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THE CLEAR ESTABLISHMENT OF THE ABSOLUTE CONFIGURATIONS IN BIPHENYL, BIANTHRYL AND BIANTHRAQUINONYL SYSTEMS

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In the previous paper[1] the absolute configuration of (+)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid dimethyl ester, (+)-(I), was proved to be that of the (R)-series by the method of anomalous X-ray diffraction. Some other binaphthyl derivatives have also been chemically correlated to (R)-(+)-I. This is the first example for the unequivocal establishment of an absolute configuration among optically active biaryl systems caused by restricted rotation.

In this paper we present the absolute configurations of other biaryl systems such as biphenyl, bianthryl and bianthraquinonyl derivatives, whose absolute configurations have only been suggested[2], by their chemical correlation with (R)-(+)-I, as shown in the Chart.

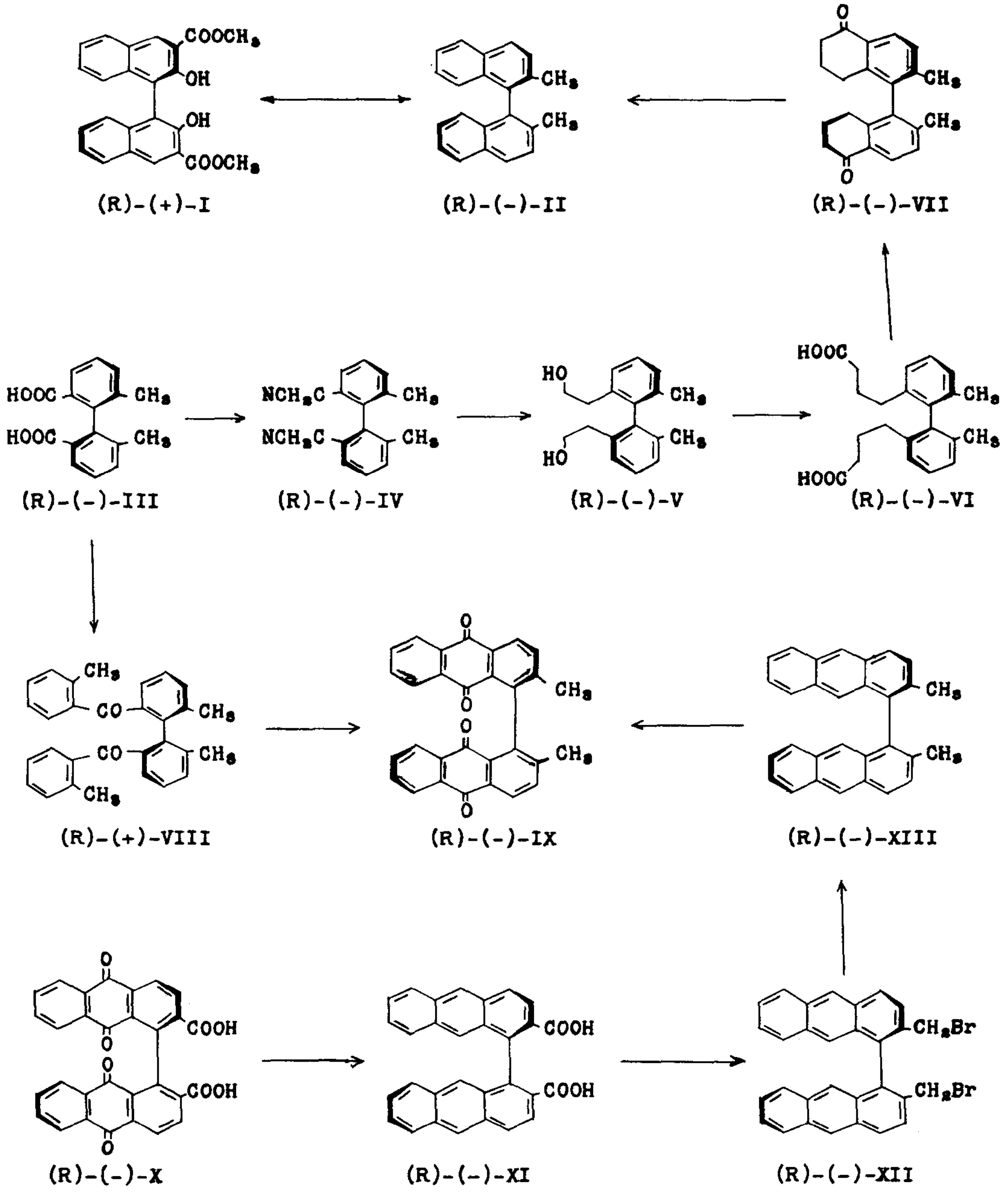
The optically active (-)-IV [m.p. 121-123°, $[\alpha]_D^{20}$ -15° (c=1.0, pyridine)] was obtained from (-)-III [m.p. 204-205°, $[\alpha]_D^{20}$ -18° (c=1.0, CH_3OH)] according to the literature[3], and the alcoholysis of (-)-IV with ethanolic hydrogen chloride followed by lithium aluminum hydride reduction gave the diol, (-)-(V), [m.p. 109-110°, $[\alpha]_D^{21}$ -25° (c=1.0, THF)], which was converted to the dibromide with phosphorus[*] tribromide, then submitted to the malonic ester synthesis under the usual reaction conditions to afford dicarboxylic acid, (-)-(VI), [$[\alpha]_D^{20}$ -20° (c=1.0, THF)]. The Friedel-Crafts reaction of acid chloride obtained from (-)-VI yielded the expected cyclic diketone, (-)-(VII), [$[\alpha]_D^{20}$ -9° (c=0.5, THF)], whose 2,4-dinitrophenylhydrazone was recrystallized from ethanol as red needles [m.p.285-290°(decomp.)]. The reduction of (-)-VII with lithium aluminum hydride gave the diol which was converted to the dibromide with phosphorus tribromide in benzene. This dibromide was further brominated with N-bromosuccinimide in carbon tetrachloride to give the tetrabromide. The dehydrobromination of the tetrabromide with potassium acetate afforded the binaphthyl derivative (-)-II, which was purified through chromatography on silica-gel to yield pure (-)-2,2'-dimethyl-1,1'-binaphthyl, (-)-(II), [m.p. 66-67°, $[\alpha]_D^{20}$ -7° (c=0.5, EtOH)]. The intermediates from (-)-VII to (-)-II were not isolated.

The configuration of (-)-II has already been correlated with (R)-(+)-I[1,2] whose absolute configuration is established to belong to the (R)-series[1], thus, the absolute configurations of biphenyl derivatives, (-)-III, (-)-IV, (-)-V, and (-)-VI, and a tetralone derivative (-)-VII were demonstrated, respectively, to belong to the (R)-series.

Subsequently, the correlation of the configuration between the biphenyl derivative and the bianthraquinonyl derivative was attempted. The reaction of (R)-(-)-III with o-tolyl lithium gave the (+)-ditoluoyl derivative, (+)-(VIII), [m.p. 120°, $[\alpha]^{19}$ +13° (c=0.8, THF)], which was converted to (-)-2,2'-dimethyl-1,1'-bianthraquinonyl, (-)-(IX), [m.p.> 300°, $[\alpha]_D^{20}$ -44° (c=0.1, THF)] by the oxidation of (+)-VIII with potassium permanganate, followed by dehydration with concentrated sulfuric acid. Hence, the absolute configurations of (+)-VIII and (-)-IX were correlated to (-)-III and proved to belong to the (R)-series.

Furthermore, chemical correlation between bianthryl and biphenyl derivatives was undertaken by way of the bianthraquinonyl derivative, (-)-(IX). The conversion of the racemic X to the racemic XI, and the resolutions of X and XI were previously reported[4]. Accordingly, optically active (-)-X was led to (-)-XI in the same way. The reduction of the dibromide, (-)-(XII), [m.p.217-219°, $[\alpha]_D^{20}$ -102° (c=1.0, benzene)] derived from (-)-XI [m.p. 250-251°, $[\alpha]_D^{20}$ -196° (c=0.8, acetone)] according to the literature[5], with lithium aluminum hydride, yielded (-)-2,2'-dimethyl-1,1'-bianthryl, (-)-(XIII), [m.p. 155-157°, $[\alpha]_D^{20}$ -284° (c=1.0, THF)], which was oxidized with sodium chlorate accompanied by a small amount of vanadium pentoxide to afford (-)-IX[6] [m.p.> 300°, $[\alpha]_D^{20}$ -163° (c=0.5, THF)]. The (-)-IX, obtained from both (+)-VIII and (-)-XIII, were found to be

Chart


COOCH₃
OH
OH
COOCH₃
(R)-(+)-I
CH₃
CH₃
(R)-(-)-II
O
CH₃
CH₃
O
(R)-(-)-VII
HOOC
CH₃
HOOC
CH₃
(R)-(-)-III
NCH₂C
CH₃
NCH₂C
CH₃
(R)-(-)-IV
HO
CH₃
HO
CH₃
(R)-(-)-V
HOOC
CH₃
CH₃
HOOC
(R)-(-)-VI
CH₃
CO
CH₃
CO
CH₃
CH₃
(R)-(+)-VIII
O
O
CH₃
O
CH₃
O
(R)-(-)-IX
CH₃
CH₃
(R)-(-)-XIII
O
COOH
O
O
COOH
O
(R)-(-)-X
COOH
COOH
(R)-(-)-XI
CH₂Br
CH₂Br
(R)-(-)-XII

identical. Thus, bianthraquinonyl derivatives, (-)-(IX) and (-)-(X), and bianthryl derivatives, (-)-(XI), (-)-(XII) and (-)-(XIII), have been correlated to the biphenyl derivative, (-)-(III), whose absolute configuration is demonstrated as above, i.e., the absolute configurations of (-)-IX, (-)-X, (-)-XI, (-)-XII and (-)-XIII were found to belong to the (R)-series.

In conclusion, according to the sequence of the above reactions, the absolute configurations of the biaryl system compounds such as biphenyl, bianthryl and bianthraquinonyl derivatives are clearly established, based on the standard reference compound (R)-(+)-I in the binaphthyl system, whose absolute configuration was firmly determined by the X-ray diffraction method

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