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DETERMINATION OF STEREOCONFIGURATION OF 1,2-DIARYLOXYCYCLOBUTANES BY OPTICAL RESOLUTION AND INTRAMOLECULAR EXCIMER FORMATION OF CIS-1,2-DIPHENOXYCYCLOBUTANE

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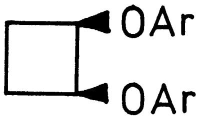
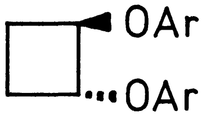
Two enantiomers of trans-1,2-diaryloxycyclobutanes were resolved by high-performance liquid chromatography (HPLC) using columns packed with chiral compounds. Measurement of fluorescence indicated that cis-1,2-diphenoxycyclobutane formed an intramolecular excimer between two phenoxy groups at ambient temperature.

Recently, we and other groups have reported the inter- and intra-molecular photocyclomerizations of aryl and alkyl vinyl ethers in the presence of various electron acceptors.[1-4] The structures of cyclobutane derivatives obtained in these photoreactions were assigned mainly from their ^1H NMR analyses. However, conflicting conclusions have been deduced about their stereochemistry because cyclobutane compounds may have both puckered and planar conformations.[5] We now report that two enantiomers of trans-1,2-diaryloxycyclobutanes can be separated by high-performance liquid chromatography (HPLC) using columns packed with chiral compounds, thereby the structures of the products are unequivocally established.[6,7] We also report that an intramolecular excimer fluorescence is observed at ambient temperature for cis-1,2-diphenoxycyclobutane in which two phenyl groups are connected by a four atom chain.[8,9]

Figure 1 shows chromatograms of two geometric isomers of 1,2-diphenoxycyclobutanes. The one geometric isomer (mp 67-68 °C) was completely resolved into two enantiomers by HPLC using a column packed with a chiral compound (Chiralcel OB).[10] Both enantiomers separated by this way exhibited opposite optical rotations to one another in polarimetric analysis. This geometric isomer was also resolved into two enantiomers by Chiralpak OT. The other geometric isomer (mp 80-81 °C) could not be resolved by the use of both chiral packings. We assigned the structure of



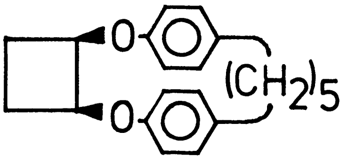
1a-d



2a-d

a; Ar = C_6H_5 b; Ar = 4-ClC_6H_4

c; Ar = 4-BrC_6H_4 d; Ar = 4-$C_3H_7C_6H_4$



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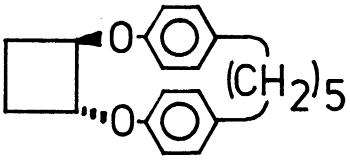

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trans-1,2-diphenoxycyclobutane to the optically resolved isomer and cis-1,2-diphenoxycyclobutane to the unresolved isomer. In a similar manner, p-substituted trans-1,2-diaryloxycyclobutanes 2b-d and trans-fused bicyclic compound 4 were resolved into two enantiomers, but the corresponding cis-isomers 1b-d and 3 could not be resolved. Recently, Farid and his co-workers have determined the structure of trans-1,2-diphenoxycyclobutane 2a by a X-ray diffraction analysis. The physical properties of this compound agreed with those of the compound assigned above.[11] Thus, the problem with regard to the stereochemical assignment of the cyclobutane derivatives has been solved by applying both optical resolution and X-ray analysis.

The stereoconfiguration of the cyclobutane compounds previously reported by us on the basis of their ^{1}H NMR data should be revised; the trans isomers should be corrected to the cis isomers and vice versa.[12] It is thus worthwhile to note that the optical resolution by means of HPLC can serve as an attractive tool for the assignment of the stereoconfiguration of compounds such as cyclobutane derivatives, in which the ^{1}H NMR spectral data may lead to erroneous conclusion.

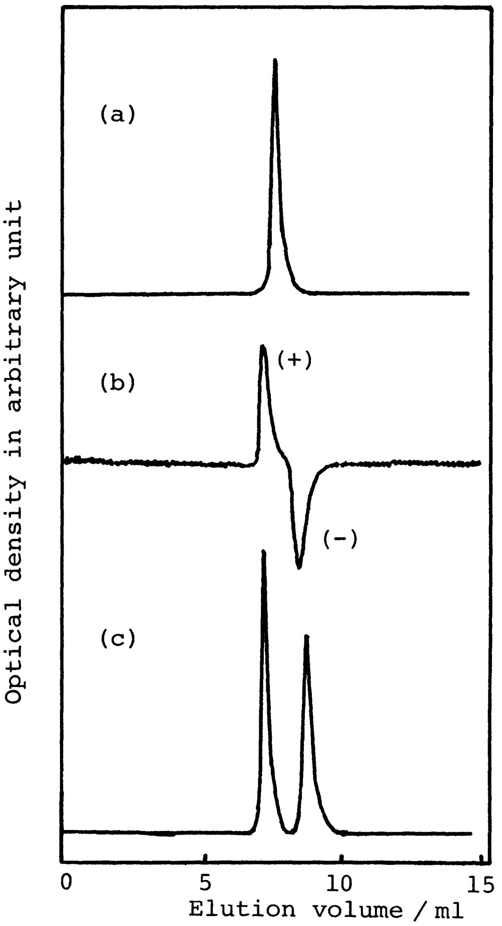


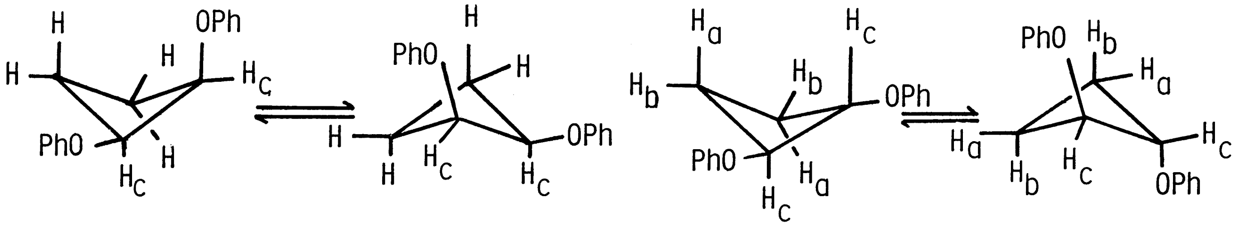
Fig. 1. Chromatograms of 1a and 2a on Chiralcel OB column (250 mm x 4.6 mm(d.i.)): Eluent, MeOH: Flow rate, 0.8 ml/min: (a) 1a (a UV (260 nm) detector was used), (b) 2a (a polarimetric detector was used), (c) 2a (a UV (260 nm) detector was used).

Table 1. ^{1}H NMR Spectral Data for the Cyclobutane Compounds in $CDCl_3$[a]

Compd	Chemical shift / δ			
	H_a	H_b	H_c	PhO or MeO
1a	2.31-2.38		4.92-4.95	6.85-6.95 7.22-7.26
2a	1.73-1.78	2.38-2.43	4.68-4.72	6.93-6.97 7.24-7.29
5	1.78-1.98		3.70-3.90	3.22
6	1.02-1.50	1.70-2.05	3.39-3.62	3.18

a) Tetramethylsilane (TMS) was used as an internal standard.

The ^{1}H NMR spectra of 1a and 2a can now be explained on the basis of the correct structures which have puckered conformations (Fig. 2): All the methylene hydrogens of 1a exhibit almost the same chemical shift due to 1,3-dipseudoaxial and 1,2-dipseudoequatorial interactions between methylene hydrogens and O-atoms of phenoxy groups. On the other hand, two methylene hydrogens of 2a (H_a) shift to upfield more than those of 1a. This is because H_a hydrogens in 2a are not affected by magnetic anisotropy of O-atoms of phenoxy groups. Interestingly, cis- and trans-1,2-dimethoxycyclobutanes (5 and 6) show very similar ^{1}H NMR spectral patterns to those of 1a and 2a (Table 1). Thus, the stereochemical structures of geometric isomers of 1,2-dialkoxycyclobutanes, 1-alkoxy-2-aryloxycyclobutanes, and cyclobutano crown ethers were assigned by comparison of their ^{1}H NMR spectral data with those of 1a and 2a, although the optical resolution of trans isomers of these compounds by HPLC failed.



1a 2a

Fig. 2. Puckered form of 1a and 2a.

To examine the relative configuration of phenoxy groups in 1a and 2a, we measured the fluorescence spectra of 1a and 2a in cyclohexane at room temperature. The results are shown in Fig. 3. The relative intensity of the monomer fluorescence of 1a was about one tenth of that of 2a and the intramolecular excimer emission was observed at longer wavelength. On the other hand, the fluorescence spectrum of 2a was very similar to that of methoxybenzene and 1,2-diphenoxyethane. In this case, no excimer emission was observed. Intramolecular excimer fluorescence has been extensively investigated in recent years.$^{9)}$ However, to our knowledge, there is no example of intramolecular excimer formation between two phenyl groups connected by a four atom chain except [4.4]cyclophane.$^{13)}$ This result indicates that the puckered conformation of 1a is obviously responsible for the formation of emmisive excimer at room temperature.

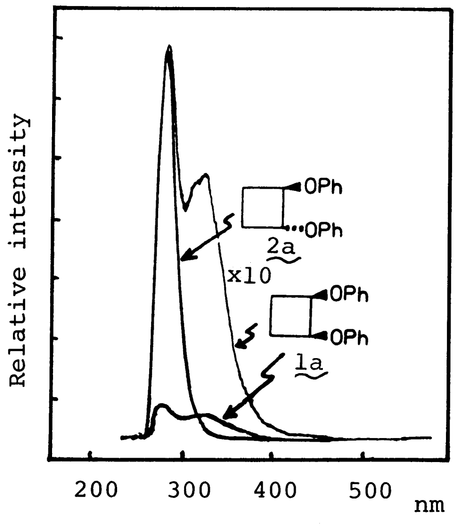


Fig. 3. Intramolecular excimer fluorescence spectra of 1a: [1a] = [2a] = 5 x 10^{-4} mol/dm^3 in deoxygenated cyclohexane solutions.

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References

1) K. Mizuno, J. Ogawa, and Y. Otsuji, Chem. Lett., 1979, 945; K. Mizuno, H. Ueda, and Y. Otsuji, ibid., 1981, 1237; K. Mizuno, H. Hashizume, and Y. Otsuji, J. Chem. Soc., Chem. Commun., 1983, 772; K. Mizuno, H. Kagano, T. Kasuga, and Y. Otsuji, Chem. Lett., 1983, 133; K. Mizuno, H. Hashizume, and Y. Otsuji, J. Chem. Soc., Chem. Commun., 1983, 977; K. Mizuno, H. Kagano, and Y. Otsuji, Tetrahedron Lett., 24, 3849(1983).

2) S. Kuwata, Y. Shigemitsu, and Y. Odaira, J. Chem. Soc., Chem. Commun., 1972, 2; J. Org. Chem., 38, 3801(1973).

3) S. Farid, S. E. Hartman, and T. R. Evans, "The Exciplex," ed by M. Gordon and W. R. Ware, Academic Press, New York(1975), p. 327; T. R. Evans, R. Wake, and O. Jaeckie, ibid., p. 345.

4) A. M. Draper, M. Ilyas, P. de Mayo, and V. Ramamurthy, J. Am. Chem. Soc., 106, 6222(1984); M. Ilyas and P. de Mayo, ibid., 107, 5093(1985); R. A. Barber, P. de Mayo, and K. Okada, J. Chem. Soc., Chem. Commun., 1982, 1073.

5) R. M. Moriarty, "Topics in Stereochemistry," ed by E. L. Eliel and N. L. Allinger, John Wiley & Sons, New York(1974), Vol. 8, p. 271.

6) Y. Okamoto, I. Okamoto, and H. Yuki, Chem. Lett., 1981, 835; Y. Okamoto, S. Honda, I. Okamoto, H. Yuki, S. Murata, and R. Noyori, J. Am. Chem. Soc., 103, 6971(1981).

7) R. Noyori, N. Sano, S. Murata, Y. Okamoto, H. Yuki, and T. Ito, Tetrahedron Lett., 29, 2969(1982); A. P. Schaap, S. Siddiqui, G. Prasad, A. F. Rahman, and J. P. Oliver, J. Am. Chem. Soc., 106, 6087(1984).

8) F. Hirayama, J. Chem. Phys., 42, 3163(1965).

9) Recent reviews of intramolecular excimer formation: F. C. De Schryver, N. Boens, and J. Put, Adv. Photochem., 10, 359(1977); S. W. Beavan, J. S. Hargreaves, and D. Phillips, ibid., 11, 207(1979).

10) The HPLC columns are commercially available from Daicel Chemical Industries, Ltd. In this study, 250 mm x 4.6 mm(d.i.) stainless steel columns packed with Chiralcel OB (microsilica coated with cellulose benzoate) and with Chiralpak OT(+) (microsilica coated with (+)-poly(triphenylmethyl methacrylate) were used.

11) S. L. Mattes, H. R. Luss, and S. Farid, J. Phys. Chem., 87, 4779(1983).

12) The mechanism and stereoselection of the photocyclodimerization of vinyl ethers will be reported in a full paper.

13) M. T. Vala, Jr., J. Haebig, and S. A. Rice, J. Chem. Phys., 43, 886(1965).

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