16: m.p. 81 – 83 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.72$ (s, 3H), 1.04 (s, 3H), 1.18 (s, 3H), 1.56 (s, 3H), 1.70 – 1.90 (m, 3H), 2.04 – 2.11 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 23.1$, 28.5, 29.3, 30.9, 39.2, 41.7, 44.2, 48.0, 90.0; IR (KBr): $\tilde{\nu} = 1123\ cm^{-1}$ (S=O); elemental analysis (%) calcd for $C_9H_{16}OS_2$: C 52.90, H 7.89; found: C 53.51, H 8.00.

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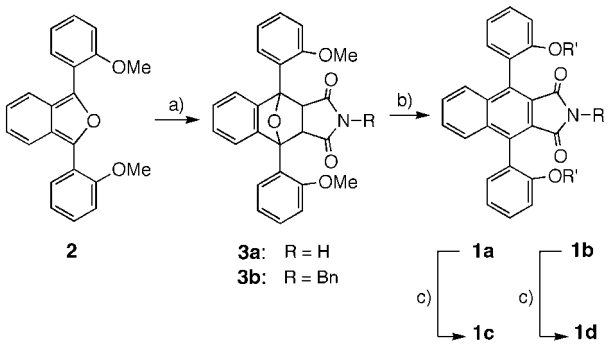
Solid-State Isomerization of Atropodiastereomers: Effective Diastereoselection through Polymorphic Transformations**

Cathy Einhorn, André Durif, Marie-Thérèse Averbuch, and Jacques Einhorn*

Polymorphism is a fascinating phenomenon accompanied by a lot of strange manifestations.[1] It is generally defined as the existence of a given compound in more than one crystalline form. In conformational polymorphs,[2] a given molecular compound adopts different conformations in different polymorphs. But, at a molecular level, conformational changes may involve quite high energy barriers, allowing in some cases the isolation of separate stereoisomers (atropisomers) which do not interconvert rapidly in solution at room temperature, but do so if enough energy is supplied. Herein we report solid-state thermal isomerizations of compounds **1**, which present such a type of atropisomerism. These isomerizations have features reminiscent of polymorphic transformations, although not involving polymorphs in the usual sense of the word.[3]

As depicted in Scheme 1, the synthesis of **1** has been achieved by Diels – Alder reactions between isobenzofuran **2** and maleimide or *N*-benzylmaleimide, giving adducts **3a** or **3b** in good yields. Their aromatization under strongly acidic conditions furnished **1a** and **1b** quantitatively. Demethylation of **1a** and **1b** gave diphenols **1c** and **1d** in high yields.



Scheme 1. Reagents, conditions, and yields: a) for **3a**: 1 equiv maleimide, toluene, RT, 6 h, 96%; for **3b**: 1 equiv *N*-benzylmaleimide, toluene, RT, 6 h, 81%; b) 6 equiv $MeSO_3H$, CH_2Cl_2, RT, 12 h, >99% for **1a**, >99% for **1b**; c) 3 equiv BBr_3, CH_2Cl_2, −78 °C to RT, 15 h, 98% for **1c**, 99% for **1d**. Full details can be found in the Supporting Information. RT = room temperature.

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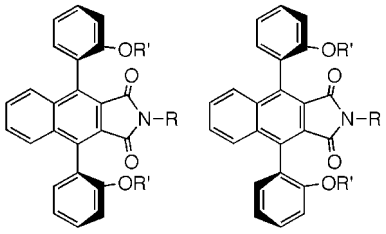


cis-**1** *trans*-**1**

a: R = H, R' = Me; **b**: R = Bn, R' = Me
c: R = H, R' = H; **d**: R = Bn, R' = H

For each compound of the series **1a**–**d**, the atropisomerization barrier was high enough to allow isolation of the diastereomeric *cis* and *trans* isomers. None of these showed noticeable interconversion in solution after one day at 20 °C. On the other hand, fast equilibration occurred in boiling toluene (b.p. 111 °C), leading, after two hours, to a 45:55 *cis*:*trans* ratio for **1a** and **1b** (Table 1, entries 1, 2 and 10), and to a nearly 50:50 ratio for **1c** and **1d** (Table 1, entries 12 and 14). As both diastereomers of **1a** are crystalline solids with high melting points (> 250 °C), we have also investigated their isomerization in the solid state. When pure *cis*-**1a**, as a microcrystalline powder, was heated at 111 °C for two hours, small amounts of *trans*-**1a** formed but the diastereomeric ratio was far from that of the solution equilibrium. The isomerization rate increased as the temperature was raised: a *cis*:*trans* ratio of about 70:30 was obtained after one hour at 180 °C. More surprisingly, after 15 hours at 180 °C, the ratio was 10:90 in favor of the *trans* isomer, having overtaken the solution equilibrium ratio! Further heating at 180 °C for two days led to an almost complete isomerization of the sample (*cis*:*trans* 1:99) (Table 1, entries 3–6). During these experiments, no macroscopic changes of the sample, in particular no melting (even partial) were noticed. When similar experiments were performed with solid *trans*-**1a**, no isomerization at all was noticed (Table 1, entry 7). Heating *cis*-**1a** or *trans*-**1a** up to complete melting (> 285 °C) and fast cooling of the samples gave the same ratio as that of the solution equilibrium (*cis*:*trans* 45:55)(Table 1, entries 8 and 9). A similar behavior was found with other compounds of the series: A 5:95 ratio was obtained after heating a 45:55 mixture of *cis*-**1b**:*trans*-**1b** in the solid state for two days at 180 °C (Table 1, entry 11). Under identical conditions, a 95:5 ratio in favor of the *cis* isomer was obtained for **1c**, and **1d** gave almost pure *cis* isomer (Table 1, entries 13 and 15).

Table 1. Thermal isomerization of compounds **1a**–**d**.

Entry	Compound	Starting *cis*:*trans* ratio[a]	Isomerization conditions *T* [°C]/*t* [h]	Final *cis*:*trans* ratio[a]
1	**1a**	100:0	111/2[b]	45:55
2	**1a**	0:100	111/2[b]	45:55
3	**1a**	100:0	111/2[c]	98:2
4	**1a**	100:0	180/1[c]	70:30
5	**1a**	100:0	180/15[c]	10:90
6	**1a**	100:0	180/48[c]	1:99
7	**1a**	0:100	180/48[c]	0:100
8	**1a**	100:0	285/0.1[d]	45:55
9	**1a**	0:100	285/0.1[d]	45:55
10	**1b**	100:0	111/2[b]	45:55
11	**1b**	45:55	180/48[c]	5:95
12	**1c**	0:100	111/2[b]	50:50
13	**1c**	50:50	180/48[c]	95:5
14	**1d**	0:100	111/2[b]	50:50
15	**1d**	40:60	180/48[c]	ca. 100:0

[a] Determined by HPLC analysis. [b] Solution isomerization in refluxing toluene. [c] Heating in the solid state. [d] Complete melting of the sample, followed by fast cooling.

On a Kofler hot bench "instantaneous" melting points of 250–252 °C for *cis*-**1a** and > 270 °C for *trans*-**1a** were obtained. For *trans*-**1a**, differential scanning calorimetry (DSC) gave sharp heat absorption at the melting point (281.4 °C) without any noticeable phase transition below this temperature. For *cis*-**1a** progressive heat absorption occurred within a large temperature interval, followed by a sharp peak with a maximum at 283.6 °C (Figure 1). These results suggest a solid-state transformation of *cis*-**1a**, yielding *trans*-**1a** in the same crystalline form as that obtained by room temperature crystallization of *trans*-**1a**, as confirmed by X-ray studies: Single-crystal X-ray diffraction analysis has been performed for both diastereomers of **1a**.[7] The crystal of *trans*-**1a** was monoclinic (space group $P2_1/n$, $a = 10.948(2)$, $b = 8.269(3)$, $c = 11.165(3)$ Å, $\beta = 90.98(2)^\circ$, $V = 1010.6(4)$ Å^3, $Z = 2$). The enantiomers of *trans*-**1a** are statistically interchangeable at each molecular site of the lattice, by exchanging the position

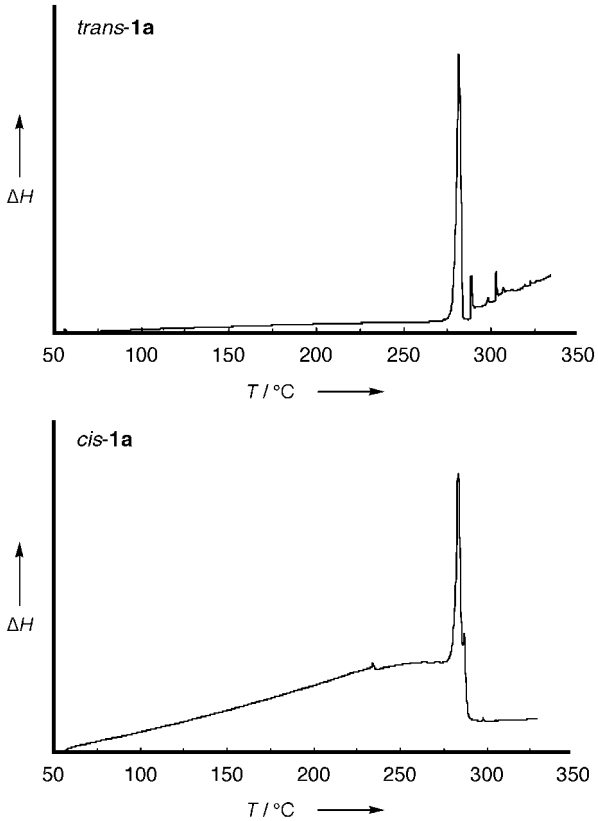


Figure 1. DSC heating thermograms of *trans*-**1a** and *cis*-**1a**. Heating rate 5 K min^{-1}.

of the fused benzene ring and that of the imide moiety. Compound *trans*-**1a** crystallized as a pseudoracemate or solid solution of enantiomers, a rather uncommon behavior of chiral compounds in the solid state (Figure 2a).[8] The

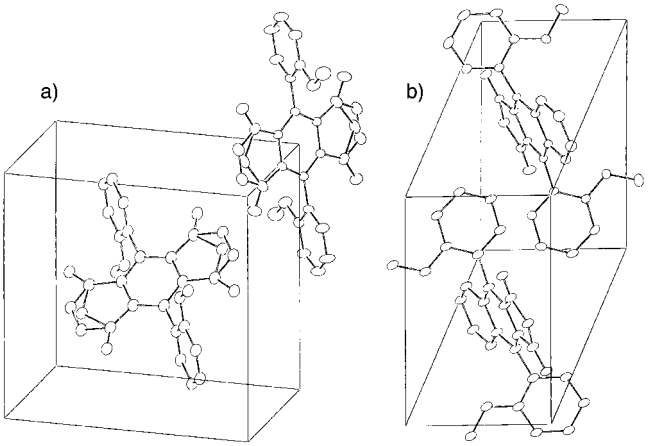
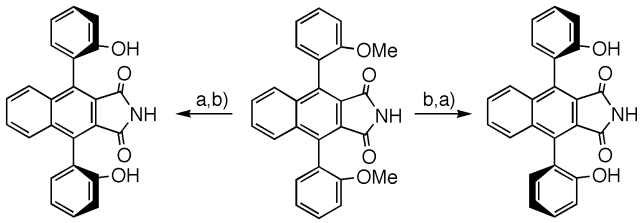


Figure 2. Crystal packing diagram of a) *trans*-**1a** and b) *cis*-**1a**. Hydrogen atoms have been omitted for clarity.

crystal of *cis*-**1a** was triclinic (space group $P\bar{1}$, $a = 9.136(4)$, $b = 11.029(5)$, $c = 10.368(5)$ Å, $\alpha = 100.37(2)$, $\beta = 111.79(2)$, $\gamma = 111.04(2)^\circ$, $V = 996.5(9)$ Å^3, $Z = 2$; Figure 2b). A sample of polycrystalline *cis*-**1a**, heated for two days at 180 °C, was next submitted to X-ray powder diffraction. The diffraction pattern of this sample was identical to that of a simulation obtained from the single-crystal X-ray diffraction data of *trans*-**1a**.

The preceding results can be rationalized as follows. At room temperature, the diastereomeric *cis* and *trans* isomers are separate compounds, in solution and in the solid state. Each of them has its own physicochemical properties, in particular its own crystalline form. At higher temperatures, the isomers interconvert rapidly in solution. Therefore, their identity as separate compounds vanishes and they should then rather be considered as two conformers of a unique compound in conformational equilibrium. Consequently, at a temperature at which interconversion is fast in solution, crystalline *cis* and *trans* isomers can be considered as two conformational polymorphs of that unique compound. Two polymorphic forms having in general different stabilities, there will be a tendency of the metastable crystals to transform into the more stable ones.[1] The consequence is that one crystalline form will disappear at the expense of the other, with, in the present case, concomitant selection of one conformer at the expense of the other. After cooling, the diastereomeric ratio of the macroscopic sample remains "frozen" at the point it had reached in the solid–solid transformation. In the melt, the ordering effect of the crystal lattice disappears and equilibration occurs very rapidly. Fast cooling "freezes" then the equilibrium reached in the melt.

An interesting point to be emphasized is that the same type of behavior has been found throughout the series **1a–d**, either the *cis* or the *trans* isomer being favored. Indeed, the driving forces that are operative in these solid-state isomerizations are related to crystal packing effects. These collective processes allow an efficient selection of stereoisomers which, otherwise, are obtained in nearly equal amounts by solution equilibration. As depicted in Scheme 2, either *cis*-**1c** or *trans*-**1c**, both in high diastereomeric purity, is obtained starting from an identical sample of **1a**, simply by carrying out solid-state isomerization *after* or *before* performing O-demethylation.



cis-**1c** dr 95:5 — **1a** *cis*:*trans* 45:55 — *trans*-**1c** dr 1:99

Scheme 2. Reagents and conditions: a) 3 equiv BBr_3, CH_2Cl_2, -78 °C to RT, 15 h; b) solid-state isomerization, 180 °C, 2 days.

As far as we know, this constitutes the first description of polymorphic transformations applied to a selection of atropisomers, which have such a long persistence in solution at room temperature.[9] It could offer new opportunities for controlling the relative stereochemistry of two or more stereogenic axes—structural features found among various natural and synthetic compounds.

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[7] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149632 (*cis*-**1a**) and CCDC-149633 (*trans*-**1a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

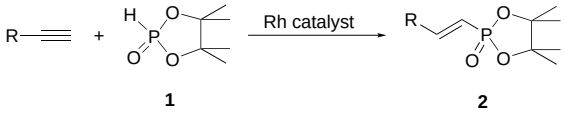
[8] *Enantiomers, Racemates and Resolutions* (Eds.: J. Jacques, A. Collet, S. H. Wilen), Wiley, New York, **1981**, pp. 104–131.

[9] A solid-state polymorphic transformation of racemic 1,1′-binaphthyl with spontaneous appearance of optical activity has been described. See ref. [6c]. See also: R. B. Kress, E. N. Duesler, M. C. Etter, I. C. Paul, D. Y. Curtin, *J. Am. Chem. Soc.* **1980**, *102*, 7709–7714. However, half-life for racemization of 1,1′-binaphthyl in solution is only about 2.5 h at 20 °C.

Rhodium-Catalyzed Hydrophosphorylation of Terminal Alkynes Leading to Highly Selective Formation of (*E*)-Alkenylphosphonates: Complete Reversal of Regioselectivity to the Palladium-Catalyzed Counterpart**

Chang-Qiu Zhao, Li-Biao Han,* Midori Goto, and Masato Tanaka*

Transition metal catalyzed addition reactions of heteroatom compounds across unsaturated carbon–carbon linkages are emerging rapidly as some of the most attractive, versatile, and clean methods for constructing carbon–heteroatom bonds.[1] However, similar methodologies for phosphorus compounds, which play an important role in our daily life, are limited.[1f] All of the successful metal-catalyzed additions of P^V compounds so far reported have been conducted by employing palladium catalysts, usually at elevated temperatures.[1f] Taking advantage of the exceptionally high reactivity of the five-membered cyclic hydrogen phosphonate **1**,[2] we found the first successful rhodium-catalyzed hydrophosphorylation of alkynes, which affords high yields of the corresponding (*E*)-alkenylphosphonates **2** with excellent regio- and stereoselectivities [Eq. (1)]. The reaction readily



1 **2** (1)

takes place even at room temperature with a complete regiochemical reversal to its palladium-catalyzed counterpart.[3] Alkenylphosphonates, which are not readily accessible by conventional methods, are key intermediates for the preparation of the commercial antibacterial agent Fosfomycin and analogues.[4] The synthetic and biological utilities of alkenylphosphonates are also well documented.[5]

A mixture of **1** and one equivalent of phenylacetylene in toluene was stirred in the presence of $[RhCl(PPh_3)_3]$ (3 mol%) at room temperature for 2 h to give a clear yellow solution, in which the corresponding product 2-phenyl-1-ethenylphosphonate (**2a**) was formed exclusively in 31% yield. Its yield increased to 43% after 24 h, but further extension to 48 h resulted in only a marginal increase. However, upon heating at 80 °C, the same mixture resumed the reaction to give a quantitative yield of **2a** after 1 h.

The solvent employed significantly influenced the progress of the reaction. In THF, the reaction kept proceeding smoothly, albeit slowly, to reach 97% yield after 48 h at room temperature. When dichloromethane, acetonitrile, and in particular, acetone were used as the solvents, great enhancement of the reaction rate was realized. Hydrophosphorylation in acetone was complete after a few hours at room temperature and gave the adduct quantitatively.

Wilkinson-type complexes $[RhX(PPh_3)_3]$ exhibited high catalytic activity. Other PPh_3-ligated Rh^I complexes such as $[RhCl(CO)(PPh_3)_2]$ also formed **2a** in moderate yields at elevated temperatures. However, the phosphane-free rhodium complexes $[\{Rh(cod)Cl\}_2]$ (cod = 1,5-cyclooctadiene) and $[\{Rh(CH_2{=}CH_2)_2Cl\}_2]$ were inactive. The cationic rhodium complex $[\{Rh(cod)_2\}]^+(OTf)^-$ ($Tf = CF_3SO_2$), used either alone or in combination with PPh_3, also did not show catalytic activity.

The rhodium-catalyzed hydrophosphorylation proved generally applicable to a variety of alkynes for synthesizing alkenylphosphonates at room temperature (Table 1).[5, 6] Thus, the $[RhBr(PPh_3)_3]$-catalyzed reaction of unsubstituted acetylene (commercial acetylene gas from a cylinder was used without purification) efficiently proceeded in acetone to form the corresponding vinylphosphonate in a high yield. Substituted terminal alkynes, both aliphatic and aromatic, reacted as efficiently to afford *trans* adducts by the regioselective attack of the phosphorus center on the terminal carbon atom of the

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