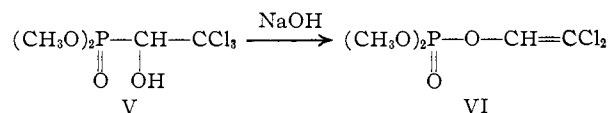


nate (V) to a phosphate (VI) under alkaline conditions.



It appears that these alkaline induced rearrangements of α -hydroxyphosphonates to phosphates may be of a general nature when the α -carbon is substituted with electron withdrawing groups such as $-\text{CN}$, $-\text{CCl}_3$, etc.

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RECEIVED DECEMBER 28, 1956

A GENERAL METHOD FOR ESTABLISHING THE ABSOLUTE CONFIGURATION OF OPTICALLY ACTIVE BIPHENYLS BY ASYMMETRIC SYNTHESIS

Sir:

We wish to report a general and direct chemical method for correlating the configuration of a biphenyl with that of a centrally asymmetric compound, and hence for the establishment of absolute configuration in the biphenyl series. The method, which is illustrated in the following sequence, involves neither creation nor destruction of biphenylic (axial) dissymmetry.

Methyl *RS*-6,6'-dinitro-2,2'-diphenate¹ was reduced with $\text{LiAlH}_4-\text{AlCl}_3$ to *RS*-6,6'-dinitro-2,2'-bis-(hydroxymethyl)-biphenyl² (m.p. 142–144°; found: C, 55.5; H, 3.9; N, 9.0) which was converted to the dibromide (m.p. 183–185°; found: C, 39.0; H, 2.5; N, 6.3) with concd. HBr . Ring closure to the iminonitrile (m.p. 304° dec.; found: C, 59.8; H, 3.2; N, 17.1) with KCN , followed by acid hydrolysis, gave *RS*-4',1''-dinitro-1,2,3,4-dibenz-1,3-cycloheptadiene-6-one (*RS*-DNDBCH-6-one), m.p. 234–236°; found: C, 60.4; H, 3.3; N, 9.2. Reduction with *i*-PrOH/ $\text{Al}(\text{i-PrO})_3$ gave *RS*-DNDBCH-6-ol, m.p. 199–200°; found: C, 60.0; H, 3.5; N, 9.2.

Treatment of *RS*-DNDBCH-6-one (951 mg.) with pinacolyl alcohol (14.0 g., $[\alpha]_{\text{D}}^{25} +7.73$)³ in the presence of $\text{Al}(\text{t-BuO})_3$ (717 mg.) in dioxane (52.4 g.) at 63° for seven hours, followed by chromatographic separation of the resulting product, afforded 139 mg. of DNDBCH-6-one, $[\alpha]_{\text{D}} +136^\circ$ (EtOAc), and 665 mg. of DNDBCH-6-ol, $[\alpha]_{\text{D}} -109^\circ$ (EtOAc). Reduction of the (+)-ketone with *i*-PrOH/ $\text{Al}(\text{i-PrO})_3$ yielded DNDBCH-6-ol, $[\alpha]_{\text{D}} +498^\circ$ (EtOAc). Finally, reduction of *RS*-DNDBCH-6-one with aluminum (+)-pinacoloxide

(1) We are here employing the nomenclature devised by R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 81 (1956), although alternative designations are also possible (G. E. McCasland, private communication).

(2) Independently prepared by D. C. Iffand (private communication) through reduction of the acid chloride with sodium trimethoxyborohydride.

(3) This enantiomer has the *S*-configuration, as shown, for example, by asymmetric synthesis; H. S. Mosher and E. La Combe, *THIS JOURNAL*, **72**, 3994 (1950).

for a twenty-five hour period gave only optically inactive DNDBCH-6-ol.

Inspection of a model of *S*-DBCH-6-one (Fig. 1 is a top view; the nitro groups are omitted for the sake of clarity) leads to the unambiguous predic-

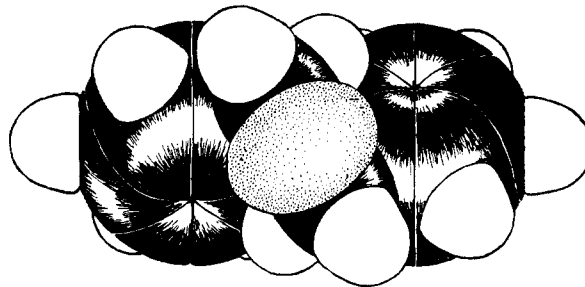


Fig. 1.

tion that hydrogen transfer to the carbonyl carbon via a Meerwein-Ponndorf-Verley type transition state⁴ on either face of the carbonyl group will be rendered energetically unfavorable owing to the necessity of accommodating the bulky *t*-butyl group on the side of the jutting phenyl, whereas for the *R*-isomer only the much smaller methyl group need thus be crowded. It can therefore be anticipated that reduction of the *R*-isomer will proceed initially more rapidly than reduction of the *S*-isomer. The experimental results are completely compatible with this view. Accordingly we assign (+)-DNDBCH-6-one the *S*-configuration and (–)-DNDBCH-6-ol the *R*-configuration.

The above transformations represent the first example of a novel and general principle for the configurational correlation of hindered biphenyls with compounds possessing only central asymmetry.⁵ Further related aspects are under active investigation in this Laboratory, as part of our program in biphenyl stereochemistry.⁶

This work was supported in part by a grant from The Trubek Laboratories.

(4) W. von E. Doering and R. W. Young, *ibid.*, **72**, 631 (1950).

(5) J. A. Berson, *ibid.*, **78**, 4170 (1956), has pointed out that analysis of transition states in the particular case of the thebaine-phenyl-dihydrothebaine interconversion permits configurational correlation of starting material and product, leading to an absolute configuration of the (generated) biphenyl moiety in the latter.

(6) K. Mislow, *Trans. N. Y. Acad. Sci.*, in press.

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RECEIVED JANUARY 23, 1957

MODIFIED NICKEL CATALYST FOR THE HYDROGENOLYSIS AND ALKYLATION OF AROMATIC HYDROCARBONS

Sir:

It was found that when small amounts of sulfur-containing compounds are added to a nickel hydrogenolysis catalyst the latter is "modified" in such a way as to catalyze reactions which until now were associated with strong acid catalysts. Some of the following reactions were observed to occur in the presence of the "modified" nickel catalyst: dealkylation, transalkylation, alkylation and internal alkylation of benzenoid hydrocarbons.

