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.

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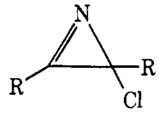
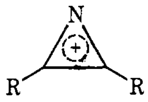
3-Chloro-1-azirines. Photochemical Formation and Thermal Isomerization[1]

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

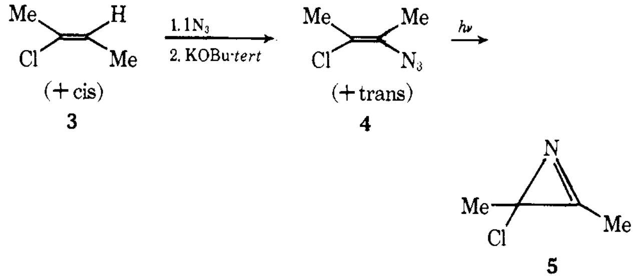


1

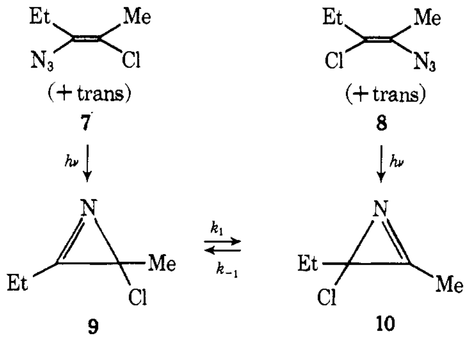


2

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);



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(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 $1.58\,\beta$ 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.

K_{eq} (k_1/k_{-1}) = 1.88 ± 0.04 (CD_3CN), 1.61 ± 0.04 (CH_2Cl_2), 1.55 ± 0.02 (CCl_4).[11] In analogy with **5**, azirines **9** and **10** afforded 2,3-pentanedione and a mixture of methoxyazirines upon treatment with water and methanol, respectively.

The thermal nature of the isomerization of the initially formed azirines **9** and **10** was revealed by conducting the photolyses at low temperature. Irradiation of **7** at −40° afforded exclusively azirine **9** by nmr. Similarly, **8** gave exclusively **10**. Warming solutions of pure **9** and **10** in the nmr probe resulted in the appearance and growth of new peaks corresponding to **10** and **9**, respectively. In a given solvent, solutions of pure **9** and **10** exhibited identical nmr spectra after thermal equilibration.

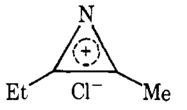
The kinetic data for the isomerizations of **9** and **10** are summarized in Table I;[12] activation parameters (CH_2Cl_2) are:[13] forward process (**9** → **10** (k_1)), E_a = 15 kcal/mol, $\Delta S^{\ddagger}$ (−15°) = −15 eu; reverse process (**10** → **9** (k_{-1})), E_a = 15 kcal/mol, $\Delta S^{\ddagger}$ (−15°) = −16 eu.

Table I. Kinetic Data for the Isomerization $\mathbf{9} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathbf{10}$

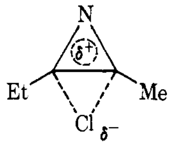
Solvent	Temp, °C	$k_1 \times 10^4$, sec^{-1}	$k_{-1} \times 10^4$, sec^{-1}	k_1, rel
CCl_4	−10	0.180[a]	0.116[a]	1
CH_2Cl_2	−10	2.13[b]	1.33[b]	12
CD_3CN	−10	14.2[b]	7.54[b]	79

[a] Extrapolated from rate data at +22 and +33°. [b] Average value of *k* calculated from forward and reverse results.

The dependence of rate on solvent polarity (see Table I) clearly establishes the polar nature of the transition state and is consistent with the intermediacy of an azacyclopropenyl ion–chloride ion pair **11** in the isomerizations of **9** and **10**.[14–16] However, an alternative mechanism involving polar bridged transition state **12** cannot be excluded.



11



12

Reaction of **5** or **9** and **10** with silver salts results in the immediate precipitation of silver chloride but thus far work-up has afforded only intractable material.[17,18]

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for partial support of this research. Helpful discussions with Professors J. O. Edwards, R. G. Lawler, and L. A. Spurlock are gratefully acknowledged. Finally we thank Mr. J. G. Henkel for the use of his computer program.

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[11] Determined by nmr integration; errors represent standard deviations.

[12] Obtained by nmr by following the change in intensity of the methyl singlet of **9** and **10** with time.

[13] Determined from Arrhenius plots of rate data on forward and reverse processes at four different temperatures, −18, −10, 0, and +15°.

[14] The solvolysis of 1,2-diaryl-3,3-dichloroaziridines involves a 1,2-intramolecular chlorine migration *via* an aziridinyl cation–chloride ion pair intermediate: R. E. Brooks, J. O. Edwards, G. Levey, and F. Smyth, *Tetrahedron*, **22**, 1279 (1966). See also, J. A. Deyrup and R. B. Greenwald, *J. Amer. Chem. Soc.*, **87**, 4538 (1965). Similarly, the thermal rearrangement of 2-chloro epoxides to 2-chloro ketones involves a 1,2-intramolecular chlorine shift: R. N. McDonald and R. N. Steppel, *ibid.*, **92**, 5664 (1970), and previous papers in the series.

[15] The degenerate isomerization of 3-chlorocyclopropene, a process which is believed to proceed *via* the cyclopropenyl cation, is not only orders of magnitude faster in similar solvents but also appears to exhibit a much larger rate dependence on solvent polarity: R. Breslow, G. Ryan, and J. T. Groves, *ibid.*, **92**, 988 (1970).

[16] Mechanisms involving elimination–addition or addition–elimination of HCl were excluded on the basis of the fact that these processes would not exhibit simple first-order kinetics. Control experiments in which HCl was added to pure solutions of **9** and **10** afforded good first-order kinetic plots and a small decrease in the first-order rate constants k_1 and k_{-1} was observed.

[17] A reported attempt by Hassner to prepare diphenylazacyclopropenyl iodide was likewise unsuccessful.[4a]

[18] Salts of the cyclopropenyl cation have been prepared from 3-chlorocyclopropene: R. Breslow and J. T. Groves, *J. Amer. Chem. Soc.*, **92**, 984 (1970).

[19] Petroleum Research Fund Graduate Fellow, 1969–1970.

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The Mechanism of the Silver-Catalyzed Reaction of Grignard Reagents with Alkyl Halides

Sir:

The coupling of alkyl groups by the reaction of Grignard reagents and alkyl halides (eq 1) is induced by

$$R'MgX + R\text{-}X \xrightarrow{MX_n} R\text{-}R' + MgX_2 \qquad (1)$$

a variety of transition metal halides (MX_n).[1] The mechanism of this facile transformation is of interest for catalytic processes generally, and has been the subject of extensive investigations.[2] The multiplicity of reactions possible with various metal catalysts, however, has precluded a general and systematic description of the elementary steps involved in the catalytic sequences. Thus, the roles of the metal catalysts, the reactions of the organometallic intermediates, and the presence of transient alkyl radicals have remained unclear.

We examined initially the *stoichiometric* reduction of transition metal salts by Grignard reagents, and then studied the *catalytic* coupling of Grignard reagents with alkyl halides. Thus, Grignard reagents in tetrahydrofuran (THF) solution reacted with stoichiometric amounts of silver(I) salts (halides, acetate, perchlorate) on mixing at 2° according to eq 2.[3,4] Similarly, when

$$RMgX + AgY \longrightarrow RAg + MgXY \qquad (2a)$$

$$2RAg \longrightarrow R\text{-}R + 2Ag \qquad (2b)$$

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[1] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Englewood Cliffs, N. J., 1954, p 122.

[2] M. H. Abraham and M. J. Hogarth, *J. Organometal. Chem.*, **12**, 1, 497 (1968); D. I. Davies, J. N. Done, and D. H. Hey, *J. Chem. Soc. C*, 1392, 2021, 2506 (1969); W. B. Smith, *J. Org. Chem.*, **26**, 4206 (1961); L. H. Slaugh, *J. Amer. Chem. Soc.*, **83**, 2734 (1961); G. Costa, G. Mestroni, and G. Boscarato, *Ric. Sci.*, **7**, 315 (1964); R. O. C. Norman and W. A. Walters, *J. Chem. Soc.*, 950 (1957).

[3] (a) *Cf.* J. H. Gardner, *et al.*, *J. Amer. Chem. Soc.*, **51**, 3375 (1929); **59**, 2583 (1937); **61**, 2551 (1939); *J. Org. Chem.*, **5**, 61, 126 (1940); (b) *cf.* also C. E. H. Bawn, *et al.*, *J. Chem. Soc.*, 3923 (1960); F. Glocking and D. Kinston, *ibid.*, 3001 (1959); and H. C. Brown, *et al.*, *J. Amer. Chem. Soc.*, **83**, 1001, 1002 (1961).

[4] (a) Hereafter solvation by THF will not be explicitly included. (b) Organometals are generally more stable in THF than in diethyl ether. (c) K. Wada, M. Tamura, and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 6656 (1970).