). Evidently, prolonged refluxing in toluene resulted in prior isomerisation of dimethyl maleate to dimethyl fumarate as has been observed.[6]

Although the thermal valence tautomerism of (I) to (II) is formally a forbidden process, substantial driving force for this process is provided by the relief of ring strain in (I) and the gain in resonance energy in (II). This process is analogous to the observed tautomerisation of 2,3-diphenylindenone oxide to the 1,3-diphenyl-2-benzopyrylium 4-oxide.[7]



(III)



(IV)

The observed opening of (I) to (II) complements the recently described allowed disrotatory opening of *N*-chloroindano[1,2-*b*]aziridine to the nitrenium ion,[8] which is an electrocyclic process with the same orbital symmetry control as the cyclopropyl–allyl cation rearrangement.[9]

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† Satisfactory analytical data were obtained on all new compounds.

‡ Line positions confirmed by specific deuterium labelling.

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