

esters are irradiated.¹¹ Clearly, an alkyl group could not function as a stable bridging group as required for the second aryl ring in II. In addition, the intermediacy of III fits very nicely with the results obtained for the unsymmetrical triaryl phosphates in which the rings bearing electron donating groups selectively couple. Additional work on the scope and mechanism of phosphate ester photoreactions is currently in progress.

(11) R. A. Finnegan and J. A. Matson, results to be published shortly. Diaryl alkyl phosphates, however, do give the biaryl on photolysis and we are studying this reaction as a potentially convenient photo-deblocking step in monoalkylphosphoric acid synthesis.

(12) This article was prepared while the senior author was Guest Professor at the Institut für Pharmazeutische Arzneimittellehre der Universität München, and he wishes to thank the Directors and their colleagues for their hospitality during this period.

R. A. Finnegan,*¹² J. A. Matson

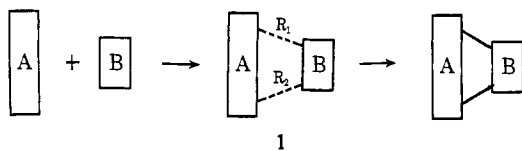
Department of Medicinal Chemistry, School of Pharmacy
State University of New York at Buffalo
Buffalo, New York 14214

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On the Existence of Symmetric Transition States for Cycloaddition Reactions

Sir:

A cycloaddition is a bimolecular reaction in which two (or more) bonds are formed. For cases in which the two bonds are equivalent (of equal length and type) in the cycloadduct, the question often arises as to whether or not these bonds are equivalent in the transition state as well. Is the transition state symmetric?



Let us assume that there exist symmetry elements such as a C_2 axis and/or a mirror plane which relate these bonds to one another in both the reactant (two isolated yet properly oriented molecules A and B in 1) and product, and let us consider only geometry variations between reactant and product which preserve this symmetry. If there is a potential energy barrier to the reaction, then it follows that there will be at least one intermediate geometry which is a point of zero potential energy gradient within this symmetry (a stationary point) and which has a totally symmetric direction of negative curvature (the decomposition direction). Moreover, this point must also be a stationary point on the complete potential energy surface since the potential energy gradient is totally symmetric.¹ Such a structure is our candidate for the symmetric transition state. For the cycloaddition reaction the direction of negative curvature will generally have a large contribution from the symmetric stretching motion of the two bonds R_1 and R_2 . It is therefore entirely reasonable to assume that the potential energy will decrease if the two bonds are simultaneously stretched (or shrunk) from their value at this stationary point.

Let us now inquire whether or not such a symmetric point is in fact a transition state, irrespective of its being

(1) J. W. McIver, Jr., and A. Komornicki, *Chem. Phys. Lett.*, **10**, 303 (1971).

“allowed” or “forbidden” by the Woodward–Hoffmann rules.² Murrell and Laidler have shown that a transition state must be a stationary point which has one and only one independent direction of negative curvature.³ In other words, the force constant matrix at the transition state must have a single negative eigenvalue. If we assume that the two bond lengths R_1 and R_2 in 1 are the only degrees of freedom of importance here, then the force constant matrix can be represented as a 2×2 with diagonal elements $K = \partial^2 E / \partial R_1^2 = \partial^2 E / \partial R_2^2$ for the bond stretching force constants and $K' = \partial^2 E / \partial R_1 \partial R_2$ for the interaction constant. The eigenvalues of this matrix are $K + K'$ for the symmetric direction and $K - K'$ for the nonsymmetric direction. If $K + K'$ is negative, as in the symmetric stationary point for the cycloaddition, then $K - K'$ will also be negative provided that $|K'| < |K|$. The eigenvalues of the 2×2 force constant matrix are upper bounds on the lowest two eigenvalues of the complete force constant matrix⁴ so that if $|K'| < |K|$, then the complete force constant matrix must have at least two negative eigenvalues. If this is true for each symmetric stationary point, then the transition state for the cycloaddition will be nonsymmetric.

Although it is true that interaction force constants are generally much smaller in magnitude than the corresponding stretching force constants in stable molecules, there is no reason to suppose that this will also be the case at other stationary points of the potential energy.⁵ It seems reasonable, however, that the magnitude of K' will decrease as the number of intervening bonds in A and B increase, whereas the stretching constant K would be expected to be roughly independent of the distance between R_1 and R_2 . Thus for $n + m$ cycloadditions, the likelihood of the transition state being nonsymmetric will increase as n and m increase.

To shed some quantitative light on this matter, we have calculated the geometries and force constants of four such symmetric points for cycloaddition reactions on MINDO/2⁶ potential surfaces using a previously described method⁷ of locating and identifying transition states: a “forbidden” (C_{2v} symmetry) structure for the addition of methylene to ethylene, an “allowed” (C_2 symmetry) and a “forbidden” (D_{2h} symmetry) structure for the dimerization of ethylene, and an “allowed” (C_s symmetry) structure for the ethylene and butadiene Diels–Alder reaction. The details will be given in a full paper. The most important result is that, in every case, the force constant matrix had two (or more) negative eigenvalues: one corresponding to the symmetric stretch of the two bonds being formed and the other

(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(3) J. N. Murrell and K. J. Laidler, *Trans. Faraday Soc.*, **64**, 371 (1968).

(4) This can be proved along the same lines as the analogous theorem for configuration interaction calculations of electronic states: cf. J. K. L. MacDonald, *Phys. Rev.*, **43**, 830 (1933).

(5) It is not the case, in fact, in the linear H_2 transition state. Here, the decomposition direction is asymmetric and the condition $|K'| < |K|$ gives rise to a “well at the top of the pass” which was found in earlier semiempirical studies and some more recent *ab initio* calculations [e.g., H. Conroy and B. L. Bruner, *J. Chem. Phys.*, **42**, 4047 (1965)]. However, more accurate calculations reveal that this structure is a saddle-point with $|K'| > |K|$ [H. Conroy and B. L. Bruner, *ibid.*, **47**, 921 (1967)].

(6) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 3854 (1970).

(7) J. W. McIver, Jr., and A. Komornicki, *ibid.*, **94**, 2625 (1972).

to the nonsymmetric stretch. The fact that this was the case for the addition of methylene to ethylene is somewhat surprising since here one might expect a large interaction constant due to the two bonds being attached to a common atom. These results, together with the discussion of the previous paragraph, indicate that, in general, transition states for cycloaddition reactions will very likely be nonsymmetric.

Finally, it is worth remarking that although transition states for cycloadditions may be nonsymmetric, this does not necessarily mean that these reactions will proceed *via* a nonconcerted (stepwise) mechanism. This can only be determined by locating the true transition states and examining the force constants.

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James W. McIver, Jr.
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214
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Synthesis of *trans*-Bicyclo[4.1.0]heptanes¹

Sir:

Since the first synthesis of a *trans*-bicyclo[*n*.1.0]alkane (1)² a considerable number of reports have appeared on the syntheses³⁻¹⁰ and reactions¹¹⁻¹⁴ of *trans*-bicyclo[6.1.0]nonanes and *trans*-bicyclo[5.1.0]octanes and their derivatives. The *trans*-bicyclo[*n*.1.0]alkanes in addition to the angle strain that is common to all cyclopropanes have a torque or twist on the zero bridge if the size of the *n* bridge is sufficiently small.¹⁵ From the reports that have appeared¹¹⁻¹⁴ the enhanced reactivity can be detected when *n* = 5 but should be much more obvious if *n* were reduced to 4.

We wish to report that we have synthesized *trans*-bicyclo[4.1.0]heptan-2-one (2) and *trans*-bicyclo[4.1.0]-

(1) Financial support from National Science Foundation Grant No. GP 15334 and an instrument grant to the Department of Chemistry for the purchase of an XL-100-15 nmr spectrometer is gratefully acknowledged. For the first paper in this series see J. V. Paukstelis and Jar-lin Kao, *Tetrahedron Lett.*, 3691 (1970).

(2) A. C. Cope and J. K. Heckt, *J. Amer. Chem. Soc.*, **85**, 1780 (1963).

(3) E. J. Corey and J. I. Schulman, *Tetrahedron Lett.*, 3655 (1968).

(4) G. Moshuk, G. Petrowski, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 2179 (1968).

(5) C. H. DePuy and J. L. Marshall, *J. Org. Chem.*, **33**, 3326 (1968).

(6) P. G. Gassman, F. J. Williams, and J. Seter, *J. Amer. Chem. Soc.*, **90**, 6893 (1968).

(7) W. Kirmse and Ch. Hase, *Angew. Chem., Int. Ed. Engl.*, **7**, 891 (1968).

(8) A. J. Ashe, III, *Tetrahedron Lett.*, 523 (1969).

(9) K. B. Wiberg and A. de Meijere, *ibid.*, 519 (1969).

(10) J. A. Deyrup, M. Betkouski, W. Szabo, M. Mathew, and G. J. Palenik, *J. Amer. Chem. Soc.*, **94**, 2147 (1972).

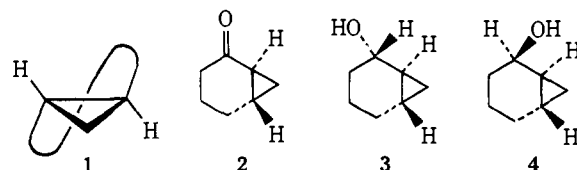
(11) K. B. Wiberg and T. Nakahira, *ibid.*, **93**, 2704 (1971).

(12) P. G. Gassman and F. J. Williams, *ibid.*, **93**, 2704 (1971).

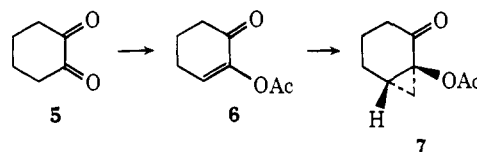
(13) P. G. Gassman, J. Seter, and F. J. Williams, *ibid.*, **93**, 1673 (1971).

(14) P. G. Gassman, E. A. Williams, and F. J. Williams, *ibid.*, **93**, 5199 (1971).

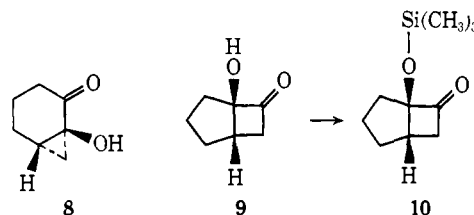
(15) P. G. Gassman, *Chem. Commun.*, 793 (1967).



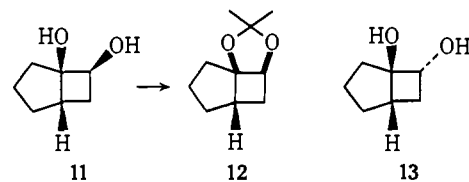
heptan-*trans*- and -*cis*-2-ols (3 and 4), the first examples of a *trans*-bicyclo[4.1.0]heptane. The synthesis was carried out starting with cyclohexane-1,2-dione (5) which on treatment with acetic anhydride gave the enol acetate 6 in 90% yield.¹⁶ Treatment of 6 under Simmons-Smith conditions gave the acetoxy ketone 7, mp 69–70°, in 20% yield.^{17,18} Reaction of 7 with



sodium methoxide at room temperature for 3 min resulted in the alcoholysis of the acetate and partial rearrangement (89%) to give a mixture of ketols 8 and 9 which had $\nu_{\text{max}}^{\text{CCl}_4}$ at 1785 and 1695 cm^{-1} .¹⁹ The mixture on reaction with trimethylchlorosilane gave in 89% yield an ether (90% purity) which was further purified by spinning band distillation (bp 93° (16 mm)) and was identified from its carbonyl stretching (CCl_4) at 1780 cm^{-1} as 10.²⁰



Reduction of 10 with lithium tri-*tert*-butoxyaluminum hydride gives two diols in 88% yield. After separation of the two diols by column chromatography on alumina the major product 11 could be converted in 79% yield to the acetonide 12 on treatment with 2,2-dimethoxypropane²¹ establishing that 11 was a *cis* diol and that the minor product, an isomer of 11, must be the *trans* diol 13.²⁰



(16) K. W. Rosenmund and G. Kositzke, *Chem. Ber.*, **92**, 486 (1959).

(17) R. J. Rawson and I. T. Harrison, *J. Org. Chem.*, **35**, 2057 (1970).

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(19) J. V. Paukstelis and D. N. Stephens, *Tetrahedron Lett.*, 3549 (1971).

(20) The alternate product, 1-trimethylsilyloxybicyclo[3.1.1]heptan-6-one, which might have a carbonyl adsorption at about the same frequency was eliminated by oxidation of 11 to 2-cyclopentanoneacetic acid and comparison of its methyl ester to an authentic sample prepared according to R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 935 (1934), and E. J. Corey and R. L. Carney, *J. Amer. Chem. Soc.*, **93**, 7318 (1971).

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