

ENANTIOSELECTIVE REARRANGEMENT OF 2,2'-HYDRAZONAPHTHALENE

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Abstract: 2,2'-Hydrazonaphthalene rearranges in the presence of (+)-camphor-10-sulfonic acid to give 2,2'-diamino-1,1'-binaphthyl with optical yields up to 15% in the (-)-enantiomer. Enantioselectivity is dependent on temperature and solvent.

Chiral binaphthyls have been the object of intensive research and a recent publication¹ reported a concise survey of methods currently available for their enantioselective production. Surprisingly, no acid-catalyzed or thermal rearrangements of hydrazoarenes (benzidine and related rearrangements) have ever, not even in theory, been considered as suitable methods for this purpose². This paper reports the preliminary results of a few experiments planned to verify this possibility. The approach was as follows: a N,N'-diarylhydrazine was needed which under very mild conditions could undergo the benzidine or a benzidine-like rearrangement to afford a chiral product endowed with good optical stability; enantioselectivity could simply be induced by an optically active acid capable of promoting rearrangement. 2,2'-Hydrazonaphthalene 1 met these requirements: it was found to rearrange to 2,2'-diamino-1,1'-binaphthyl 2 in the presence of (+)-camphor-10-sulfonic acid at very low temperatures (-40/-50). Under these conditions the formation of 7H-dibenzo[c,g]carbazole 3, the only by-product of thermal and acid-catalyzed rearrangement of 1 to 2³, is considerably reduced. The evaluation of the optical yields was greatly facilitated due to the fact that 2 is optically stable at room temperature⁴ and its specific rotation⁵ is very high ($[\alpha]_D = \pm 183^\circ$, 1% benzene). Furthermore the absolute configuration of pure enantiomers is already known⁶.

Preliminary experiments (summarized in the Table) demonstrated that the levorotatory enantiomer of 2 (absolute configuration S) was invariably produced in larger quantities; furthermore, although the enantiomeric excess is not impressive it is certainly significant and in line with other enantioselective routes to binaphthyl systems⁶.

Experimental parameters such as solvent and temperature influence the optical yields. Solvent effects are notable: the solvent that proved inefficient in producing a meaningful enantiomeric excess probably segregated the protonated substrate from the chiral acid anion, which was responsible for optical induction; the best results were obtained in dipolar aprotic solvents where optical yields up to 15% were observed. A decrease in the reaction temperature led to an increase in the optical yields. Experiments are currently under way to obtain additional information concerning the effect of the structure of the substrate, that of chiral acid and the nature of the solvent, in order to draw an appropriate picture of the transition state controlling the reaction path.

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SOLVENT	TEMPERATURE, C°	TIME, h	% YIELD	% ee ^{b,c}
CH ₃ CN	-20	immediate	89	9
CH ₃ CN	-35	0.5	89	13
C ₂ H ₅ CN	-45	6	75	15
CH ₃ NO ₂	-20	immediate	65	7
CH ₃ COCH ₃	-55	3	89	12
C ₂ H ₅ OH	-40	1.5	90	2

a) Yields and % ee were not significantly influenced whether 1 or 2 moles of (+)-camphor-10-sulfonic acid were used.

b) Relative to (-)-S-enantiomer.

c) Rotations were determined in 2% benzene solution.

EXPERIMENTAL. A solution of (+)-camphor-10-sulfonic acid (anhydrous or monohydrate) (1.5 or 3.0 mmoles) in a suitable solvent (10-30 mL) was rapidly added to a cold stirred solution of 2,2'-hydrazonaphthalene³ **1** (0.5 mmoles) in the same solvent (10-30 mL). When the reaction was complete (TLC analysis), the solution was poured onto ice-cold 5% NH₄OH solution; the precipitate was extracted with Et₂O and the organic layer in turn was exhaustively extracted with a cold 5% HCl solution. Combined aqueous extracts were made alkaline with a cold 5% NH₄OH solution and the crude **2** was extracted several times with Et₂O. Combined organic layer were dried (Na₂SO₄) and evaporated under reduced pressure; the white solid residue, pure **2**, as shown by HPLC analysis (column: Merck LiChrosorb RP8; eluent: MeOH 65% - Ammonium phosphate pH 7.5 buffer solution 35%; UV detector: 254 nm), was submitted directly to rotation measurements^{7,8}.

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- 7) As **2** can crystallize as a conglomerate⁹, final crystallization was avoided so as not to affect the optical yields.
- 8) Blank experiments demonstrated the complete elimination of the (+)-camphorsulfonic acid.
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