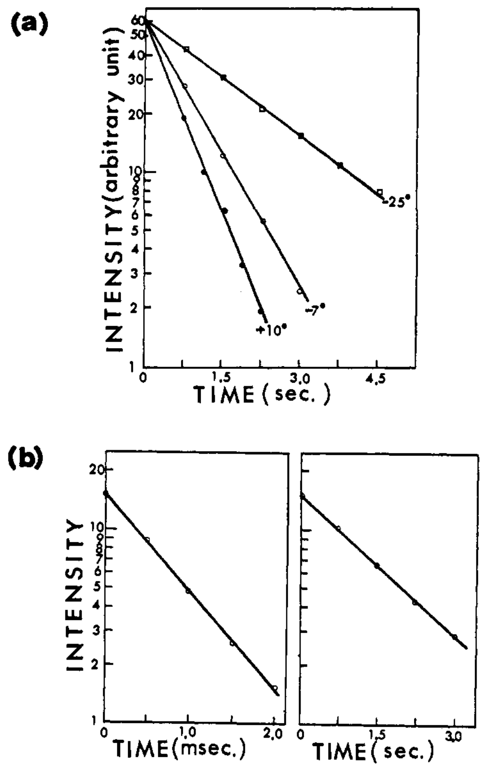


Figure 1. First-order decay plots of iminoxy radicals, log (intensity) *vs.* time: (a) diphenyliminoxy generated by chloranil in dichloromethane at −25, −7, and +10°; (b) 2,4,6-trimethylphenyliminoxy in dichloromethane, generated by duroquinone (left) and chloranil (right).

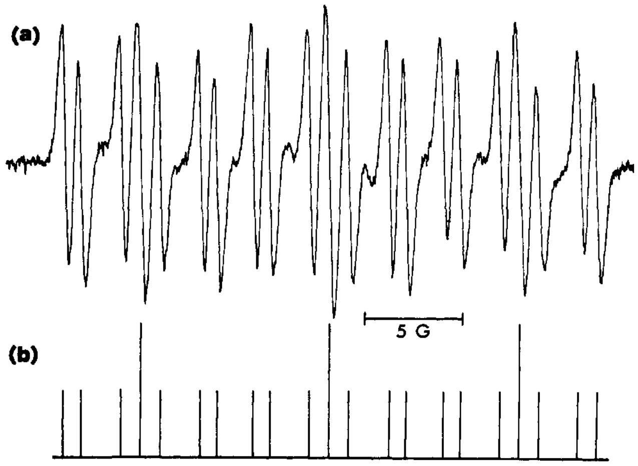


Figure 2. (a) Epr spectrum of nitroxide resulting from decay of diphenyliminoxy with benzoquinone; (b) reconstructed spectrum using $a_N = 9.70$, $a_{H_1} = 3.75$, $a_{H_2} = 3.00$, and $a_{H_3} = 0.95$ G.

decay. Thus the lifetime of 2,4,6-trimethylphenyliminoxy is only 0.86 msec when generated from the corresponding oxime with duroquinone, compared with 1.3 sec when generated with chloranil. This is consistent with the relatively high activation energy found for radical decay with chloranil, *e.g.*, +4.6 kcal/mol for diphenyliminoxy.

Nitroxide formation during diphenyliminoxy decay is particularly informative, as a reversible equilibrium between iminoxy and nitroxide radicals is observed

$$\text{quinone} + (C_6H_5)_2C{=}NO\cdot \underset{\text{light}}{\overset{\text{dark}}{\rightleftarrows}} \text{nitroxide}$$

With benzoquinone the nitroxide spectrum is complex (Figure 2), but can be assigned to splitting arising from three nonequivalent protons which presumably originated with the quinone superimposed on the characteristic $^{14}N$ triplet. This interpretation is supported by the observation of a simple sharp three line nitroxide spectrum when chloranil is substituted for benzoquinone.

Radical production from benzaldoximes is complicated by the facile abstraction of the aldehydic as well as the hydroxyl proton by photoexcited quinones. Thus a clean spectrum can be obtained from the sterically hindered 2,4,6-trimethylbenzaldoxime using benzoquinone but not from benzaldoxime unless sterically hindered quinones such as chloranil or duroquinone are used. These steric effects also influence radical stability, as shown by the enhanced lifetimes, ~1.3 sec, of the hindered 2,4,6-trimethylphenyl- and 2,6-dichlorophenyliminoxy radicals generated with chloranil compared with the 1.2 msec lifetime of the *p*-nitrophenyliminoxy radical prepared under the same conditions. This lifetime enhancement implicates aldehydic proton abstraction as an additional pathway for aldoxime iminoxy radical decay.

**Acknowledgment.** We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. One of us (N. O.) was supported as a National Science Foundation Centers of Excellence postdoctoral fellow.

**Tien-Sung Lin, Stephen H. Mastin,* Noboru Ohkaku**
*Department of Chemistry, Washington University*
*St. Louis, Missouri 63130*

*Received May 25, 1973*

## Interpretation of the Pseudocontact Model for Nuclear Magnetic Resonance Shift Reagents. V. Collinearity in the Structural Elucidation of Nitriles

*Sir:*

The transformation of Hinckley's[1] widely applicable method of lanthanide-induced shifts (LIS) into an instrument for making distinctions among structures with statistical criteria of reliability[2,3] was recently applied to the structure assignment of the four diastereoisomeric nitriles **1**–**4**, as reported by Doering and Birladeanu.[4] We report here an important and useful extension to the application of this method—the assumption of collinearity of lanthanide with the nitrile bond and the consequent improvements in confidence levels for structure assignment.

Minimum values of $R^{2,3}$ were obtained for all 16 binary combinations of the four structural possibilities with the four sets of experimental relative slopes (obtained by least-squares treatment of the Eu(fod)$_3$ LIS data with six or more dopings), with the assumed N–Eu distance ranging from 2.0 to 3.5 Å and the C–N–Eu

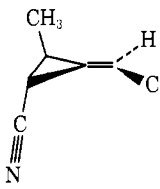
---

[1] C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

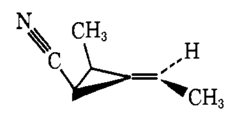
[2] (a) M. R. Willcott III, R. E. Lenkinski, and R. E. Davis, *J. Amer. Chem. Soc.*, **94**, 1742 (1972). (b) A FORTRAN computer program for carrying out the calculations according to this method is now available from the authors (R. E. D.).

[3] R. E. Davis and M. R. Willcott III, *J. Amer. Chem. Soc.*, **94**, 1744 (1972).

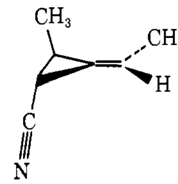
[4] W. von E. Doering and L. Birladeanu, *Tetrahedron*, **29**, 499 (1973).



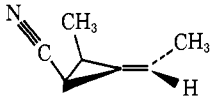
1, (*Z*)-*trans*



2, (*Z*)-*cis*



3, (*E*)-*trans*



4, (*E*)-*cis*

angle ranging from 0 to 90°. These minimum *R* values are shown in Table I, together with *R*-factor ratios for the (second best)/best models and confidence levels at which each second best model may be rejected. The confidence levels are obtained by routine application of the tables for significance of the *R*-factor ratios for one degree of freedom (five experimental observations minus the four parameters *x*, *y*, *z*, and scale).[3,5] It may be recalled that rejection of a hypothesis at a given confidence level $\alpha\%$ means that we risk rejecting a true hypothesis $\alpha\%$ of the time. Table II presents chemical shifts and observed and calculated relative slopes for these isomers. Examination of the C–N–Eu angles at minimum *R* consistently reveals angles less than 10° for each best model, and larger angles (>30°) and generally erratic Eu positions at the 12 larger values of *R*. This observation has led us to propose and explore the hypothesis of collinearity of the lanthanide and cyano group.[6]

**Table I.** Minimum *R* Values (%) for Binary Combinations of Models **1–4** with Sets of Relative Slopes; No Restraint of Lanthanide Position

| | LIS data set | | | |
|---|---|---|---|---|
| | **1** | **2** | **3** | **4** |
| Model (*Z*)-*trans* | 4.2 | 22.0 | 12.6 | 31.0 |
| Model (*Z*)-*cis* | 15.0 | 6.2 | 20.1 | 10.1 |
| Model (*E*)-*trans* | 13.2 | 25.7 | 4.7 | 20.1 |
| Model (*E*)-*cis* | 21.0 | 12.2 | 14.8 | 4.7 |
| Second best/best | 3.14 | 1.96 | 2.68 | 2.14 |
| Confidence level (%) for rejection of second best model | 20 | 34 | 24 | 31 |

**Table II.** Chemical Shifts and Observed and Calculated Relative Slopes for Compounds **1–4** with Eu(fod)$_3$

| Type of hydrogen | Chem shift (δ) | Rel slopes | | Chem shift (δ) | Rel slopes | |
|---|---|---|---|---|---|---|
| | | Obsd | Calcd | | Obsd | Calcd |
| | | **1**, (*Z*)-*trans*[a] | | | **2**, (*Z*)-*cis*[b] | |
| $H_1$ | 1.47 | 10.00 | 9.93 | 1.97 | 10.00 | 9.67 |
| $H_2$ | 1.99 | 6.19 | 6.13 | 2.02 | 4.06 | 4.78 |
| $(CH_3)_2$ | 1.22 | 3.23 | 3.17 | 1.33 | 5.39 | 5.30 |
| $H_0$ | 5.95 | 2.50 | 2.68 | 5.93 | 3.03 | 3.08 |
| $(CH_3)_0$ | 1.90 | 2.69 | 3.01 | 1.89 | 3.00 | 3.02 |
| | | **3**, (*E*)-*trans*[c] | | | **4**, (*E*)-*cis*[d] | |
| $H_1$ | 1.48 | 10.00 | 9.83 | 1.96 | 10.00 | 9.88 |
| $H_2$ | 1.96 | 6.21 | 6.09 | 1.90 | 4.31 | 4.83 |
| $(CH_3)_2$ | 1.24 | 2.66 | 3.17 | 1.37 | 5.31 | 5.04 |
| $H_0$ | 6.00 | 3.53 | 3.70 | 6.06 | 3.51 | 3.51 |
| $(CH_3)_0$ | 1.84 | 1.47 | 1.56 | 1.84 | 1.59 | 1.59 |

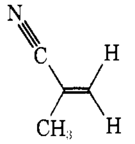
[a] *R* = 4.2%. [b] *R* = 6.2%. [c] *R* = 4.7%. [d] *R* = 4.7%.

Minimum *R* values obtained by imposition of this restraint are given in Table III. The ratios between second best and best have suffered a slight deterioration, but now all correspond to confidence levels at least as good as 11%, thanks to the increase in the number of degrees of freedom from one to three (five observations minus the two parameters, distance and scale).

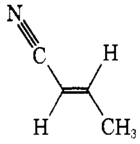
**Table III.** Minimum *R* Values (%) for Binary Combinations as in Table I, with Collinearity Restraint

| | LIS data set | | | |
|---|---|---|---|---|
| | **1** | **2** | **3** | **4** |
| Model (*Z*)-*trans* | 8.3 | 27.0 | 13.4 | 26.9 |
| Model (*Z*)-*cis* | 22.3 | 6.5 | 26.0 | 12.0 |
| Model (*E*)-*trans* | 14.1 | 28.7 | 8.4 | 25.2 |
| Model (*E*)-*cis* | 25.8 | 12.6 | 22.7 | 6.7 |
| Second best/best | 1.70 | 1.94 | 1.59 | 1.79 |
| Confidence level (%) for rejection of second best model | 10 | 7 | 11 | 8 |

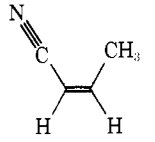
Support for the collinearity hypothesis has been obtained from examination of the isomeric set of methylacrylonitriles **5–7**, each member of which provides a unique set of three relative slopes. Analysis by the original procedure,[2,3] which would have been statistically meaningless, minus one degree of freedom (three observations minus four parameters), gives inconsistent results, as shown in Table IV. The assumed N–Yb distance ranges from 2.0 to 3.5 Å and the C–N–Yb angle ranges from 0 to 90°. An obvious discrepancy is that the 1-methylacrylonitrile model is the one which gives the best fit with LIS data both for **5** and for **7**. Again, many of the incorrect model–data pairs exhibit C–N–Yb angles deviating more than 25° from col-



**5**



**6**



**7**

**Table IV.** Minimum *R* Values (%) for Binary Combinations of Methylacrylonitrile Models **5–7** with Sets of Relative Slopes; No Restraint of Lanthanide Position

| | LIS data set | | |
|---|---|---|---|
| | **5** | **6** | **7** |
| Model 1-CH$_3$ | 2.8 | 14.4 | 0.3 |
| Model *cis*-2-CH$_3$ | 6.0 | 22.6 | 2.5 |
| Model *trans*-2-CH$_3$ | 29.2 | 0.7 | 23.9 |

---

(5) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(6) This hypothesis has recently been applied to four pairs of (*E*)- and (*Z*)-cinnamonitriles by R. Seux, G. Morel, and A. Foucaud, *Tetrahedron Lett.*, 1003 (1972).

linearity. Analysis under the restraint of collinearity, however, can be fruitful—one degree of freedom (three observations minus two parameters)—as is seen in Table V. In this event, minimum *R* values are clearly associated with the correct structures and higher *R* values with mismatched structures. Chemical shifts and observed and calculated relative slopes, assuming collinearity, appear in Table VI.

**Table V.** Minimum *R* Values (%) for Binary Combinations of Methylacrylonitrile Models **5–7** with Sets of Relative Slopes, with Collinearity Restraint

| | LIS data set | | |
|---|---|---|---|
| | **5** | **6** | **7** |
| Model 1-$CH_3$ | 2.9 | 31.7 | 9.7 |
| Model *cis*-2-$CH_3$ | 6.0 | 26.6 | 2.8 |
| Model *trans*-2-$CH_3$ | 29.3 | 1.5 | 27.1 |
| Second best/best | 2.06 | 17.7 | 3.46 |
| Confidence level (%) for rejection of second best model | 27 | 4 | 19 |

**Table VI.** Chemical Shifts and Observed and Calculated Relative Slopes, Methylacrylonitrile:Yb(dpm)$_3$, with Collinearity Restraint

| Type of hydrogen | Chem shift ($\delta$) | Rel slopes Obsd | Rel slopes Calcd |
|---|---|---|---|
| | 1-Methylacrylonitrile[a] | | |
| $CH_3$ | 1.96 | 8.17 | 8.34 |
| $H_1$ cis | 5.74 | 10.00 | 10.10 |
| $H_1$ trans | 5.60 | 6.94 | 6.56 |
| | *cis*-2-Methylacrylonitrile[b] | | |
| $CH_3$ | 2.04 | 6.59 | 6.74 |
| $H_1$ | 5.26 | 10.00 | 10.08 |
| $H_2$ | 6.46 | 5.83 | 5.49 |
| | *trans*-2-Methylacrylonitrile[c] | | |
| $CH_3$ | 1.96 | 4.02 | 3.86 |
| $H_1$ | 5.32 | 10.00 | 9.96 |
| $H_2$ | 6.62 | 8.20 | 8.32 |

[a] $R = 2.9\%$. [b] $R = 2.8\%$. [c] $R = 1.5\%$.

We are encouraged to believe that the collinearity hypothesis will receive support from additional studies now underway, and that the potentially exciting opportunities in structure determination offered by the nitrile group may be realized.

**Acknowledgment.** We acknowledge with gratitude the financial support of this work provided by the National Science Foundation (to W. von E. D.) and by the Robert A. Welch Foundation (Grant E-183 to M. R. W. and Grant F-233 to R. E. D.).

(7) John Simon Guggenheim Fellow, 1972–1973.

**Raymond E. Davis***
*Department of Chemistry, University of Texas at Austin*
*Austin, Texas 78712*

**M. Robert Willcott III,[7] Robert E. Lenkinski**
*Department of Chemistry, University of Houston*
*Houston, Texas 77004*

**W. von E. Doering, L. Birladeanu**
*Department of Chemistry, Harvard University*
*Cambridge, Massachusetts 02138*

*Received December 29, 1972*

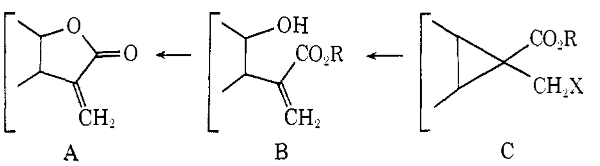
---

## Synthesis of α-Methylene-γ-butyrolactones by Rearrangements of Functionally Substituted Cyclopropanes

*Sir:*

The wide variety[1] and biological activity[2] of natural products, particularly sesquiterpenes, containing the α-methylene-γ-butyrolactone ring have been of much interest recently. Although this ring system has been the objective of synthetic projects in a number of laboratories,[3] the number of basically different approaches is not large. In many syntheses,[3b,c,f,h,i,m–q] the methylene group is constructed on a preformed lactone ring. We now report a new synthesis of α-methylene-γ-butyrolactones, utilizing a novel acid or metal-ion promoted cyclopropane rearrangement.

The rationale for our synthetic approach is the fact that the desired lactone ring (A) can be considered as a derivative of a homoallylic alcohol (B), which should be derivable from a suitable cyclopropylcarbinyl derivative (C).[4]



For an initial test of this hypothesis, the synthesis of the unsubstituted α-methylene-γ-butyrolactone (**4**), a natural product isolated from tulips,[5] was attempted.

---

(1) For reviews, see (a) W. Parker, J. S. Roberts, and R. Ramage, *Quart. Rev., Chem. Soc.*, **21**, 331 (1967); (b) J. Romo and A. Romo de Vivar, *Progr. Chem. Org. Natur. Prod.*, **25**, 90 (1967); (c) T. A. Geissman and M. A. Irwin, *Pure Appl. Chem.*, **21**, 167 (1970); (d) W. Stöcklin, T. G. Waddell, and T. A. Geissman, *Tetrahedron*, **26**, 2397 (1970), and references cited therein.

(2) For example, (a) antibiotic activity, C. J. Cavallito in "Medicinal Chemistry," Vol. I, C. M. Suter, Ed., Wiley, New York, N. Y., 1951, pp 221–235; (b) root promotion, H. Shibaoka, M. Shimokoriyama, S. Iriuchijima, and S. Tamura, *Plant Cell Physiol.*, **8**, 297 (1967); (c) dermatitis, G. A. W. Verspyck Mijnssen, *Brit. J. Dermatol.*, **81**, 737 (1969); (d) cytotoxic activity, S. M. Kupchan, *Trans. N. Y. Acad. Sci.*, **32**, 85 (1970); K.-H. Lee, E.-S. Huang, C. Piantadosi, J. S. Pagano, and T. A. Geissman, *Cancer Res.*, **31**, 1649 (1971); S. M. Kupchan, M. A. Eakin, and A. M. Thomas, *J. Med. Chem.*, **14**, 1147 (1971).

(3) (a) E. R. H. Jones, T. Y. Shen, and M. C. Whiting, *J. Chem. Soc.*, 230 (1950); (b) W. J. McGraw, U. S. Patent 2624723; *Chem. Abstr.*, 47, 11232*h* (1953); (c) E. E. van Tamelen and S. R. Bach, *J. Amer. Chem. Soc.*, **80**, 3079 (1958); (d) V. B. Piskov, *J. Gen. Chem. USSR*, 30, 1421 (1960); (e) J. A. Marshall and N. Cohen, *J. Org. Chem.*, **30**, 3475 (1965); (f) H. Minato and I. Horibe, *Chem. Commun.*, 531 (1965); (g) A. Löffler, R. D. Pratt, J. Pucknat, G. Gelbard, and A. S. Dreiding, *Chimia*, **23**, 413 (1969); (h) J. Martin, P. C. Watts, and F. Johnson, *Chem. Commun.*, 27 (1970); (i) E. S. Behare and R. B. Miller, *ibid.*, 402 (1970); (j) E. Öhler, K. Reininger, and U. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **9**, 457 (1970); (k) J. W. Patterson and J. E. McMurry, *Chem. Commun.*, 488 (1971); (l) V. R. Tadwalkar and A. S. Rao, *Indian J. Chem.*, **9**, 1416 (1971); *Chem. Abstr.*, 77, 34710 (1972); (m) L. K. Dalton and B. C. Elmes, *Aust. J. Chem.*, **25**, 625 (1972); (n) A. E. Greene, J.-C. Muller, and G. Ourisson, *Tetrahedron Lett.*, 2489, 3375 (1972); (o) P. A. Grieco and K. Hiroi, *J. Chem. Soc., Chem. Commun.*, 1317 (1972), 500 (1973); (p) A. D. Harmon and C. R. Hutchinson, *Tetrahedron Lett.*, 1293 (1973); (q) K. Yamada, M. Kato, M. Iyoda, and Y. Hirata, *J. Chem. Soc., Chem. Commun.*, 499 (1973).

(4) The nature of the intermediates in the solvolytic interconversions of cyclopropylcarbinyl, cyclobutyl, and homoallyl systems has attracted much interest in the past two decades. For leading references, see V. Buss, R. Gleiter, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3927 (1971); G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *ibid.*, **94**, 146 (1972); C. D. Poulter and S. Winstein, *ibid.*, **94**, 2297 (1972); W. J. Hehre and P. C. Hiberty, *ibid.*, **94**, 5917 (1972); Y. E. Rhodes and V. G. DiFate, *ibid.*, **94**, 7582 (1972).

(5) U. W. Brongersma-Oosterhoff, *Recl. Trav. Chim. Pays-Bas*, **86**, 705 (1967); B. H. H. Bergman, J. C. M. Beijersbergen, J. C. Overeem, and A. Kaars Sijpesteijn, *ibid.*, **86**, 709 (1967). See also C. J. Cavallito and T. H. Haskell, *J. Amer. Chem. Soc.*, **68**, 2332 (1946), and ref 2c.