Influence of Vibrational Excitation Energy on the Cyclisation Stereochemistry of Triplet 1,3-Biradicals

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Summary 1,4-Hydrogen migration in triplet 3-methylbut-1-ene produces the triplet 1,2-dimethyl-1,3-trimethylene biradical which can subsequently cyclise to *trans*- and *cis*-1,2-dimethylcyclopropane in a ratio strongly dependent on its internal vibrational energy.

THE triplet 1,2-dimethyl-1,3-trimethylene biradical (DMTMB) has been postulated as an intermediate in the triplet-sensitized decomposition both of 2,3-dimethylcyclobutanones[1,2] and of 3,4-dimethyl-Δ^1-pyrazolines,[3,4] and in the reaction of CH_2 ($^3B_1$) with but-2-ene.[5,6] Known reactions of this species include decomposition by CH_3 loss[6] and ring closure yielding *trans*- and *cis*-1,2-dimethylcyclopropane (DMCP).[1-5] While the influence of excitation energy on the stereochemistry of the cyclisation reaction, in addition to that for the fragmentation process, has been recognised, its extent is reportedly small.[2,3] Results pertinent to this latter reaction are now presented which demonstrate that the magnitude of this effect is much greater than hitherto realised. The biradical was obtained by the Hg(6^3P_1)-photosensitized rearrangement of 3-methylbut-1-ene. The reaction is analogous to those leading to methylcyclopropane (MCP) and DMCP in the Hg(6^3P_1)-photosensitized isomerization of but-1-ene[7] and pent-1-ene[8] respectively, and presumably proceeds by an intramolecular 1,4-hydrogen shift in the triplet olefin.

Photolyses were carried out at low conversion with a Hanovia low-pressure mercury resonance lamp and the numerous reaction products analysed by g.l.c. A study of the DMCP product yields over the pressure range 12—789 Torr† showed that the total DMCP mercury photosensitization quantum yield, Φ_{DMCP}, passed through a maximum at *ca.* 80 Torr as the pressure increased, in a manner analogous to that for MCP formed from but-1-ene,[7] and, more interestingly, the ratio of *trans*- to *cis*-DMCP varied continuously from 1·58 at 11·8 Torr to 3·44 at 789 Torr† as shown in the Figure. The variation of Φ_{DMCP} with pressure can be explained by postulating that there are two excited species, both subject to collisional deactivation, that are involved consecutively in the mechanism forming DMCP. They can be identified as the excited triplet parent olefin and the 'hot' DMTMB.

The extensive variation in the *trans*-DMCP–*cis*-DMCP ratio with pressure demonstrates that the excited DMTMB is sufficiently long lived so as to be collisionally intercepted, thereby undergoing internal energy degradation, and that the ring closure becomes more stereospecific as the biradical excitation decreases. The effective competition between biradical fragmentation and collisional deactivation implies a lifetime of a similar magnitude.[6] While the pressure dependence of the *trans*-DMCP–*cis*-DMCP ratio observed here is much larger than that previously reported in other systems[2,3] it does mirror that found in experiments using CH_2 ($^3B_1$) and but-2-ene as the DMTMB precursors.[9] It therefore seems likely that the same triplet biradical, differing only in internal energy content, is present in both these systems. The triplet nature of the biradical is also supported by the results of a crude R.R.K. calculation of the rate of DMCP formation from singlet DMTMB of equivalent excitation energy.‡ The calculation shows that singlet biradicals would cyclise so rapidly as to preclude their prior collisional deactivation in the pressure range of the experiments. Thus hydrogen migration in the triplet olefin conserves spin and, furthermore, it is the rate of intersystem crossing of the biradicals so produced which largely determines their overall rate of cyclisation.

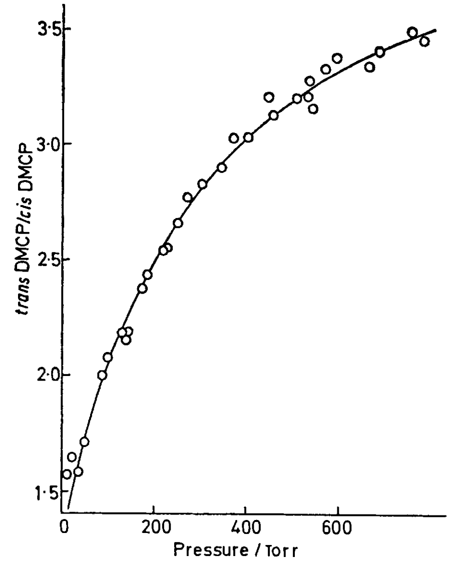

FIGURE. *Ratio of the mercury photosensitization quantum yields of* trans- *to* cis-DMCP vs. *pressure.*

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† 1 Torr = 133·3 N m^{-2}.

‡ ΔH_f^0 (DMTMB) may be estimated (H. E. O'Neal and S. W. Benson, *Internat. J. Chem. Kinetics*, 1969, **1**, 238) as *ca.* 213·0 kJ mol^{-1} resulting in a calculated initial biradical excitation energy of 230 kJ mol^{-1} assuming total energy transfer from Hg (6^3P_1) and using ΔH_f^0 (3-methylbut-1-ene) = − 28·95 kJ mol^{-1}. Suggested Arrhenius parameters for DMTMB ring-closure (H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 1968, **72**, 1866) are $\log_{10} A = 13{\cdot}6$ and $E_a = 38{\cdot}9$ kJ mol^{-1}; using $s = 18$ leads to a calculated specific rate constant for cyclisation of *ca.* $10^{12\cdot1}$ s^{-1}.

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