

- (3) D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **29**, 2702 (1964); G. K. Helmkamp, H. N. Cassey, B. A. Olsen, and D. J. Pettitt, *ibid.*, **30**, 933 (1965); H. Meerwein, K. F. Zenner, and R. Gipp, *Justus Liebig's Ann. Chem.*, **688**, 67 (1965); G. K. Helmkamp, B. A. Olsen, and J. R. Koskinen, *J. Org. Chem.*, **30**, 1623 (1965).
- (4) M. L. Kline, N. Beutow, J. K. Kim, and M. C. Caserio, details to be published.
- (5) Label distribution was determined from NMR spectrum of products in benzene. **3a**: δ 1.68 (CH₃S at C-2, s), 1.81 (CH₃S at C-3, s), 2.65 (SCH₂CH, m), and 3.55 ppm (CH₂Cl, m).
- (6) The chemical shifts of the two nonequivalent CH₃S groups cannot be resolved cleanly.
- (7) Product composition was determined by demethylation of the adducts with trimethylamine to a mixture of tri(alkylthio)propanes which were analyzed by GPC, NMR, and mass spectrometry.
- (8) (a) J. K. Kim and M. C. Caserio, *J. Am. Chem. Soc.*, **96**, 1930 (1974); (b) S. H. Smallcombe and M. C. Caserio, *ibid.*, **93**, 5826 (1971); (c) J. L. Kice and N. A. Favstritsky, *ibid.*, **91**, 1751 (1969).
- (9) C. G. Moore and M. Porter, *J. Chem. Soc.*, 2890 (1958); *Tetrahedron*, **9**, 58 (1960). F. Pietra and D. Vitali, *J. Chem. Soc. B*, 623 (1970). J. L. Kice, *Prog. Inorg. Chem.*, **17**, 147 (1972). B. Miller and C. H. Han, *J. Org. Chem.*, **36**, 1513 (1971).
- (10) H. Minato, T. Miura, F. Takagi, and M. Kaboyashi, *Chem. Lett.*, 211 (1975).
- (11) Composition was determined from 90-MHz and 220-MHz NMR spectra. A single ABX pattern was observed that was assigned to CH₃SCD₂C(SC₂H₅)CH₂Cl by comparison with authentic unlabeled material: δ_A 3.68, δ_B 3.52 ppm ($J_{AB} = 7.6$, $J_{AX} = 3.6$, $J_{BX} = 4.6$ Hz). No ABX signals corresponding to C₂H₅SCD₂C(SCH₃)CH₂Cl were evident.
- (12) J. E. Baldwin, R. E. Hackler, and D. P. Kelley, *Chem. Commun.*, 537, 538 (1968); G. M. Blackburn, W. D. Ollis, J. D. Plackett, C. Smith, and I. O. Sutherland, *ibid.*, 186 (1968); R. B. Bates and D. Feld, *Tetrahedron Lett.*, 417 (1968); B. M. Trost and R. LaRoche, *ibid.*, 3327 (1968); B. M. Trost and L. S. Melvin, Jr., "Sulfur Ylids", Academic Press, New York, N.Y., 1975, Chapter 7.
- (13) R. W. Jemison and W. D. Ollis, *Chem. Commun.*, 294 (1969).
- (14) V. Rautenstrauch, *Chem. Commun.*, 4 (1970); J. E. Baldwin and J. E. Patrick, *J. Am. Chem. Soc.*, **93**, 3556 (1971); U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970).
- (15) J. E. Baldwin and F. J. Urban, *Chem. Commun.*, 165 (1970).
- (16) R. Tang and K. Mislow, *J. Am. Chem. Soc.*, **92**, 2100 (1970); D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 147 (1974).
- (17) G. A. Russell and G. J. Mikol, *Mech. Mol. Migr.*, **1**, 157 (1968); R. A. W. Johnstone, *ibid.*, **2**, 249 (1969); A. R. Lepley and A. G. Giunani, *ibid.*, **3**, 271 (1970).
- (18) I. D. Brindle and M. S. Gibson, *Chem. Commun.*, 803 (1969); J. E. Baldwin, J. E. Brown, and R. W. Cordell, *ibid.*, 31 (1970); J. E. Baldwin, J. E. Brown, and G. Höfle, *J. Am. Chem. Soc.*, **93**, 788 (1971).
- (19) A. S. F. Ash, F. Challenger, and D. Greenwood, *J. Chem. Soc.*, 1877 (1951).
- (20) (a) R. D. Baechler, J. P. Hummel, and K. Mislow, *J. Am. Chem. Soc.*, **95**, 4442 (1973); R. D. Baechler, S. K. Daley, B. Daly, and K. McGlynn, *Tetrahedron Lett.*, 105 (1978); (b) see also M. B. Evans, G. M. C. Higgins, C. G. Moore, M. Porter, B. Saville, J. F. Smith, B. R. Trego, and A. A. Watson, *Chem. Ind. (London)*, 897 (1960).

Jhong K. Kim, Margaret L. Kline, Marjorie C. Caserio*

Department of Chemistry, University of California
Irvine, California, 92717

Received April 21, 1978

Photochemical Interconversion of Phenylnitrene and the Isomeric Pyridylmethylenes

Sir:

Recently we demonstrated that irradiation (>2160 Å) of phenyl azide matrix isolated in argon produces 1-aza-1,2,4,6-cycloheptatetraene (**1**).¹ The question whether phenylnitrene (**2**) was formed in competition with **1** prompted us to follow the irradiation of phenyl azide using electron spin resonance.² Irradiation (>2160 Å) of phenyl azide matrix isolated in argon at 12 K produced the characteristic, intense *X,Y* transition of the triplet phenylnitrene (Figure 1: *D*, 1.027 cm⁻¹; *E*, 0 cm⁻¹).^{3,4} The excellent signal to noise ratio permitted observation of the weak $\Delta m = 2$ transition and the *Z*₁ transition which had not been observed in previous studies. Continued irradiation of the sample produced a new triplet species (Figure 1) with zero-field parameters (*D*, 0.537 cm⁻¹; *E*, 0.027 cm⁻¹) rather similar to those of phenylmethylene (*D*, 0.5098 cm⁻¹; *E*, 0.0249 cm⁻¹).⁵ The similarity in zero-field parameters suggested that the new triplet species might be 2-pyridylmethylene (**3**). This possibility was confirmed by independent generation of 2-pyridylmethylene. Irradiation (λ

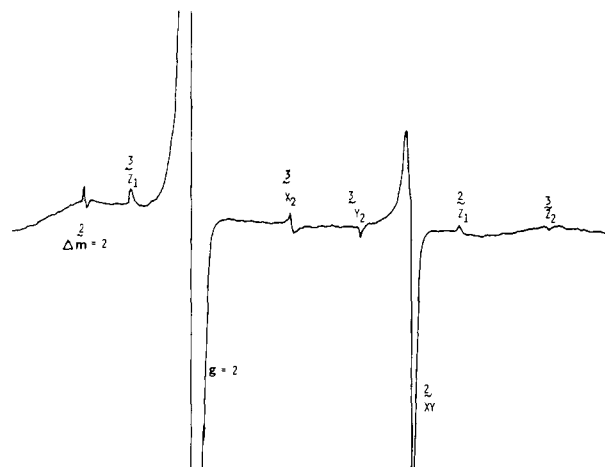


Figure 1. ESR spectrum produced upon irradiation of phenyl azide (>2160 Å) matrix isolated in argon at 10 K. The observed field positions for **2** are $\Delta m = 2$, 1668 G; *XY*, 6914 G; *Z*₁, 7639 G. The field positions for **3** are *Z*₁, 2377 G; *X*₂, 4934 G; *Y*₂, 6057 G; *Z*₂, 9068 G. The $g = 2$ region is due to the adventitious formation of free radicals.

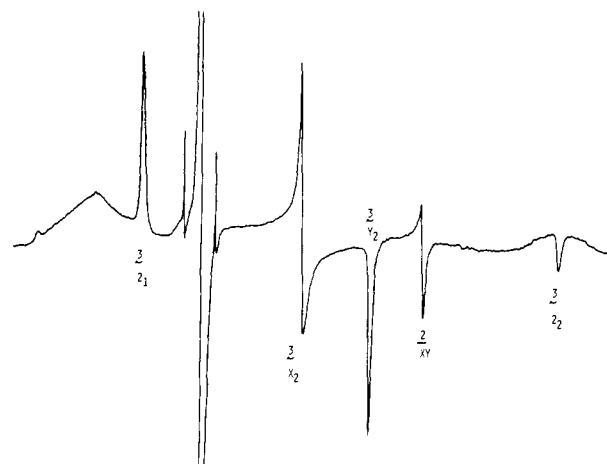


Figure 2. ESR spectrum produced on irradiation of *vic*-triazolopyridine (**4**, >2000 Å) matrix isolated in argon at 10 K. The field positions are identical with those given in Figure 1. The sharp signals symmetrically disposed about the $g = 2$ signal are due to hydrogen atoms.

> 2000 Å) of *vic*-triazolopyridine (**4**) matrix isolated in argon is known to give first 2-diazomethylpyridine then 1-aza-1,2,4,6-cycloheptatetraene.¹ When this irradiation is monitored by ESR, the signals characteristic of triplet 2-pyridylmethylene (**3**) are observed (Figure 2). Continued irradiation produces the signals of triplet phenylnitrene (Figure 2). Blank experiments showed the vacuum system and the ESR cell to be free of cross contamination.⁶

Irradiation (>2000 Å) of 4-diazomethylpyridine^{6,7} matrix isolated in argon at 12 K gave triplet 4-pyridylmethylene (**5**: *D*, 0.533 cm⁻¹; *E*, 0.0248 cm⁻¹). Continued irradiation produces 3-pyridylmethylene (**6**, *vide infra*), 2-pyridylmethylene (**3**), and phenylnitrene (**2**) as well (Figure 3). Similar irradiation of argon matrix isolated 3-diazomethylpyridine^{6,7} gives 3-pyridylmethylene (**6**: *D*, 0.513 cm⁻¹; *E*, 0.0241 cm⁻¹), 4-pyridylmethylene, 2-pyridylmethylene, and phenylnitrene (Figure 4). The three isomeric pyridylmethylenes can be clearly distinguished in the *Z*₁ and *Y*₂ transitions. The *Z*₁ transition of 3-pyridylmethylene is complex owing to the presence of two conformers.⁸ Only one conformer is possible for 4-pyridylmethylene, and only one of the two possible conformers is observed for 2-pyridylmethylene. This observation is probably due to an effect of the nitrogen lone pair. When the irradiation of either 4-diazomethylpyridine or 3-diazo-

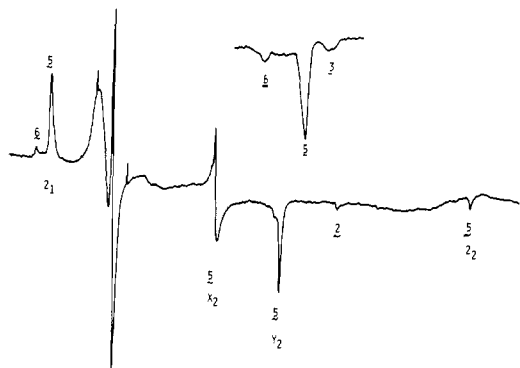


Figure 3. ESR spectrum obtained on irradiation of 4-diazomethylpyridine ($>2000 \text{ \AA}$) matrix isolated in argon at 10 K. The field positions for **5** are Z_1 , 2335 G; X_2 , 4966 G; Y_2 , 6006 G; Z_2 , 9025 G. The inset shows an expansion of the Y_2 region.

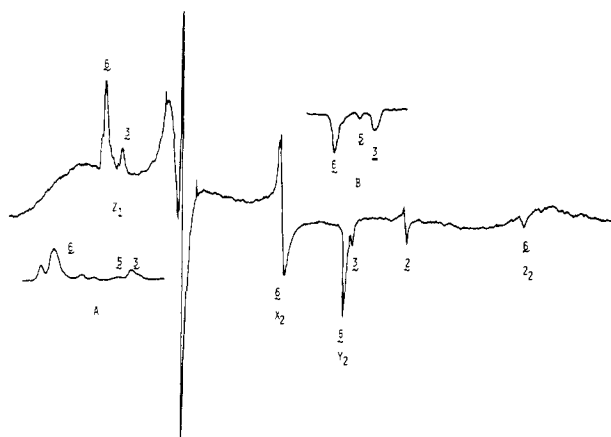
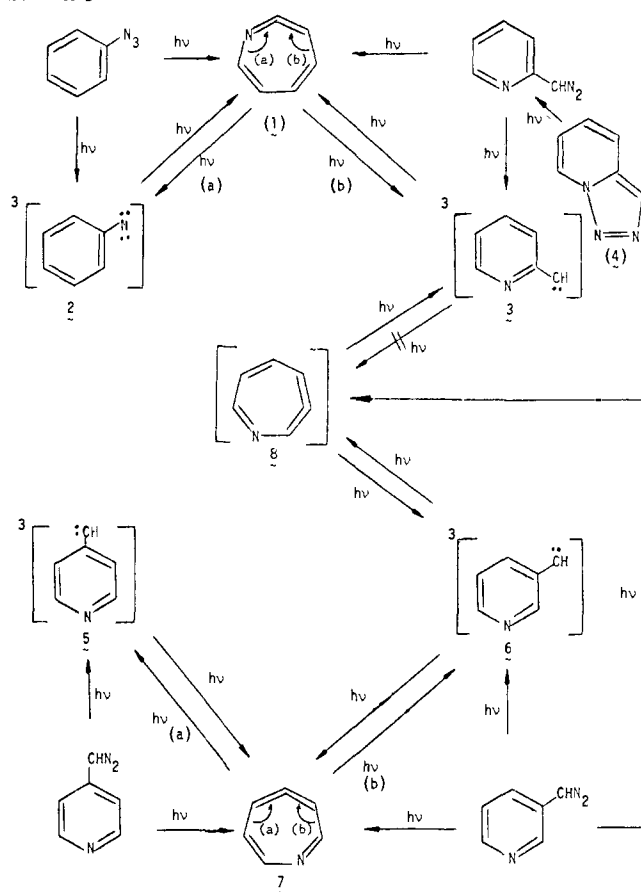


Figure 4. ESR spectrum obtained on irradiation of 3-diazomethylpyridine ($>2000 \text{ \AA}$) matrix isolated in argon at 10 K. The field positions for **6** are Z_1 , 2123 G; X_2 , 4924 G; Y_2 , 5923 G; Z_2 , 8817 G. Inset A shows an expansion of the Z_1 region. Inset B shows a similar expansion of the Y_2 region.

methylpyridine is monitored by infrared spectroscopy, the same primary photoproduct is observed. This photoproduct shows bands at 1810 and 850 cm^{-1} which we attribute to the presence of a strained allene. The formation of a common intermediate from 3- and 4-diazomethylpyridine severely limits the structures which may be considered.⁹ Ring expansion to the allene (**7**) seems most plausible, and we tentatively conclude that this is the species with the 1810 - and 850-cm^{-1} bands. Continued irradiation destroys this species with the formation of unidentified products. In the irradiation of 3-diazomethylpyridine, formation of a small amount of 1-aza-1,2,4,6-cycloheptatetraene (**1**) is observed (infrared spectrum). This observation provides a valuable clue to the crossover point in the mechanism.

The observations given above can be understood in terms of the transformations shown in Scheme I. This mechanism is appealing in its simplicity, and it accounts for all of the observations. It is consistent with, but not required by, the data. Simple 1,2 shifts in **1** give phenylnitrene (**2**) or 2-pyridylmethylene (**3**). Use of 1-aza-1,2,4,6-cycloheptatetraene (**1**) as the vehicle for interconverting phenylnitrene and 2-pyridylmethylene has the appealing feature of providing a reason why phenylnitrene and 2-pyridylmethylene are not converted to the 3- and 4-pyridylmethylenes (**5** and **6**). Ring expansion of 2-pyridylmethylene to **1** is a process in which the nitrogen lone pair participates, and this ring expansion is clearly favored over the alternate expansion to **8** in which the nitrogen lone pair cannot play a role. Interconversion of 3- and 4-pyridylmethylene is possible via 1,2 shifts in the allene (**7**). The crossover point between the two almost independent systems (**1**–**3** and

Scheme I



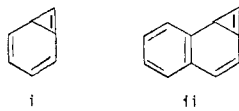
5–**7**) is the allene (**8**) which we have not observed. It must be a minor product which does not build up.

Thermolysis of phenyl azide and *vic*-triazolopyridine gives virtually identical products.¹⁰ The same is true for the thermolysis of the 3- and 4-diazomethylpyridines.¹¹ Interconversions of the isomeric pyridylmethylenes and phenylnitrene by various schemes have been considered as possible mechanisms for formation of the thermolysis products. It is probable that Scheme I is relevant to the thermolysis mechanisms since the 1,2 shifts can occur photochemically or thermally.

Acknowledgment. This research was supported by Grant 75-10939 from the National Science Foundation and Grant GM-24427 from the National Institute of General Medical Sciences, U.S. Department of Health, Education, and Welfare.

References and Notes

- O. L. Chapman and J.-P. LeRoux, *J. Am. Chem. Soc.*, **100**, 282 (1978).
- Electron spin resonance spectra were obtained on a modified Varian E-12 ESR spectrometer. In all experiments argon and substrate were codeposited on an oxygen-free high conductivity copper leaf cooled to 10–20 K with an Air Products "Helitran" liquid helium transfer system. Samples were irradiated with a 1000-W high pressure mercury arc lamp.
- (a) G. Smolinsky, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3220 (1962); (b) R. M. Moriarty, M. Rahman, and G. J. King, *ibid.*, **88**, 842 (1966).
- Zero-field splitting parameters were calculated from the observed field positions using an iterative computer program based on the equations given by E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).
- A. M. Trozzolo, R. W. Murray, and E. Wasserman, *J. Am. Chem. Soc.*, **84**, 4990 (1962).
- The pyridine aldehydes used in the synthesis of 2-, 3-, and 4-diazomethylpyridines were free of contamination by the isomeric aldehydes and were $>99.9\%$ pure (analysis by vapor phase chromatography).
- B. Elstert, W. Kurze, and G. W. Müller, *Justus Liebigs Ann. Chem.*, **732**, 1 (1970).
- A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **87**, 129 (1965); R. S. Hutton, M. L. Manion, H. D. Roth, and E. Wasserman, *ibid.*, **96**, 4680 (1974).
- A common cyclopropene from 3- and 4-diazomethylpyridine is not possible without rearrangement. The $\nu_{C=C}$ for fused-ring cyclopropenes of this type



is observed at 1760 cm^{-1} (i and ii; unpublished observations of J.-P. LeRoux and P. R. West). The assignment of the 1810-cm^{-1} band to an allene has no precedent. The shift to lower frequency is, however, in accord with the frequency shift observed in the ketenimine system (1).¹ The 850-cm^{-1} band is a standard allene C-H deformation mode. Replacement of the diazomethyl hydrogen in 3- and 4-diazomethylpyridine produced deuterated derivatives of 7 which are not identical. The 1810-cm^{-1} absorption is shifted to 1800 cm^{-1} in each case. This shift is reasonable for deuterated allenes but far below the 50-cm^{-1} shift characteristic of deuterated cyclopropenes (G. L. Gloss, *Adv. Alicycl. Chem.*, 1, 53 (1966)).

- (10) W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 6149 (1968); C. W. Wentrup, *Chem. Commun.*, 1386 (1969); W. D. Crow and M. N. Paddon-Row, *Tetrahedron Lett.*, 2231 (1972); W. D. Crow, M. N. Paddon-Row, and D. S. Sutherland, *ibid.*, 2239 (1972); C. Thetaz and C. Wentrup, *J. Am. Chem. Soc.*, 98, 1258 (1976). For excellent reviews, see W. M. Jones and U. H. Brinker in "Pericyclic Reactions", A. P. Marchand and R. E. Lehr, Ed., Academic Press, New York, N.Y., 1977, p 110, and C. Wentrup, *Top. Curr. Chem.*, 62, 173 (1976).
- (11) W. D. Crow, A. N. Khan, and M. N. Paddon-Row, *Aust. J. Chem.*, 28, 1741, 1755, 1763, (1975).

O. L. Chapman,* R. S. Sheridan, J. P. LeRoux

Contribution No. 4008

Department of Chemistry, University of California
Los Angeles, Los Angeles, California 90024

Received April 7, 1978

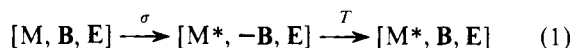
Effects of Electric and Magnetic Fields on Prochiral Chemical Reactions: Macroscopic Electric and Magnetic Fields Can Cause Asymmetric Synthesis¹

Sir:

We address the question of whether the application of uniform and constant electric and magnetic fields to an achiral or racemic (prochiral) reaction mixture can lead to asymmetric synthesis of products.

The literature contains one report of asymmetric syntheses in the presence of magnetic and presumed electric fields.² Small optical rotations (maximum 0.024°) were obtained for various reactions and field orientations. In spite of the fact that the macroscopic electric field must have been zero³ in the reactions conducted by Gerike, the theoretical possibility of applied field effects on prochiral reactions is quite interesting.

In answer to the question of the theoretical possibility of such field effects on asymmetric synthesis, Mead, Moscowitz, Wynberg, and Meuwese have presented a theorem⁴ which shows that, in the presence of constant and uniform electric and magnetic fields, a molecule M and its enantiomer M* have states of the same energy. Consequently, they conclude that asymmetric synthesis under the specified conditions is impossible. Their argument is based on the application of two symmetry operations to the entire system (reaction and applied fields): a plane of reflection, σ , and time reversal, T . The electric field, E , and magnetic field, B , have arbitrary relative directions. Successive application of σ (chosen to contain E and B) and T have the following effect:

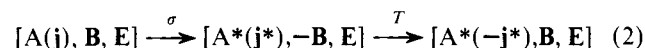


Thus, the net effect of the two operations is to transform M into M*, showing that the two enantiomers have (stationary) states with the same set of energy levels in the presence of the fields.

The conclusion that such fields cannot induce asymmetric synthesis is based on the condition of complete thermodynamic equilibrium, whereby, in accordance with the above theorem, equal concentrations of enantiomeric products, P, and P*, are

attained. In many systems, however, the actual concentrations of reaction components may be kinetically, rather than thermodynamically, controlled. This is the case, in particular, if given reactants can produce different products by reaction paths having different activation energies, and if equilibrium strongly favors product formation. Such reactions can essentially go to "completion" without reaching complete thermodynamic equilibrium. In these cases the theorem above does not apply.

We will show below that parallel E and B fields, which are constant and uniform, can differentially affect the rate constant for the formation of enantiomeric products, P and P*, from an optically inactive mixture of reactants. The argument depends on the existence of a current density (or magnetic moment) in the transition states which are precursors to products. We denote the current density by j and the precursor molecule with current density by $A(j)$. Now consider the effect of the operations σ and T as defined above:



The symbol j^* represents σj , the reflected current density. This result shows that molecule A with current density j has the same energies in the fields as does molecule A* with current density $-j^*$.

Let us assume that $A(j)$ is the precursor to product P and that $A^*(j^*)$ is the precursor to the enantiomeric product P*. While it is true that $A(j)$ and $A^*(-j^*)$ have the same energy, it follows that, in general, $A(j)$ and $A^*(j^*)$ do not have the same energy if j and j^* are not superimposable in space. Therefore, at thermal equilibrium, the concentrations of the two species will differ and, consequently, so will the rates of formation of P and P*.

The current density in the precursor molecule may be intrinsic to the molecule (such as a stationary magnetic moment) or it may be induced by the applied fields or by molecular interactions. Induced currents may be due either to adiabatic (stationary) response or to nonadiabatic (transient) response of the molecule. Nonadiabatic responses may be particularly important in transition states.

The adiabatic response to the applied field B is of particular interest. Formulation of the second-order response tensor, $K^{(2)}$, for the response of j to B shows⁵ that, for molecules having no current density in the absence of the field, $K^{(2)} = 0$. This implies that, for such molecules, $\Delta j(A, B) = \Delta j^*(A, -B) = \Delta j^*(A, B^*)$, where $\Delta j(A, B)$ is the current response of molecule A to B and $B^* \equiv \sigma B$. However, it follows that $\Delta j^*(A, B^*)$ is identical with $\Delta j(A^*, B)$; therefore,

$$\Delta j(A, B) = \Delta j(A^*, B)$$

which shows that the adiabatic current response of A and A* are the same. Consequently, if the unperturbed A has no current density, adiabatic current response to B cannot, of itself, contribute to asymmetric synthesis.

The above argument reduces the number of possible sources of effective current density to (1) the presence of an intrinsic stationary magnetic moment and (2) the nonadiabatic response of a (transient) magnetic moment.

An example of the first is a precursor molecule A having only one plane of symmetry and a magnetic moment perpendicular to the symmetry plane. The magnetic moment could be due to spin. There are two possible species, denoted by $A(j)$ and $A(-j)$, having opposite magnetic polarizations relative to the molecular plane. One is produced from the other by the successive operations of reflection and time reversal. In the absence of magnetic interactions, $A(j)$ and $A(-j)$ are degenerate. Distortions of molecule A which destroys the symmetry plane lead to P and P* depending on the direction of distortion. If the electric field influences the direction of distortion (be-