Topology of the Photochemical 'Bicycle' Reaction. Mechanistic and Exploratory Organic Photochemistry[1]

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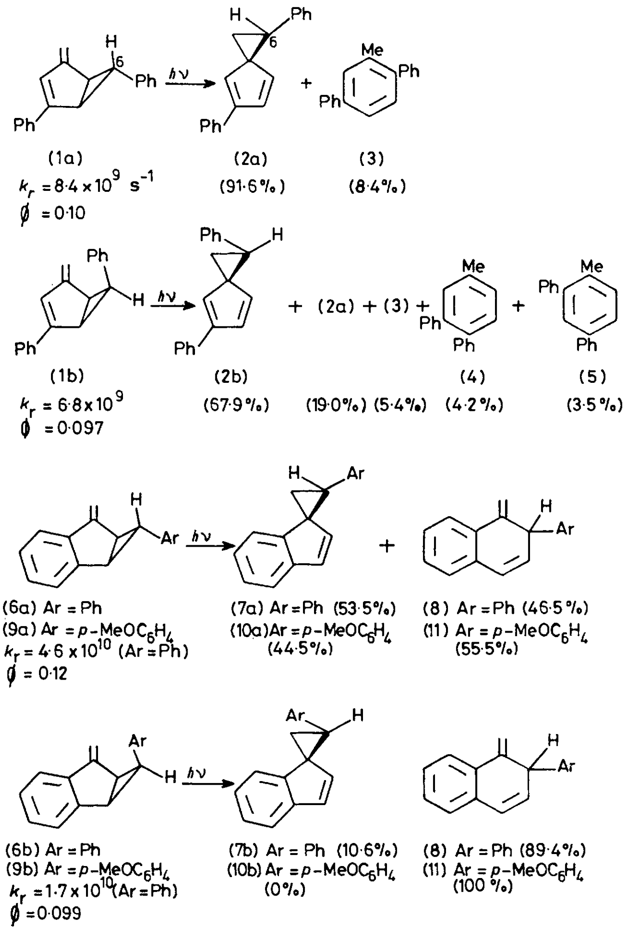
Summary We report some new examples of the 'bicycle' reaction, the corresponding quantum yields and exceptionally rapid S_1 reaction rates, evidence for lack of clockwise bicycling but in favour of an overshoot plus backup mechanism to account for loss of stereochemistry, a test excluding an even number of pivot steps as alternative to bicycling, and the effect of interposition of an aromatic unit along the track.

PREVIOUSLY we described a photochemical rearrangement in which C-6 of a 2-methylenebicyclo[3.1.0]hex-3-ene slithers along the π system of a fulvene unit to the exocyclic π bond, thus giving a spiro[2.4]hepta-4,6-diene.[2] The rearrangement can be envisaged as involving a carbenoid carbon (*i.e.* C-6) 'bicycling' on the fulvene π system using its sp^5 hybrid orbitals as 'wheels' and its *exo* and *endo* substituents as 'handlebars.'†

We now report: (a) information on the generality of the bicycle reaction; (b) evidence for lack of clockwise bicycling and in favour of an overshoot plus backup mechanism leading to some loss of stereospecificity; (c) the effect of interposing a high energy aromatic π unit along the bicycle track; (d) a test excluding an even number of pivots as an alternative to bicycling; (e) evidence against an intriguing alternative mechanism; and (f) an SCF–CI calculation of the hypersurfaces involved in the reaction.

Scheme 1 delineates three new examples of the bicycle reaction. It also includes some rates and quantum yields derived from our initial studies. The reaction can be seen to be a rapid excited singlet process comparable in rate to our di-π-methane rearrangement.[3] From the reaction stereospecificity it is concluded that the carbenoid carbon cannot be ejected followed by recapture to give spiro product, since the bimolecular recombination would not 'remember' the reactant stereochemistry.



SCHEME 1. New examples of the bicycle reaction.

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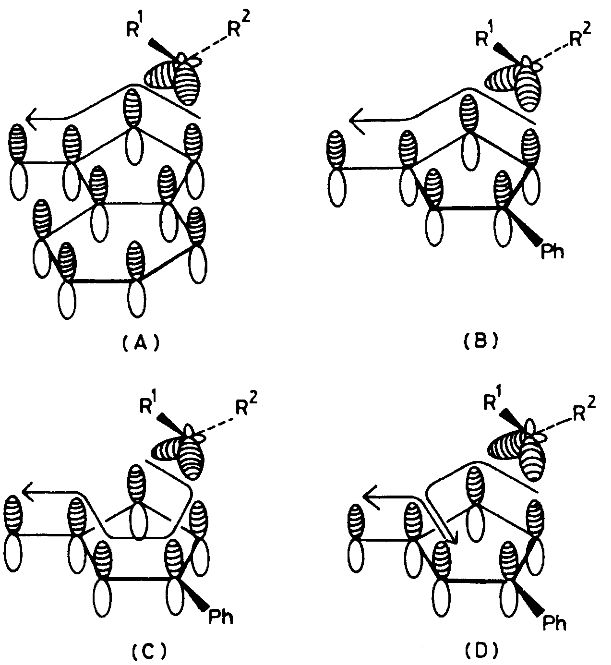
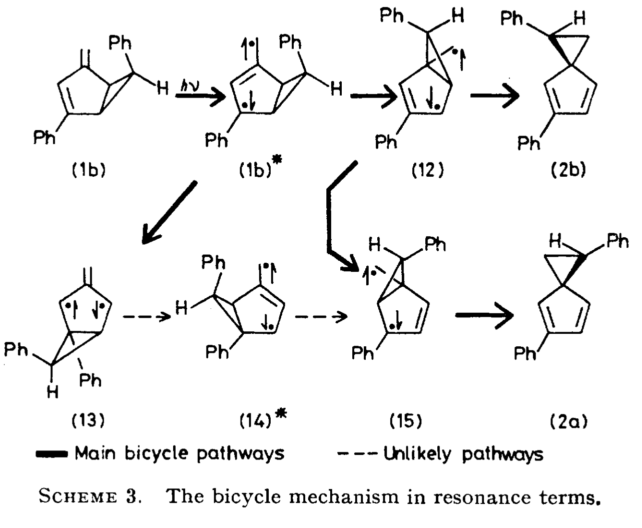
† We prefer a change in nomenclature from 'slither' to 'bicycle; the two are equivalent.



Scheme 2. Bicycling topology.

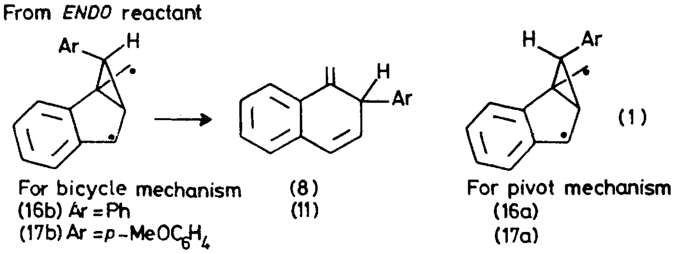
The reaction topology is depicted in Scheme 2. The observed reaction stereospecificity is accounted for by paths A and B. Minor loss of stereospecificity in the case of *endo*-2-methylene-4,6-diphenylbicyclo[3.1.0]hex-3-ene (**1b**) can *a priori* be rationalised in a competing mechanism following the topology of either path C or path D. Path C utilizes clockwise bicycling while path D has the bicycling carbon proceeding beyond the *exo*-methylene side chain and backing up on to this double bond to give the spiro-product. Scheme 3 gives the mechanism in more traditional organic terms.

In considering the clockwise bicycling pathway C, we note that this mechanism proceeds *via* species (**14**)* in Scheme 3. This is just the excited state of *endo*-2-methylene-5,6-diphenylbicyclo[3.1.0]hex-3-ene (**14**) whose photochemistry we have previously studied.[2] However, the 115 kcal mol^{-1} singlet energy of (**14**)* precludes its formation from the starting excited state with 94 kcal mol^{-1} energy. The overshoot plus backup pathway D does not pose comparable difficulties.



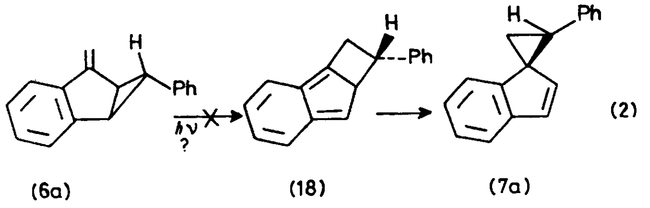
Scheme 3. The bicycle mechanism in resonance terms.

One might ask if there is any bicycling of C-6 around or on to the aromatic benzo-ring in the cases of benzo-bicyclic olefins (**6**) and (**9**). The contrasting essentially total stereospecificity in these benzo examples indicates that pathways C and D, losing stereospecificity, are not available. Pathways C and D require loss of aromaticity *en route*, and a high energy portion of the excited state hypersurface is avoided by the bicycle. One notable result is the dominant internal bond fission of 1,4-diradical species to give 1-methylene-2-aryl-1,2-dihydronaphthalenes (**8**) and (**11**) only for the *endo* isomers of the benzo bicyclic olefins (**6**) and (**9**) (*cf.* Scheme 1). This reaction is shown in equation (1).



The general enhancement of Grob fragmentation may derive from greater localization of the two electrons due to replacement of the double bond by a benzo-ring. However, steric relief of strain accounts for the preferential diversion of *endo* 1,4-diradicals (**16b**) and (**17b**). Now, were a series of pivot steps utilized, instead of bicycle steps, at this point one pivot step would have taken place and the *exo*-aryl 1,4-diradical (**16a**) or (**17a**) would be present with no steric driving force for molecular flattening and internal bond fission.

Concerning point (e) already mentioned, applying an intriguing mechanistic alternative[4] to the benzo examples, we obtain the sequence in equation (2). In contrast with the ordinary bicyclic examples in Scheme 3 benzo-aromaticity is lost in this mechanism. Yet Scheme 1 shows the benzo-bicyclic excited states rearrange slightly more rapidly rather than more slowly as predicted from the mechanism in equation (2).



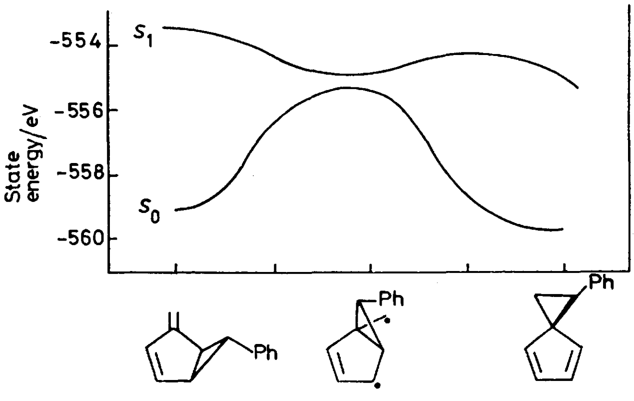


FIGURE. Hypersurfaces for the bicycle reaction. (Energies are relative since only those σ bonds involved in the reaction are included.)

Finally, we report the results of SCF–CI calculations utilizing three-ring Walsh orbitals and *p*-orbitals for one phenyl group and the rest of the π system using singly and doubly excited configurations. Calculations were carried out on each species along the reaction co-ordinate.[1b] Thus the mechanism involves S_1 proceeding exothermically along the reaction co-ordinate until the penultimate biradical (**20**) is formed, whereupon conversion of electronic excitation into vibrational energy leads to product. The results are summarized in the Figure.

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[1] (a) For previous paper in this series, see H. E. Zimmerman, T. P. Gannett, and G. E. Keck, *J. Amer. Chem. Soc.*, 1978, **100**, 323; (b) Full experimental details and details of the calculations, will be given in our full paper. Satisfactory elemental analyses were obtained on all new compounds except for the methylene-dihydronaphthalenes for which high resolution mass spectra were obtained.

[2] (a) H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, 1971, **93**, 3662; (b) *ibid*, 1970, **92**, 3474.

[3] H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, *J. Amer. Chem. Soc.*, 1974, **96**, 439.

[4] N. K. Hamer and M. Stubbs, *Chem. Comm.*, 1970, 1013.