$$C_n + M \longrightarrow C + M \qquad (5)$$

$$C_n \longrightarrow D \qquad (6)$$

$$D_m{}^1 \longrightarrow D \qquad (7)$$

With the usual steady-state assumptions, it can be derived that

$$1/\Phi_C = \frac{k_3k_6 + (k_4 + k_7)k_5}{k_4k_5} + \frac{k_6(k_4 + k_7)}{k_4k_5}[M^{-1}] + \frac{k_3}{k_4}[M] \qquad (8)$$

The Stern–Volmer plot would hence have a minimum, as the data in Table I actually display. At the minimum $k_4 = (k_3k_5[M]^2/k_6) - k_7$, which makes it possible to calculate k_4, the rate constant for the valence isomerization process, if k_3, k_5, k_6, and k_7 are known. The first two were calculated from simple kinetic theory on the assumption that every collision between $D_m{}^1$ or C_n and M will lead to deactivation.[7] k_6 was calculated from the known[4] parameters for the thermal decomposition of 1,3,3-trimethylcyclobutene. This led to a value for k_6 of $10^{8.92}$ sec^{-1}.[8] k_7 was taken to be $19k_4$ since the quantum yield for reaction 1 had a maximum value of 0.05. By inserting these values, it was calculated that

$$k_4 = 2 \times 10^9 \text{ sec}^{-1}$$

The effects that the various assumptions that were made in this calculation had on the accuracy of k_4 will be as follows. (i) In setting $k_7 = 19k_4$, there was an implicit assumption that $k_7 >> k_3[M]$. Errors created by this simplification will tend to underestimate the value for k_4. However, since the maximum for Φ_C is only a factor of 2 smaller than the maximum quantum yield realized for the valence isomerization of a linear 1,3-diene, *i.e.*, 2,3-dimethyl-1,3-butadiene in solution,[1a] it is reasonable to assume that the deactivation step 3 is an insignificant route for the loss of $D_m{}^1$ at that pressure. (ii) In the calculation of k_6, the principal uncertainty is in the magnitude of the vibrational energy possessed by the activated molecule C_n. The value of 101 kcal/mol that was used must represent the maximum possible. If this value is less, the net result will be to increase the magnitude of k_4. For example, if the activation energy possessed by C_n is only 96 kcal/mol, k_4 will be increased by a factor of 2.2. (iii) The assumed rate of k_5 will lead to an overestimate in the value of k_4[7] and partially compensate for the error from ii. The value of k_4 is probably a minimum, accurate to wihin a factor of 5.

The rate of radiative decay for the diene that can be calculated from its absorption spectrum is of the order of, and smaller than, 10^9 sec^{-1}. The value of k_4 given above is hence a reasonable one as linear conjugated dienes have not been observed to fluoresce[9] and reactions from the excited state would be expected to be faster than the rate of radiative decay.

A remarkable implication of this result is that dienes such as the one in this study, although sterically hindered by methyl groups at the C_4 position, can cyclize with a quantum yield comparable to that of 2,3-dimethyl-1,3-butadiene, *provided activation energy is available to overcome some internal energy barrier.* This barrier may be the rotation of the *cis*-methyl group on C_4, but this does not seem likely in view of other data.[1,2] A more attractive possibility is that some rotation around the C_2–C_3 bond does occur in the excited singlet state of this diene. A comparison of the quantum yields for ring closure as a function of pressure in other 1,3-dienes may be of considerable interest.

We intend to use the photochemical closure of linear 1,3-dienes as a reference and measure rates of the reactions such as cyclopropene formation and dimerization relative to it.

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(7) This assumption is probably wholly valid in estimating k_3, as the vibrational energy possessed by $D_m{}^1$ is less than 15 kcal/mol. Since C_n may have considerably more vibrational energy (see ref 8), the estimate of k_5 may be high by a factor of 2–4. An average collision diameter of 4 Å was used in both calculations.

(8) The photon used in the reaction corresponded to 112 kcal/mol. The conversion of a linear 1,3-diene to a cyclobutene can be taken to be endothermic by 11 kcal/mol [K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, 90, 3305 (1968)], so that C_n may possess 101 kcal/mol of vibrational energy. k_6 was calculated from the expression $k_6 = A(1 - E/E^*)^{s-1}$, where log A = 13.9, E = 37.0,[4] and S was set equal to 26.

(9) R. Srinivasan, *Advan. Photochem.*, **4**, 115 (1966).

Electronic Effects on the Ring Opening of Cyclopropylidenes

Sir:

Some years ago[1] we reported that the ring opening of diphenylcyclopropylidene gave rise to optically active 1,3-diphenylallene.[2] It was further pointed out that the cause for the retention of dissymmetry is dominated (and probably limited to) a steric effect.[3]

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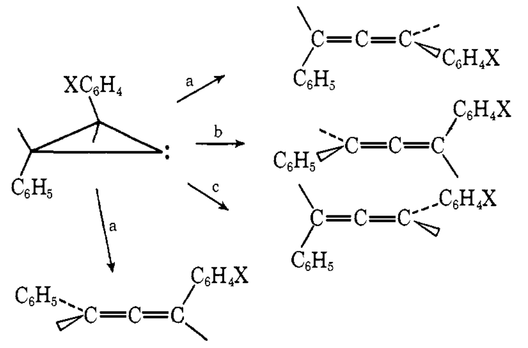
(1) *Cf.* J. M. Walbrick, J. W. Wilson, Jr., and W. M. Jones, *J. Amer. Chem. Soc.*, **90**, 2895 (1968); and W. M. Jones and J. W. Wilson, Jr., *Tetrahedron Lett.*, 1587 (1965).

(2) Ring opening of a cyclopropylidene (or its carbenoid) to give an allene was first reported by W. von E. Doering and P. M. Laflamme (*Tetrahedron*, **2**, 75 (1958)). For more recent examples of this ring opening—a number of which occur from free carbenes as well as carbenoids—see: W. M. Jones and J. M. Walbrick, *J. Org. Chem.*, **34**, 2217 (1969); L. Skattebol, *Tetrahedron Lett.*, 2175 (1965); P. S. Skell and R. R. Engel, *J. Amer. Chem. Soc.*, **89**, 2912 (1967); K. D. Bayes, *ibid.*, **85**, 1730 (1963); M. Marshall, R. Wolfgang, and C. McKay, *Tetrahedron Lett.*, 2033 (1963); L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, **83**, 3159 (1961); E. T. Marquis and P. D. Gardner, *Tetrahedron Lett.*, 2793 (1966); J. Maier, *ibid.*, 3603 (1965); H. Ward, R. G. Lawler, and H. Y. Loken, *J. Amer. Chem. Soc.*, **90**, 7359 (1968), and references cited in the above.

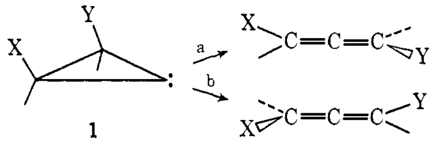
(3) In fact, it is difficult to visualize an electronic effect in any way influencing the retention of dissymmetry in the opening of a *trans*-disubstituted cyclopropylidene. Thus, placing a substituent on a phenyl ring that has no effect on its steric bulk may be expected to promote or retard its rotation (due to electronic effects) relative to the other ring (for example, path "a" over path "b"), but this would leave the optical purity of the product allene unaffected. Only if the substituent changed the amount of product arising from path "c" plus path "d" would any effect on optical purity be observed, and there is no obvious way an electronic effect would cause this.



In this communication we would like to report a clear demonstration of an electronic effect influencing the retention of dissymmetry in the opening of optically active cyclopropylidenes.

Dissymmetry in a cyclopropylidene can be achieved by either trans 2,3 disubstitution[1] or unsymmetrical cis 2,3 disubstitution. Whereas changes in the electronic nature of the substituents in the trans-disubstituted cyclopropane should have little, if any, effect on the retention of dissymmetry,[3] the opposite is true in the cis case. In fact, if the two substituents in an unsymmetrically disubstituted *cis*-cyclopropylidene have identical size, steric bulk is immaterial and any dissymmetry in the product allene *must* originate from electronic effects. In other words, if X and Y (Chart I) in optically active **1** have identical size and if ring opening were unaffected by electronic effects, then paths "a" and "b" must occur with exactly equal probability (and also the corresponding inward rotations) and, since the two paths lead to enantiomers, the product must be optically inactive. If, on the other hand, the proportion proceeding by either path were affected by the electronic nature of X or Y, then the product should be active.

Chart I

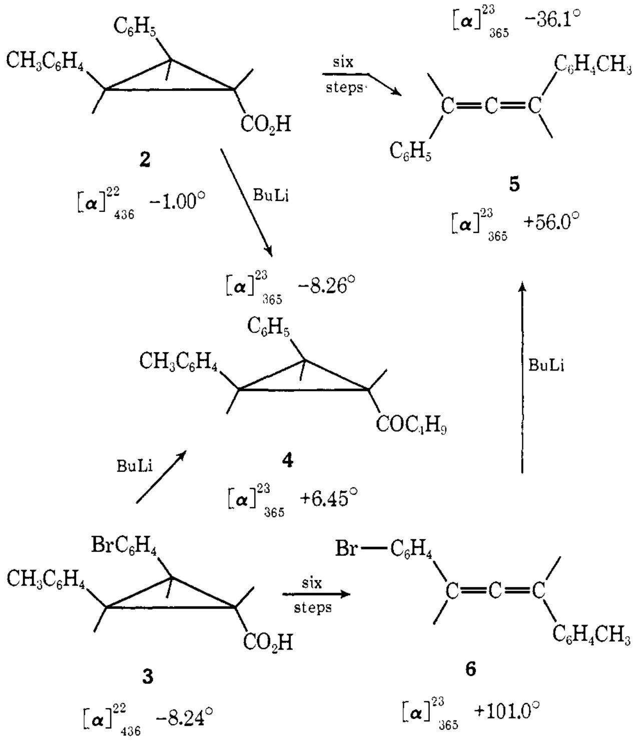


To minimize steric differences, unsymmetrical para-substituted *cis*-diarylcyclopropylidenes were generated.[4,5] Three systems were studied—*cis*-2-phenyl-3-*p*-chlorophenylcyclopropylidene (from the acid), the *p*-methyl derivative (from **2**), and the *p*-methyl-*p'*-bromocarbene (from **3**).[6] The optically active *p*-chloro-substituted cyclopropylidene for which precursors happened to be most readily available was generated first to determine if dissymmetry could be carried to the allene. From the acid showing a rotation of $[\alpha]^{22}_{436}$ $-5.73°$ there was obtained 1-phenyl-3-*p*-chlorophenylallene showing a rotation of $[\alpha]^{22}_{436}$ $+5.95°$.[7] From this result it is apparent that dissymmetry is carried to the allene although probably not very efficiently.[8]

Although para substituents should have little if any steric influence on the ring opening process, the low optical activity (and probable low optical purity)[8] motivated us to seek an unequivocal method to exclude the possibility of dissymmetry retention arising from steric effects. The method selected is summarized in Scheme I.[10]

If retention of dissymmetry resulted from a steric effect and inasmuch as bromine is larger than hydrogen, the cyclopropylidene resulting from **3**—in which a bromine has been substituted for a hydrogen—must lead to allene of either lower optical purity or reversed configuration when compared with the diphenylcyclopropylidene substituted with a methyl group only. From the results in Scheme I,[7] it is obvious that, in fact, **3** leads to an allene of higher activity and the same relative configuration as that derived from **2**—results that are opposite to those expected for a steric effect. From these results it can be concluded that the retention of dissymmetry *cannot* derive from steric effects and must reflect electronic effects in the ring-opening process, and thus prove that a substituent

Scheme I



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(4) Although it is highly likely, there is no conclusive evidence that the product arises from the free carbene. Even indirect evidence is not available since the ring opening occurs so rapidly (probably due to steric effects) that the carbene cannot be trapped. Evidence for carbene involvement in allene formation from trans-disubstituted diazocyclopropanes is relatively sound.[2]

(5) Both the generation of the carbenes from the corresponding nitrosocarbamates and syntheses of all precursors were accomplished by standard procedures.[2] Resolutions were effected by recrystallization of the ephedrine salts of the carboxylic acids from CH_2Cl_2 or CH_2Cl_2–hexane.

(6) Properties of new materials follow: *cis*-2-phenyl-3-*p*-chlorophenylcyclopropanecarboxylic acid: mp 151–153°; nmr τ -0.9 (s, 1),[7] 2.96 (m, 9), 6.90 (d, 5 Hz, 2), 7.52 (t, J = 5 Hz, 1); *m/e* 272. *Anal.* Found: C, 70.36; H, 4.85; Cl, 12.80. 1-*p*-Chlorophenyl-3-phenylallene: mp 51–53°; ir 1929, 1879 cm^{-1}; nmr τ 2.78 (m, 9), 3.48 (s, 2); *m/e* 226; instability precluded analyses. **2**: mp 119–121°; nmr τ -2.2 (s, 1), 3.08 (m, 9), 6.97 (d, J = 5 Hz, 2), 7.57 (t, J = 5 Hz, 1), 7.80 (s, 3); *m/e* 252. *Anal.* Found: C, 81.08; H, 6.43. **3**: mp 151–153°; nmr τ -1.35 (s, 1), 3.15 (m, 8), 7.02 (d, J = 5 Hz, 2), 7.68 (m, 4); *m/e* 331. *Anal.* Found: C, 61.91; H, 4.64; Br, 23.85. **4**: oil; nmr τ 3.12 (m, 9), 7.42 (m, 7), 8.74 (m, 7); *m/e* 292. *Anal.* Found: C, 86.38; H, 8.17. **5**: mp 51–52°; ir 1933 cm^{-1}; nmr 2.83 (m, 9), 3.50 (s, 1), 7.67 (s, 3); *m/e* 206; instability precluded analyses. **6**: mp 95–96°; ir 1935, 1903 cm^{-1}; nmr τ 2.78 (m, 8), 3.53 (s, 2), 7.67 (s, 3); *m/e* 285; instability precluded analyses.

(7) In all cases extreme caution was taken to avoid possible fractionation at any point. For example, from carboxylic acid to allene no intermediate was isolated. The allene was purified by column chromatography, assaying cuts by thin-layer chromatography. All allene cuts were combined and the rotation was determined. The solid residue remaining after solvent evaporation was weighed to give specific rotations and was also shown to be quite pure allene by normal spectral procedures. Allene **5** was shown to be stable to BuLi under reaction conditions.

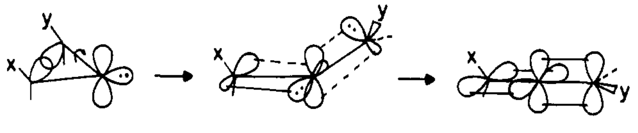
(8) Optical purities of both reactants and products are unknown. However, since optically pure 1,3-diphenylallene[1] has a rotation at 589 nm in excess of 1000° it is likely that the optical purities of the allenes reported here are low.[9]

(9) In all cases studied, starting materials were very carefully analyzed for traces of trans isomers since these are known to give allenes of high activity.

(10) In Scheme I, the structures used are for convenience only and do not connote absolute configurations.

group can promote or retard—by electronic effects—the rotation of one group relative to the other during the ring-opening process. In other words, in Scheme I, paths "a" and "b" cannot be occurring to exactly the same extent.

Preference for one path over the other (Chart I) can be rationalized as follows. Applying a correlation diagram based approach to the problem of this type of interconversion, Borden[11,12] has concluded that singlet cyclopropylidene opens by preferentially rotating only one terminal carbon. Assuming the carbene is sp^2 hybridized, then the carbon that rotates becomes the one that furnishes the pair of electrons to the carbene center. This process would certainly be expected to be sensitive to electronic effects. The question of which type of group (electron withdrawing or electron donating) promotes rotation must remain open until anticipated absolute configuration studies are completed.



Acknowledgment. The authors are grateful to the National Science Foundation for support of this work.

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(11) Private communication from W. T. Borden of Harvard University. Some of Professor Borden's results have also been discussed in H. R. Ward and E. Karafiath, *J. Amer. Chem. Soc.*, **91**, 7474 (1969). See also W. T. Borden, *Tetrahedron Lett.*, 447 (1967), for a discussion of ring opening of the triplet. We are deeply indebted to Professor Borden for communicating his results to us.

(12) The ring opening has also been treated theoretically by M. J. S. Dewar, E. Haselbach, and M. Shanshal, *J. Amer. Chem. Soc.*, **92**, 3505 (1970).

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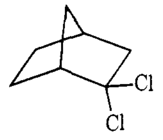
Anomalous Proton Donor Effects in Dimethylformamide

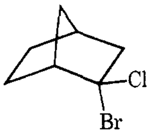
Sir:

Phenols and carboxylic acids, although largely undissociated in dimethylformamide (DMF), are nevertheless good proton donors in this solvent toward electrochemically generated radical anions of aromatic hydrocarbons and carbonyl compounds.[1] By contrast, water is known to be a rather poor proton donor toward aromatic radical anions in DMF.[2,3] Mark has suggested that the low proton-donating ability of water in DMF is due to the high degree of structure in water–DMF solutions, demonstrated, *e.g.*, by such data as the large amounts of heat evolved upon mixing water and DMF, and the substantially increased viscosity of the resulting solutions relative to the viscosities of the individual components. On the other hand, water and acetonitrile are not strongly associated, and indeed water is a much better proton donor in this solvent.[3] Likewise, methanol and DMF are not strongly associated, and methanol is a much better proton donor than water in DMF.[3] We wish to report discovery of a system in which the proton-donating ability of phenols and acetic acid is extremely low relative to water, methanol, or even tetraethylammonium ion.

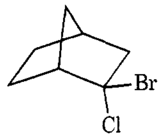
Electrochemical reduction of dihalides **1**–**3**[4] in DMF containing tetraethylammonium bromide (TEAB)[5] affords in each case the same mixture of nortricyclene (**4**) (62%) and *endo*-norbornyl chloride (**5**) (38%).[6] We interpret isolation of the same products in the same ratio from all three dihalides as convincing evidence for generation of the same intermediate, equilibrating anion **6**, from all three (Scheme I). Ejection of chloride ion from **6** would lead to carbene **7**, which is known to undergo efficient intramolecular insertion to form **4**.[7] Alternatively, protonation of **6** from the less hindered exo side[8] would afford **5**. Evidence that TEAB is a proton donor in the latter path is the formation of ethylene, demonstrated by vpc analysis. This process has been observed by others during electrochemical reduction of alkyl halides.[9] A corollary of the mechanism suggested in Scheme I is that addition of a proton donor to the medium should increase the ratio of **5** to **4** by capturing **6** before it can eject chloride ion. We have found that added methanol or water does indeed increase the ratio of **5** to **4**. This ratio, as expected, is dependent upon the concentration of added proton donor; the ratio of **5** to **4** is increased from the original 38:62 to 80:20 when the water con-



1

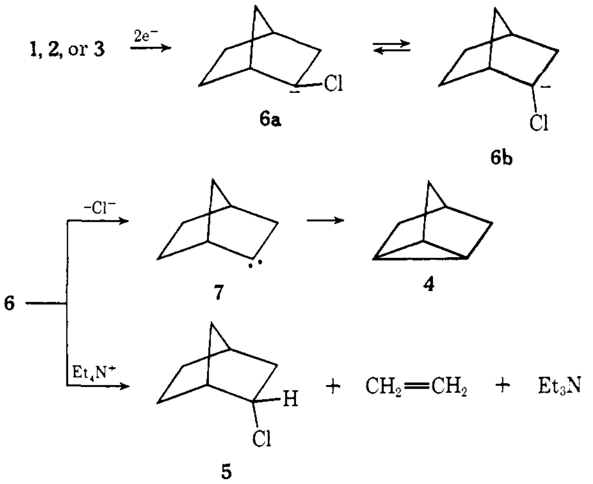


2



3

Scheme I



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(1) For a recent review, see M. J. Peover, *Electroanal. Chem.*, **2**, 1 (1967).

(2) D. L. Maricle, *Anal. Chem.*, **35**, 683 (1963).

(3) J. R. Jezorek and H. B. Mark, Jr., *J. Phys. Chem.*, **74**, 1627 (1970).

(4) A. J. Fry, W. B. Farnham, B. J. Holstein, M. A. Mitnick, and L. C. Riggs, *J. Org. Chem.*, **34**, 4195 (1969).

(5) Dimethylformamide was purified by reflux over 4A molecular sieve, followed by distillation *in vacuo* from molecular sieve; water content, determined by vpc analysis (5 ft × 1/4 in., Porapak Q, 210°), is typically 2–4 m*M*. DMF is very hygroscopic; the actual water content of the electrolysis mixtures is 15–20 m*M*. TEAB was recrystallized from ethanol–ether and dried overnight in a vacuum desiccator.

(6) 2% of *exo*-norbornyl chloride could easily have been detected under our vpc conditions (50 ft × 1/8 in. column, packed with 7% Zonyl E-7 on Chromosorb G, 75°, flow rate 25 ml/min).

(7) W. G. Dauben and F. G. Willey, *J. Amer. Chem. Soc.*, **84**, 1497 (1962).

(8) *E.g.*, (a) H. C. Brown and K.-T. Liu, *ibid.*, **92**, 200 (1970); (b) H. C. Brown and J. H. Kawakami, *ibid.*, **92**, 201 (1970).

(9) J. L. Webb, C. K. Mann, and H. M. Walborsky, *ibid.*, **92**, 2042 (1970).