Ph_3PAuCl and Ph_3PAgCl do not form adducts with tetrachloro-1,2-benzoquinone.

Acknowledgment. This research was supported by Grant No. AM 12182 from the U. S. Public Health Service.

found in $(1,4\text{-}O_2C_6H_4)M(PPh_3)_2$ (M = Pd, Pt) and $(1,4\text{-}O_2C_{10}H_6)Pd(PPh_3)_2$: S. Takahashi and N. Hagihara, *J. Chem. Soc. Jap.*, **88**, 1306 (1967). In these complexes the *p*-quinones are undoubtedly coordinated through their olefinic portions[1] since $\nu_{C=O}$ suffers only a slight decrease of about 30 cm^{-1}. Their nmr spectra are also consistent with this mode of bonding.

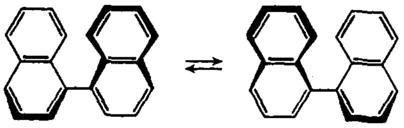
Y. S. Sohn, A. L. Balch*
Department of Chemistry, University of California
Davis, California 95616

Received October 22, 1970

Solid State Resolution of Racemic 1,1′-Binaphthyl

Sir:

1,1′-Binaphthyl is a dissymmetric molecule and the rotation which interconverts enantiomers is only moderately hindered. The *S*-(+) form[1] has been obtained by resolution of the 4,4′-diamino derivative using α-bromo-π-camphorsulfonic acid followed by low-temperature deamination (through diazotization and hypophosphorous acid reduction).[2] (*S*)-(+)-1,1′-Binaphthyl has a half-life for racemization in solution of *ca.* 15 min at 50°.[2b,3]



S-(+) *R*-(−)

We report here that racemic binaphthyl may be resolved spontaneously into either of its optically active enantiomers simply by heating neat crystalline samples at 105–150°. Solid racemic binaphthyl can develop optical rotations as high as $[\alpha]_D$ ±245° and subsequently be held at temperatures up to its melting point of 159° without loss of activity.[4] Three experimental approaches demonstrate the remarkable ability of binaphthyl to resolve in the absence of any external influence.

Partial resolution of 1,1′-binaphthyl occurs during solidification of melted samples. For example, ten samples of 20 mg each in sealed vials were totally immersed in a bath at 175° for several minutes in order to melt and destroy all seed crystals. The completely melted samples were transferred to a 150° bath and crystallization was induced by touching each sample vial with a piece of Dry Ice. After 20 hr at 150°, the samples were dissolved in benzene and the specific rotations obtained were $[\alpha]_D$ −128, −17, +5, −76, −170, −124, −147, −115, +94, and −97° (benzene, 7 mg/ml). Other sets of samples gave similar scatterings of + and − rotations.[5]

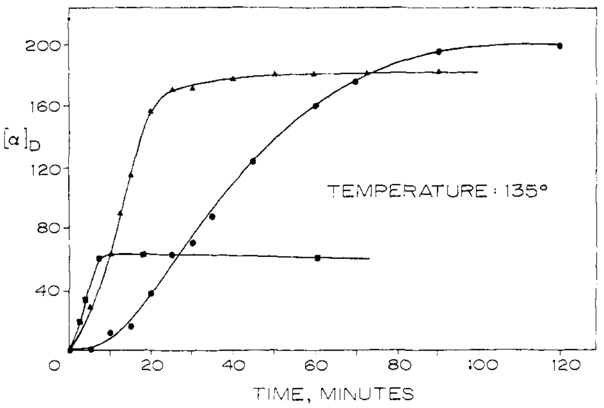


Figure 1. Development of optical activity in samples of neat, crystalline 1,1′-binaphthyl at 135°: ●, samples as crystallized from acetone;[8] ▲, same material ground into smaller crystals; ■, more finely ground samples. $[\alpha]_D$ is the specific rotation of an individual sample dissolved in benzene for analysis of optical activity.

A second approach utilizing the polymorphic nature[6] of the (*R*,*S*)-binaphthyl system involves systematic enhancement of optical activity and produces larger quantities of highly resolved binaphthyl. Solid samples containing the low-melting form (mp 145°) were heated to 150°. At this temperature the racemic low form melts to a metastable liquid, which in turn crystallizes to the high melting (mp 159°) potentially[7] optically active form. An optical activity is produced which is at least as great as that of starting material. For example, binaphthyl with an initial rotation of $[\alpha]_D$ 0.0° gave, after 2 hr at 150°, material with a specific rotation of +42°. Recrystallization from pentane is easily carried out so that there is no appreciable loss of optical activity. A crystalline mixture of racemic low-melting form and resolved high-melting form is obtained so that alternately recrystallizing from pentane between 35 and 0° and heating the neat solid to 150° for 2 hr boosted the rotation successively to +112, +186, and +194°. Initial use of + or − seed leads to production of the corresponding enantiomer.

The conversion of racemic solid binaphthyl to the optically active *S*-(+) or *R*(−) form is also possible at temperatures below 145° where liquid phase is less stable than any solid form, *i.e.*, the resolution occurs in the solid state. Figure 1 shows the development of optical rotation in a set of sealed neat samples of binaphthyl held at 135°. The binaphthyl used had $[\alpha]_D$ +1.4° and was obtained by crystallization from acetone at −70° from a 0.056 *M* solution with initial activity of $[\alpha]_D$ +9.4°.[8] X-Ray powder photographs

---

(1) H. Akimoto, T. Shioiri, Y. Iitaka, and S. Yamada, *Tetrahedron Lett.*, 97 (1968).

(2) (a) W. Theilacker and R. Hopp, *Chem. Ber.*, **92**, 2293 (1959); (b) A. S. Cooke and M. M. Harris, *J. Chem. Soc.*, 2365 (1963); A. K. Colter and L. M. Clemens, *J. Amer. Chem. Soc.*, **87**, 847 (1965).

(3) A. K. Colter and L. M. Clemens, *J. Phys. Chem.*, **68**, 651 (1964).

(4) This behavior is in contrast to that of *trans*-5-norbornene-2,3-dicarboxylic acid, which undergoes racemization in the solid state; R. E. Pincock, M.-M. Tong, and K. R. Wilson, *J. Amer. Chem. Soc.*, in press.

(5) The highest rotation at 5893 Å reported for samples of (+)-binaphthyl obtained by the classical resolution procedure is $[\alpha]_D$ +192°.[2c] Cooke and Harris[2b] report [α] +245° at 5791 Å.

(6) Two crystalline forms of 1,1′-binaphthyl, with mp 145 and 159°, are known: Y. Badar, C. C. K. Ling, A. S. Cooke, and M. M. Harris, *J. Chem. Soc.*, 1543 (1965). The low-melting form is established as an *R*,*S* racemic compound: K. A. Kerr and J. M. Robertson, *ibid.*, *B*, 1146 (1969).

(7) From our results the high-melting form is a eutectic system of various amounts of (*R*)- and (*S*)-binaphthyl. If the sample produced were an equimolar mixture of *R* and *S* crystals it would be optically inactive. If, as is experimentally almost always the case, an excess of *R* (or *S*) crystals were produced the sample would be optically active.

(8) Samples of binaphthyl obtained by this procedure do not always develop high rotations in an orderly manner as illustrated in Figure 1. However, similarly seeded samples of binaphthyl develop some activity in the desired direction.

and differential scanning calorimetry show this sample to be essentially all in the low-melting form. When heated at 105–140° the solid → solid transformation of the low- to high-melting forms of binaphthyl occurs and an optimum distribution of + seed crystals promotes the solid state resolution. At 105° a final rotation of $[\alpha]_D$ +220° (benzene) is attained in 12 days.

The last two experiments described are made possible by the polymorphic phase properties of binaphthyl. These are: (1) a racemic *R,S* compound, mp 145° (*i.e.*, the "low-melting form") which is easily obtainable at room temperature by crystallization from pentane but is metastable above *ca.* 90°; and (2) a eutectic type mixture of separate crystals of *R* and *S* enantiomers, mp 159°[9] (*i.e.*, "high-melting form") which is the stable phase above *ca.* 90° and which is produced readily either by solidification of the metastable melt or by maintaining the low-melting form at 105–145°. The results show that resolutions are possible during the following phase changes: transformation of the supercooled melt to high-melting form; transformation of the low-melting form to melt and then to the high-melting form; and the direct solid state transformation of the metastable low-melting form to the stable high-melting form.

These resolutions also depend on the interconversion of enantiomers which occurs rapidly in the melt and apparently also at the interface of the solid → solid phase transformation. Autocatalytic growth of predominantly one enantiomeric solid is prompted by seed crystals which have been added (or otherwise happen to develop first). Even though the two enantiomers have equivalent free energy, the growth of one may be kinetically induced by the presence of only one enantiomeric surface. The kinetic details of this type of resolution are complex (*e.g.*, see Figure 1). However, it is clear that the highly stereospecific character of the solid state promotes the development of optically active binaphthyl even at temperatures near 150° where the half-life for racemization in the melt is about 0.5 sec.

This solid state resolution illustrates some possibilities of specific melt → solid and solid → solid reactions. The solid → solid resolution definitely depends on the special properties of the binaphthyl phase system (*i.e.*, on the existence of a metastable racemate which transforms into a eutectic-type form). However, the growth of one of two rapidly interconverting enantiomers by spontaneous crystallization from a melt or solution[10] may be more general than commonly supposed and the method may be especially useful with compounds difficult to resolve by other means. It is also of interest that this example of binaphthyl resolution is an illustration of a hypothetical scheme for the selection of one enantiomorph in the genesis of optically active molecules.[11]

Acknowledgments. Financial aid from the National Research Council of Canada and the Air Force Office of Scientific Research (U.S.) is gratefully acknowledged. We thank the Alfred P. Sloan Foundation for a fellowship (to R. E. P.) and the National Research Council and the H. R. MacMillan Family Fund (University of B. C.) for fellowships (to K. R. W.).

---

[9] In this eutectic system of (*R*)- and (*S*)-binaphthyl, the melting points of samples with any per cent composition are experimentally the same (*ca.* 159°). This is because a very rapid development of racemic melt depresses the melting point of resolved or partially resolved binaphthyl to that of the 50% *R*–50% *S* optically inactive mixture (mp 159°). The equilibrium melting point of pure *R* (or *S*) compound is unobtainable.

[10] For spontaneous resolution from solution, Havinga has described the necessary conditions and presented the example of spontaneous deposition of optically active methylethylallylanilinium iodide; see E. Havinga, *Biochim. Biophys. Acta*, 13, 171 (1954). Partial resolutions of rapidly interconverting enantiometers have also been achieved by mechanical separations of single crystals: A. C. D. Newman and H. M. Powell, *J. Chem. Soc.*, 3747 (1952). Resolution of optical isomers by crystallization procedures is reviewed by R. M. Secor, *Chem. Rev.*, 63, 297 (1963).

[11] M. Calvin, "Chemical Evolution," Oxford University Press, Oxford, England, 1969, p 150.

Richard E. Pincock,* Keith R. Wilson
Department of Chemistry, University of British Columbia
Vancouver 8, Canada

Received November 5, 1970

Thermal Reorganization of *cis*-Bicyclo[6.2.0]deca-2,4,6-triene. Energetics of Allowed and Nonallowed Thermal $6\pi + 2\sigma \rightarrow 8\pi$ Electrocyclic Reactions

Sir:

Recently, a number of groups[1–7] have considered the important question of the energetic advantage of allowed relative to related nonallowed thermal electrocyclic reactions.[8] A major difficulty encountered in the problem concerns the fact that nonallowed processes are generally not observed and therefore only a minimum energy difference between alternate pathways can be obtained. We now report a slightly different approach to this problem which leads to a considerably larger estimate for the value for $6\pi + 2\sigma \rightarrow 8\pi$ electrocyclic reactions than previously reported.[5]

When *cis*-bicyclo[6.2.0]deca-2,4,6-triene (**1**)[9] was heated at 154° (1% (v/v) in octane) a single product, **3**, was initially observed. The structure of **3** was assigned on the basis of its uv ($\lambda_{\max}^{\text{hexane}}$ 259.5 nm (ϵ 3700)) and nmr (CCl_4, τ 3.91–4.48 (6 H, olefinic), 7.33 (d, 1 H, diallylic bridgehead, J = 18 Hz), 7.53–8.03 (3 H, allylic), 8.75–9.03 (2 H, methylene)) spectra and catalytic hydrogenation (3 mol equiv) to >94% *trans*-decalin.

The almost exclusive formation of a trans-fused product, **3**, from **1** is in marked contrast to the thermal behavior of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**5**) which affords *cis*-8,9-dihydroindene as the major product.[10] A reasonable mechanism for the former conversion, which is analogous to mechanisms suggested for the rearrangements of **6**[11] and of 9,9-dialkyl derivatives of

---

(1) G. R. Branton, H. M. Frey, D. C. Montague, and I. D. R. Stevens, *Trans. Faraday Soc.*, 62, 659 (1966).

(2) J. I. Brauman and D. M. Golden, *J. Amer. Chem. Soc.*, 90, 1920 (1968).

(3) E. C. Lupton, Jr., *Tetrahedron Lett.*, 4209 (1968).

(4) G. A. Doorakian and H. H. Freedman, *J. Amer. Chem. Soc.*, **90**, 5310, 6896 (1968).

(5) A. Dahmen and R. Huisgen, *Tetrahedron Lett.*, 1465 (1969).

(6) N. Rieber, J. Alberts, J. A. Lipsky, and D. M. Lemal, *J. Amer. Chem. Soc.*, 91, 5668 (1969).

(7) W. L. Mock, *ibid.*, 92, 3807 (1970).

(8) For a review see R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim, 1970.

(9) S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **92**, 7612 (1970).

(10) (a) E. Vogel and H. Kiefer, *Angew. Chem.*, 73, 548 (1961); (b) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Lett.*, 673 (1963); (c) W. Grimme, *Chem. Ber.*, **100**, 113 (1967).

(11) (a) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Amer. Chem. Soc.*, **89**, 4804 (1967); 90, 1680 (1968); (b) S. Masamune,