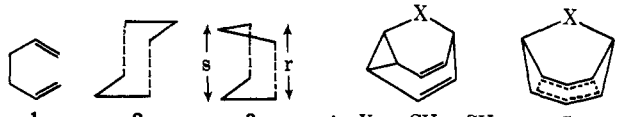
Communications to the Editor

Cope Rearrangements in the Bullvalene Series[1]

Sir:

The Cope rearrangements of acyclic 1,5-hexadienes (**1**) are known[2] to take place preferentially *via* chair transition states **2**, the energy of the boat isomer **3** being, in a typical case,[2] at least 5.7 kcal/mol greater than that of **2**. On the other hand, the analogous rearrangements of bullvalene (**4a**), barbaralene (**4b**), and semibullvalene (**4c**) take place with extreme facility, although they must proceed through transition states **5** that are derivatives of **3**.

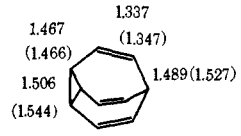


1 **2** **3** **4a**, X = -CH=CH- **b**, X = $-CH_2-$ **c**, X = — **5**

Recent work in these laboratories has led to the development of a semiempirical SCF–MO treatment (MINDO/2[3]) which seems to give good estimates of heats of atomization and activation energies.[4] Application[4a] of this to the Cope rearrangement of **1** not only reproduced the difference in energy between the transition states **2** and **3**, but also the difference in energy between chair transition states **3** with a methyl substituent in the axial or equatorial positions. The calculated absolute activation energy for the reaction was, however, low (24 instead of 35 kcal/mol), due to a known failing of MINDO/2 at its present stage of development, *i.e.*, a tendency to overestimate the stability of cyclic compounds.

In the case of the bullvalene series **4**, the geometries of the transition states **5** must be very similar to those of the reactants, due to their rigid polycyclic structures. It therefore seemed likely that MINDO/2 could be applied even more successfully to their rearrangements since errors due to the presence of rings should cancel.

The geometries of the parent molecules **4** were calculated by minimizing the total energy, using a computer program (SIMPLEX) written by Brown.[4a] That for bullvalene is given below, together with (in parentheses) the electron-diffraction values of Andersen and Marstrander.[5] According to MINDO/2, the bonds in the cyclopropane ring should have almost the same lengths as those in cyclopropane[3b] (calcd, 1.496; obsd, 1.51 Å) and the single bonds in the C=CC C=C units lengths typical of sp^2–sp^3 C–C bonds (calcd[3b] for $PhCH_3$, 1.497; obsd, 1.51 Å). According to Andersen and Marstrander, these bonds are unaccountably lengthened by 0.034 and 0.017 Å, respectively.



As in the case of the Cope rearrangement of biallyl,[4a] it was assumed that the transition states **5** have two planes of symmetry passing through X. The energies calculated on this basis are compared with the available experimental evidence in Table I. The calculated distances between the terminal atoms of the allyl units in the transition states (*r* in **3**) are also listed, together with values for rearrangement of **1** *via* the boat transition state **3**.

Table I

Compound	Activation energy, kcal/mol Calcd	Activation energy, kcal/mol Obsd	Interatomic distances, Å *r*	Interatomic distances, Å *s*
Biallyl (**1**)	30.6	41.2[a]	1.628	2.577
Bullvalene (**4a**)	11.3	11.8;[b] 12.8[c]	1.626	2.808
Barbaralene (**4b**)	5.9	8.6[d]	1.720	2.680
Semibullvalene (**4c**)	2.3		1.752	2.806

[a] Calculated on the assumption that a minor reaction product was correctly identified; Doering and Roth[2] cautiously quote the difference in energy between **2** and **3** as "greater than 5.7 kcal/mole," in case of a misidentification. [b] M. Saunders, *Tetrahedron Lett.*, 1699 (1963). [c] A. Allerhand and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **87**, 4092 (1965). [d] W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).

Evidently our calculations reproduce in a very satisfactory way the great increase in rate in passing from **1** to the rigid derivatives **4**. As anticipated, the absolute activation energies for **4** are also in much better agreement with experiment. The calculations correctly predict a rapid decrease in activation energy with decreasing size of the group X; in the limit when X vanishes (*i.e.*, semibullvalene (**4c**)), the calculated activation energy is only 2.3 kcal/mol. The nmr spectrum of **4c** indicates that rearrangement is still rapid on the nmr time scale at −110°.[6]

The great increase in the rate of rearrangement on passing from **1** to **4** is probably due mainly to the relief of ring strain in going from **4** to **5**. However, an additional factor is the decrease in the antibonding interaction[7] between the central atoms of the allyl moieties along the series, due to an increase in the distance *s*. This interaction is responsible[4a] for the relative instability of the boat transition state **3**. Note also the increase in the distance *r* along the series;

(1) This work was supported by the Air Force Office of Scientific Research through Contract No. F44620-70-C-0121.

(2) W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

(3) (a) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970); (b) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

(4) (a) A. Brown, M. J. S. Dewar, and W. W. Schoeller, *ibid.*, **92**, 5516 (1970); (b) M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **91**, 7521 (1969); (c) M. J. S. Dewar, E. Haselbach, and M. Shanshal, *ibid.*, **92**, 3505 (1970).

(5) B. Andersen and A. Marstrander, *Acta Chem. Scand.*, **21**, 1676 (1967).

(6) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **91**, 3316 (1969).

(7) See M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969; *Angew. Chem.*, in press.

as the overall activation energy decreases, the transition state approximates more and more closely a pair of uncoupled allyl radicals.

The properties[6] of semibullvalene (**4c**) have led to the suggestion[6] that this might be the first case of a fluxional organic molecule where the mesovalent intermediate is actually the stable form. Indeed, EH calculations predict this to be so for **4c**.[8] Our results make this very unlikely, as also does[6] the uv spectrum of **4c**, since while the calculated activation energy for **4c** is very low (2.3 kcal/mol), the MINDO/2 values for Cope rearrangements in general seem to be systematically too small. However, one might expect suitable substituents to stabilize the transition states **5** relative to the classical structures **4**; if so, a suitable derivative of **4c** might well prove the first example of such a mesovalent molecule.

The choice of "suitable substituents" seems an ideal problem for MINDO/2, given that it seems to account so well for the course of reactions of this type and given that the calculations can be carried out much more quickly, and at much less expense, than the synthesis of the compounds in question.

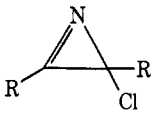
(8) D. S. Wulfman, personal communication.
(9) DAAD (German Academic Exchange Service), 532 Bad Godesberg, West Germany.

Michael J. S. Dewar,* Wolfgang W. Schoeller[9]
Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712
Received November 14, 1970

3-Chloro-1-azirines. Photochemical Formation and Thermal Isomerization[1]

Sir:

3-Chloro-1-azirines (**1**) are potential precursors to the theoretically interesting 2π-electron azacyclopropenyl (azirinium) ion **2**.[2] We wish to report a con-

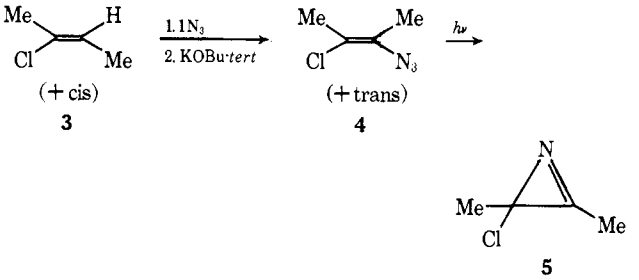


1

2

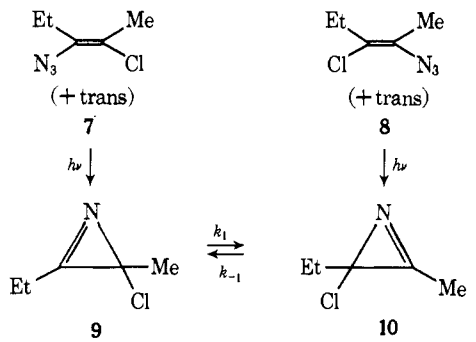
venient photochemical synthesis and some properties including the facile thermal isomerization of dialkyl derivatives of this previously unknown system.[3]

Addition of iodine azide (IN_3) to a mixture of *cis*- and *trans*-2-chloro-2-butene (**3**) followed by the elimination of hydrogen iodide with potassium *tert*-butoxide yielded a mixture of *cis*- and *trans*-2-azido-3-chloro-2-butene (**4**):[4] spectral data, ir (ν_{max}, neat) 2110, 1655 cm^{-1}; nmr (δ, neat) 1.96–2.23 (multiplet). Photolysis



at 3500 Å afforded 2,3-dimethyl-3-chloro-1-azirine (**5**),[5] isolated as a colorless liquid by preparative gas chromatography:[6] spectral data, ir (ν_{max}, CCl_4) 1745 cm^{-1}; nmr (CD_3CN, δ) 1.87 (3 H, s), 2.57 (3 H, s); mass spectrum *m/e* 105, 103, 68 (dimethylazirinium ion). Chemical evidence was provided by aqueous hydrolysis of **5** to biacetyl and by conversion of **5** with methanol to 3-methoxy-2,3-dimethyl-1-azirine (**6**). The nmr spectrum of **6** (CD_3CN) exhibited three singlets of equal intensity at δ 1.57, 2.66, and 3.43. As expected, hydrolysis of **6** with 5% aqueous hydrochloric acid afforded biacetyl.

In order to investigate the possible interconversion of the 3-chloro-1-azirine isomers **9** and **10**,[7] the requisite chlorovinyl azide precursors **7** (cis + trans) and **8** (cis + trans) were synthesized from 2-chloro-2-pentene (cis + trans) and 3-chloro-2-pentene (cis + trans), respectively: spectral data, ir (**7**) (ν_{max}, CCl_4) 2105,



1650 cm^{-1}; (**8**) 2105, 1655 cm^{-1}. The nmr spectra of **7** and **8** each showed absorption for two sets of methyl and ethyl groups. The regiospecificity[8] of the IN_3 addition to the above chloropentenes was established by conversion of **7** and **8** to 3-pentanone and 2-pentanone, respectively, by treatment with zinc and acetic acid.[9] Photolysis of either **7** or **8** at room temperature produced an equilibrium mixture of 2-ethyl-3-methyl-3-chloro-1-azirine (**9**) and 2-methyl-3-ethyl-3-chloro-1-azirine (**10**):[10] spectral data, ir (**9** + **10**) (ν_{max}, CCl_4) 1745 cm^{-1}; nmr (**9**) (CD_3NO_2, δ) 1.29 (3 H, t), 1.83 (3 H, s), 2.89 (2 H, q); (**10**) 0.88 (3 H, t), 2.14 (2 H, q), 2.53 (3 H, s); mass spectrum (**9** + **10**) *m/e* 119, 117, 82 (methylethylazirinium ion);

(1) This work was presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 13–18, 1970, Abstracts, ORGN-067.
(2) Simple Hückel LCAO–MO calculations indicate a delocalization energy of 1.58 β for the parent system: G. R. Harvey and K. W. Ratts, *J. Org. Chem.*, **31**, 3907 (1966), footnote 13.
(3) Perfluoroazirines have been prepared: C. S. Cleaver and C. G. Krespan, *J. Amer. Chem. Soc.*, **87**, 3716 (1965); R. E. Banks and G. J. Moore, *J. Chem. Soc. C*, 2304 (1966).
(4) The elegant procedure of Hassner was employed: (a) F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, **89**, 2077 (1967); (b) A. Hassner and F. W. Fowler, *J. Org. Chem.*, **33**, 2686 (1968); (c) A. Hassner, F. P. Boerwinkle, and A. B. Levy, *J. Amer. Chem. Soc.*, **92**, 4879 (1970).
(5) (a) A. Hassner and F. W. Fowler, *Tetrahedron Lett.*, 1545 (1967); (b) A. Hassner and F. W. Fowler, *J. Amer. Chem. Soc.*, **90**, 2869 (1968).
(6) A 0.25 in. × 10 ft column packed with 15% SE-30 Chromosorb W DMCS acid-washed 80–100 mesh was employed for preparative work.
(7) The isomerization of **5** would be degenerate and therefore invisible by nmr if the rate were slow relative to the nmr time scale.
(8) A. Hassner, *J. Org. Chem.*, **33**, 2684 (1968).
(9) A. Hassner, R. J. Isbister, and A. Friederang, *Tetrahedron Lett.*, 2939 (1969).
(10) Azirines **9** and **10** like **5** can be isolated as a colorless liquid by preparative gas chromatography.[6] However, due to their instability in the neat form these azirines are best handled in solution.