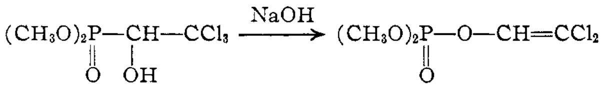
nate (V) to a phosphate (VI) under alkaline conditions.



$$(CH_3O)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{OH}{|}}{CH}-CCl_3 \xrightarrow{NaOH} (CH_3O)_2\underset{\underset{O}{\|}}{P}-O-CH=CCl_2$$

V VI

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—CN,—CCl_3, etc.

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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′-diphenate[1] was reduced with $LiAlH_4$–$AlCl_3$ to *RS*-6,6′-dinitro-2,2′-bis-(hydroxymethyl)-biphenyl[2] (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; H, 9.2. Reduction with *i*-PrOH/Al(*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., $[\alpha]^{29}\text{D}$ +7.73)[3] in the presence of Al(*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° (EtOAc), and 665 mg. of DNDBCH-6-ol, $[\alpha]\text{D}$ −109° (EtOAc). Reduction of the (+)-ketone with *i*-PrOH/Al(*i*-PrO)$_3$ yielded DNDBCH-6-ol, $[\alpha]\text{D}$ +498° (EtOAc). Finally, reduction of *RS*-DNDBCH-6-one with aluminum (+)-pinacoloxide 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 prediction that hydrogen transfer to the carbonyl carbon *via* a Meerwein–Ponndorf–Verley type transition state[4] 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.

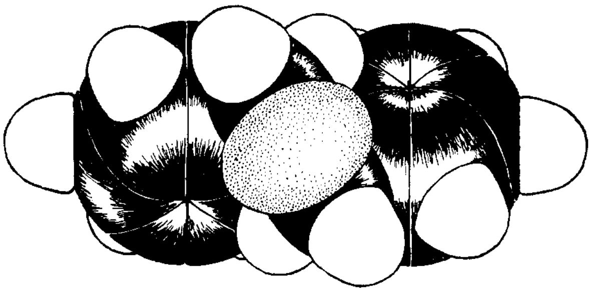

Fig. 1.

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]

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[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. Iffland (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).

[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 statesi n the particular case of the thebaine–phenyldihydrothebaine 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.

MODIFIED NICKEL CATALYST FOR THE HYDROGENOLYSIS AND ALKYLATION OF AROMATIC HYDROCARBONS

Sir:

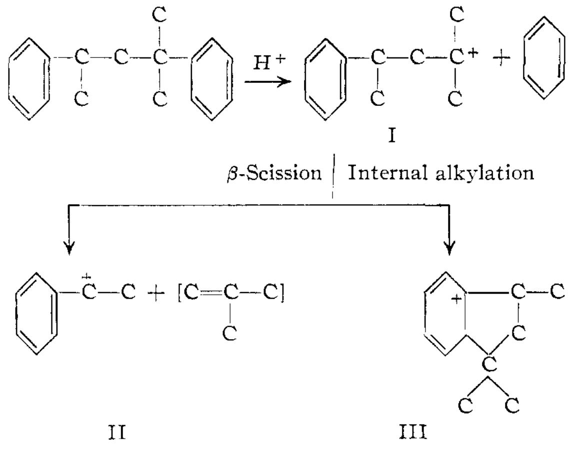
It was found that when small amounts of sulfur-containing compounds are added to a nickel hydrogenolysis catalyst the latter is "modified" in such a way as to catalyze reactions which until now were associated with strong acid catalysts. Some of the following reactions were observed to occur in the presence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

In the presence of the "modified" catalyst and hydrogen tertiary alkyl or cycloalkylarenes undergo hydrogenolysis (reductive dealkylation) most readily, secondary alkylarenes undergo only a partial hydrogenolysis while primary alkylarenes are stable under these conditions. The decreasing order of reactivity of alkylbenzenes, III > II > I, is characteristic of acid reactions.

The hydrogenolysis takes place under pressure of 10–75 atmospheres, at temperatures of 300–350° and in the presence of either nickel–kieselguhr, precipitated nickel or Raney nickel catalyst, "modified" by the addition of small amounts of thiophene to the reaction mixture. Thus, *tert*-butylbenzene yields at 350° 80% benzene 2-(*p*-tolyl)-2,4-dimethylpentane about 80% of toluene and 2,4-dimethylpentane and 1-methylcyclohexylbenzene yields 80% benzene and methylcyclohexane. Isopropylbenzene under similar conditions forms only 20% of benzene. This type of hydrogenolysis does not occur in the absence of sulfur-containing compounds.

This hydrogenolysis method can be used for a selective removal of one of the aromatic groups from a diarylcyclane in which one of the phenyl groups is attached to a tertiary and the other to a secondary carbon atom, *e.g.*, 1-methyl-1,3-diphenylcyclopentane formed benzene and 1-methyl-3-phenylcyclopentane. The hydrogenolysis can thus serve as a novel degradation method for determining structures of complex hydrocarbons.

The modified nickel catalyst can also act as a cycloalkylating catalyst. The hydrogenolysis of 10 g. of 2-methyl-2,4-diphenylpentane under 70 atmospheres of hydrogen and in the presence of 1.1 g. of nickel–kieselguhr catalyst and 0.2 g. of thiophene yielded a mixture of hydrocarbons which was composed of 41 mole % benzene, 24% ethylbenzene, 4% isopropylbenzene and 15% of about equal amount of 1,1,3-indan and hexylbenzene, the latter being composed mainly of 2-methyl-2-phenylpentane. The reactions leading to the various hydrocarbons may be explained by the usual acidic mechanism[1]



I, II and III may then form the corresponding hydrocarbons.

The formation of isopropylbenzene can be explained by the initial removal of the phenyl which is attached to the secondary carbon atom of the diphenylhexane and this is then followed by a β-scission with the elimination of propylene and formation of a phenylisopropyl carbonium ion.

A transalkylation reaction was observed when *tert*-butylbenzene was hydrogenolyzed under 10 atmospheres of hydrogen. The products of the reaction contain *para*- and possibly also *meta*-di-*t*-butylbenzene.

Similarly toluene was alkylated with isobutylene in the presence of "modified" nickel catalyst at 350° and under an initial pressure of 5–8 atmospheres of hydrogen. About 35% of the isobutylene reacted to form a mixture of *m*- and *p*-*t*-butyltoluene. In the absence of thiophene the yield of *t*-butyltoluene was less than 4%.

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RECEIVED JANUARY 28, 1957

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[1] The possible source of protons in reactions catalyzed by nickel was discussed in a previous paper: H. Pines, M. Shamaiengar and W. S. Postl, THIS JOURNAL, **77**, 5099 (1955).

AN EXCEPTION TO THE RULE OF *trans*-NUCLEOPHILIC ADDITION[1]

Sir:

In the course of testing our "Rule of *trans*-Nucleophilic Addition"[1] over a wider range of systems, an exception to it was observed in the addition of sodium *p*-toluenethiolate to sodium propiolate.

When an alcoholic solution of sodium *p*-toluenethiolate is added to a cooled aqueous alcoholic solution of sodium propiolate, there is obtained a quantitative yield of product consisting of two *p*-tolylmercaptoacrylic acids, m.p. 144.5–145.5° (85–90% of total; *Anal.* Calcd. for $C_{10}H_{10}O_2S$: C, 61.83; N, 5.18. Found: C, 61.83; H, 5.25) and m.p. 136–137° (10–15% of total; Found: C, 62.07; H, 5.22). The compounds were assigned the structures, *trans*- and *cis*-β-*p*-tolylmercaptoacrylic acids, respectively, on the basis of the following evidence.

Infrared spectra of the two acids revealed a band at 7.80μ for the low-melting isomer, and a band at 8.42 μ for the high-melting isomer, indicative[1] of *cis* and *trans* configurations, respectively; bands associated with $>C{=}CH_2$ were absent. Furthermore, treatment of both isomers under Friedel–Crafts conditions[2] gave, from the low-melting isomer, an approximately 90% yield of 6-methylthiochromone, b.p. 138.0° (1.0 mm.), m.p. 69–70° (lit.[3] b.p. 194° (12 mm.), m.p. 69–70°). *Anal.* Calcd. for $C_{10}H_8OS$: C, 67.99; H, 5.12. Found: C, 68.09; H, 4.90. Essentially all of the high-melting isomer was recovered unchanged.

The fact that the above nucleophilic addition proceeds primarily *cis* may be due to the coulombic

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[1] This constitutes Paper V in the series on Stereospecific Reactions of Nucleophilic Agents with Acetylenes and Vinyl-type Halides; refer to W. E. Truce, *et al.*, THIS JOURNAL, **78**, 695, 2743, 2748, 2752, 2756 (1956).

[2] S. Ruhemann and H. E. Stapleton, *J. Chem. Soc.*, **77**, 1197 (1900).

[3] F. Krollpfeiffer, *et al.*, *Ber.*, **58B**, 1654 (1925).