

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Synthesis and Complete Resolution of 2-Hydroxy-1,1'-binaphthyl and the Reaction of its Phenylglyoxylate with Methylmagnesium Iodide^{1,2}

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RECEIVED SEPTEMBER 3, 1957

The synthesis of 2-hydroxy-1,1'-binaphthyl is accomplished readily by reaction of 2-methoxy-1-naphthylmagnesium bromide with 1-tetralone, followed by dehydration, dehydrogenation and ether cleavage. Complete resolution of the phenol *via* the quinine salts of the acid succinate is described. The phenylglyoxylate of the (+)-isomer reacts with methylmagnesium iodide to give (-)-atrolactic acid in 85% optical yield. This result provides support for the previous supposition that the high optical yields observed in Grignard additions to phenylglyoxylates of the phenyldihydrothebaine series are not due to specific chelate complexing with methoxyl groups.

Previous papers^{2b,c} reported that the phenylglyoxylates of phenyldihydrothebaine and its derivatives reacted with methylmagnesium iodide to give, after saponification, (-)-atrolactic acid in high optical yields. It was proposed that the direction and magnitude of these asymmetric inductions were controlled principally by compression effects which came into play as the keto carbonyl group of the phenylglyoxylate began to achieve tetrahedral geometry in the transition state. Nevertheless, the presence of two methoxyl groups in positions close to the reaction site in these molecules introduced undesirable complications. In particular, the possibility could not be rigorously excluded that specific chelate complexing of the phenylglyoxylate carbonyl groups with the methoxyl oxygens by the Grignard reagent was restricting the reacting substance to a particular conformation. One of these chelate-"frozen" conformations (XIV of reference 2c) had one face of the keto carbonyl group almost completely masked, and therefore could have accounted for the high optical yields. The desirability of examining asymmetric inductions with α -ketoesters of simple 2-hydroxybiphenyls lacking extraneous complexable groups was therefore evident.

We chose to work with 2-hydroxy-1,1'-binaphthyl (I) for the following reasons: (i) The substance has the desired structural simplicity, and it was anticipated that its synthesis in quantity would present no difficulty. (ii) A number of 2,2'-disubstituted-1,1'-binaphthyls have been resolved and all show exceptional resistance to thermal racemization.³⁻⁸ Further, even 1,1'-binaphthyl-5,5'-dicarboxylic acid, 4,4'-biquinolyl and 5,5'-biquinolyl, all of which have only hydrogens in (the steric equivalent of) 2,2'-blocking positions, have been resolved, although their optical stability is low.^{9,10,11} We anticipated, therefore, that I and

its derivatives would have conveniently high optical stability. (iii) It was desirable that the difference in compression energy between the transition state in which the phenylglyoxylate chain is compressed against hydrogen and that in which it is compressed against a substituent group be about the same as those in the phenyldihydrothebaine series. In the earlier series,^{2c} the contending pairs were (a) H *vs.* alicyclic-CH₂-CH₂-, (b) H *vs.* vinyl and (c) H *vs.* ethyl, whereas in the case of I, the contending pair is (d) H *vs.* the 8-position of a naphthalene nucleus. It is difficult to give a quantitative estimate of the magnitude of $\Delta\Delta F^*$ for case (d) in comparison with $\Delta\Delta F^*$ for cases a, b and c. If the vinyl group in case b is considered to be coplanar with the benzene ring, the purely mechanical bulk comparison with case d is good. However, it seems clear^{2c} that the entropy decrease associated with compression against a group that enjoys essentially free rotation in the ground state is a factor aside from mechanical bulk that also contributes to the observed optical yield. Thus, the optical yields for cases b and c are appreciably higher than that for a. In the latter, the entropy decrease in passing to the transition state from a ground state in which rotational motion of the -CH₂-CH₂- group is already restricted by inclusion in a ring is smaller than that in cases b and c, in which the vinyl or ethyl group rotation is unrestricted. On this basis, the effective bulk of vinyl would be expected to be greater than that of the 8-position of the naphthalene nucleus. On the other hand, a large part of the minimization of the compression energy contribution to the activation energy is undoubtedly accomplished by bond bendings.¹⁵ It is to be expected¹⁵ that bending of the single bond that attaches the vinyl group to the aromatic ring in case b would require less energy than the deformation of the relatively stiff naphthalene nucleus in case d. This factor qualitatively balances the entropy factor discussed above.

It was therefore anticipated that if compression effects were the principal determining factor, the

(1) This work was supported by a grant, G-1838, from the National Science Foundation.

(2) Paper IV of the Series "Asymmetric Induction Studies with Optically Active Biphenyls." For previous papers, see (a) J. A. Berson, *THIS JOURNAL*, **78**, 4170 (1956); (b) J. A. Berson and M. A. Greenbaum, *ibid.*, **79**, 2340 (1957); (c) *ibid.*, **80**, 445 (1958).

(3) R. Kuhn and O. Albrecht, *Ann.*, **465**, 282 (1928).

(4) R. Kuhn and P. Goldfinger, *ibid.*, **470**, 183 (1929).

(5) W. M. Stanley and R. Adams, *Rec. trav. chim.*, **48**, 1035 (1929).

(6) W. L. F. Armarego and E. E. Turner, *J. Chem. Soc.*, 13 (1957).

(7) D. Muriel Hall and E. E. Turner, *Chemistry & Industry*, 1177 (1953).

(8) D. Muriel Hall, E. E. Turner and K. E. Howlett, *J. Chem. Soc.*, 1242 (1955).

(9) F. Bell, W. H. D. Morgan and I. F. B. Smyth, *Chemistry & Industry*, 634 (1951).

(10) F. Bell and W. H. D. Morgan, *J. Chem. Soc.*, 1716 (1954).

(11) Bell and Morgan¹⁰ have pointed out that the purely mechanical interpretation of relative optical stabilities in the 1,1'-binaphthyl series is jeopardized by the finding that the 8,8'-¹²⁻¹⁴ and 5,5'-¹⁰ dicarboxylic acids do not differ much in racemization rate.

(12) W. M. Stanley, *THIS JOURNAL*, **53**, 3104 (1931).

(13) A. Corbellini, *Atti della Reale Accad. Lincei*, **13**, 702 (1931).

(14) J. Meisenheimer, *Ber.*, **65**, 32 (1935).

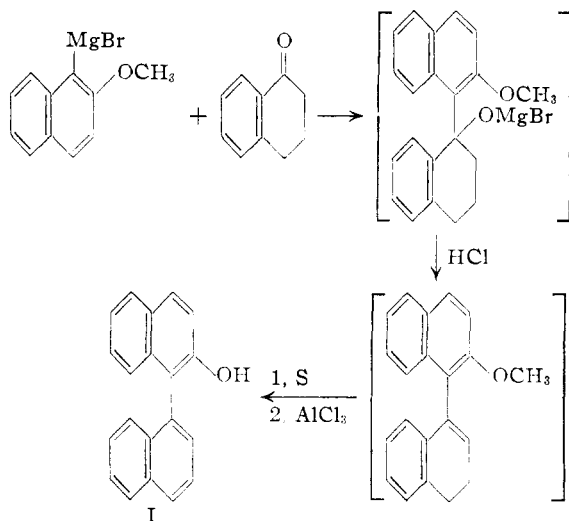
(15) F. H. Westheimer in "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, Chapt. 12, and references therein cited.

TABLE I
 PROPERTIES OF (+)-, (-)- AND RACEMIC I AND THEIR DERIVATIVES

	Racemic series M.p., °C.	M.p., °C. (+)-Series	[α] _D	M.p., °C. (-)-Series	[α] _D
Quinine salt	200.5-201	-84.22°	181-182	-165.4°
Acid succinate	221-221.5	238.5-239	+37.61	238-239	-37.45
Phenol	188-189	199-199.5	+21.70	198.5-199	-21.65
Phenylglyoxylate	141.5-142.5	156-157	+32.50

optical yield in case d would be roughly comparable to those (70-93%) observed in cases a, b and c, whereas, if chelate complexing with methoxyl groups had caused the high optical yields in the latter cases, the optical yield for case d, in which no such complexing was possible, would fall markedly.

The synthesis of I was accomplished readily. 2-Methoxy-1-naphthylmagnesium bromide and 1-tetralone reacted smoothly in refluxing ether. The Grignard complex was decomposed with 5 *N* hydrochloric acid and the resulting two-phase system was stirred for several hours. This process apparently effected dehydration, and the resulting crude product, after distillation *in vacuo* to remove tar, was directly dehydrogenated by heating with sulfur at 250-275°. It was found that milder conditions in the decomposition of the Grignard complex did not effect complete dehydration, with the result that dehydration accompanied the dehydrogenation step. This lowered the boiling point of the mixture and, consequently, the rate of dehydrogenation was slow. The dehydrogenated product, 2-methoxy-1,1'-binaphthyl, was converted to the phenol I with aluminum chloride in benzene. The over-all yield of I from 1-bromo-2-methoxynaphthalene was 35%.



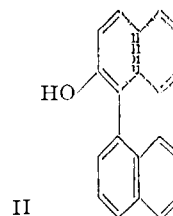
The acid succinate of (\pm)-I, prepared with succinic anhydride in pyridine, was converted to a mixture of crystalline diastereomeric quinine salts. Resolution of the isomers proved to be remarkably easy; the quinine salt of (+)-I acid succinate was readily soluble in hot acetone, whereas that of (-)-I acid succinate was virtually insoluble. Recrystallization of the salts from acetone and acetonitrile, respectively, was carried to constant m.p. and rotation of each, whereupon regeneration of the acid succinates gave materials of equal and opposite rotation. Regeneration of the (+)- and

(-)-phenols I was accomplished with lithium aluminum hydride. Again, materials of equal and opposite rotation were obtained. Recrystallizations of the acid succinates or of the phenols failed to change the properties of the substances. Since the salts had also reached constant properties and since the high optical stability of both I and its acid succinate (*vide infra*) made it extremely unlikely that any of our manipulations had caused partial racemization, the completeness of the optical resolution was established (see Table I).

The acid succinate was racemized only with difficulty. A benzene solution of the (-)-isomer lost 4.9% of its optical activity in 24 hours at reflux, which, assuming first-order kinetics, corresponds to an optical half-life of about two weeks at 80°. The (+)-phenol I, under the same conditions, had a half-life of about two days. The chemical identity of (+)-I was established by boiling it in *p*-cymene for three days. This caused complete racemization and gave material identical with (\pm)-I.

The phenylglyoxylates of racemic and optically pure (+)-I were prepared. The racemic phenylglyoxylate was treated with methylmagnesium iodide in ether. Saponification gave chemically virtually pure (\pm)-atrolactic acid in 70% yield and a neutral fraction in 27% yield (calculated as 1,1,2-trimethyl-2-phenylethyleneglycol). The phenol was recovered in 94% yield. These experiments eliminated the possibility of contamination of the acid fraction with gross amounts of impurities. The (+)-phenylglyoxylate, after the same treatment, gave in 66% yield (-)-atrolactic acid of 85% optical purity.

The observed optical yield provides support for the previous hypothesis^{3c} that asymmetric inductions in systems of this type are controlled by compression effects and not by chelate complexing. The predominant product presumably is formed *via* a transition state in which the phenylglyoxylate chain is compressed against hydrogen rather than against the 8-position of the naphthalene nucleus. If one may rely upon analogy between this case and those in the phenyldihydrothebaine series, the assignment of the absolute configuration II to (+)-I then follows.



This analogy appears valid at present, but we consider the absolute configurational assignment ten-

tative until a more thorough investigation of asymmetric inductions with simple binaphthyls has been completed.

Experimental¹⁶

2-Methoxy-1,1'-binaphthyl.—2-Methoxy-1-naphthylmagnesium bromide¹⁷ was prepared as follows. About 25 ml. of a solution of 123 g. of 1-bromo-2-methoxynaphthalene in 1500 ml. of anhydrous ether was added to a suspension of 13 g. of magnesium in 500 ml. of anhydrous ether. A few ml. of methyl iodide were added to start the reaction and the remainder of the bromide solution was then added with vigorous stirring at such a rate that refluxing occurred spontaneously. After about one-third of the bromide solution had been added, refluxing ceased, and the solution was then heated at reflux until the addition had been completed (2 hours) and for an additional two hours. The clear yellow Grignard solution was stirred and treated during 2 hours at room temperature with 75.9 g. of 1-tetralone in 450 ml. of anhydrous ether. During the addition, the ether refluxed gently and a white solid separated from the reaction mixture. The Grignard complex was decomposed by very slow addition of 5 *N* hydrochloric acid, which caused a very vigorous reaction. The precipitate dissolved, and the resulting two-phase mixture was stirred vigorously at room temperature for an additional hour, during which time the color of the ether solution changed from yellow to reddish-yellow. The ether layer was separated, the aqueous layer was extracted with 500 ml. of fresh ether, and the combined ether solutions were dried over calcium sulfate and evaporated. The residue was distilled at 30 mm. (bath at 190–240°) and the bright red distillate, b.p. *ca.* 170–200°, was heated in a Woods metal-bath under a reflux condenser with 16 g. of sulfur. Evolution of hydrogen sulfide began at about 150°. The bath temperature was raised to 250–275° and, after 2 hours, hydrogen sulfide evolution was complete. The reaction mixture was cooled, taken up in acetone, and filtered to remove a small quantity of unreacted sulfur. The filtrate was evaporated and the dark, viscous residue was subjected to steam distillation. Three grams of 2-methoxynaphthalene was recovered from about 5 l. of distillate. The non-volatile material was taken up in chloroform, dried, and evaporated to give a black viscous oil. The oil was distilled in a solids distillation apparatus (bulb-to-bulb) at 30 mm., bath at 250–285°. The distillation residue was a black tar. The thick reddish oil which had distilled crystallized upon standing at room temperature. (Crystalline material had been obtained, in an earlier small-scale run, after chromatography on alumina in benzene-pentane 1:2). The crude product weighed 94 g. Recrystallization from aqueous methanol gave 76 g. of white leaflets, m.p. 109–110°. An analytical sample of 2-methoxy-1,1'-binaphthyl had m.p. 110.5–111°.

Anal. Calcd. for C₂₁H₁₆O: C, 88.73; H, 5.63. Found: C, 88.90; H, 5.73.

In another run in which the Grignard complex was decomposed with *N* hydrochloric acid and the product extracted immediately, the dehydrogenation was accompanied by evolution of water, with consequent foaming. The temperature of the dehydrogenation mixture (140–180°) could not be raised as high as before, and hydrogen sulfide evolution continued for 6 hours.

(±)-2-Hydroxy-1,1'-binaphthyl (I).—A solution of 75 g. of 2-methoxy-1,1'-binaphthyl in 400 ml. of dry benzene was treated with 100 g. of anhydrous aluminum chloride (added in one portion). Heat was evolved and the solution turned very dark. After 24 hours at room temperature, the reaction mixture was poured onto crushed ice and the benzene layer was extracted with 25% aqueous sodium hydroxide. The pale yellow aqueous extract was chilled in ice and acidified with 2 *N* hydrochloric acid. Recrystallization of the resulting precipitate from aqueous methanol gave 53.4 g. of white needles, m.p. 188–189°.

Anal. Calcd. for C₂₀H₁₄O: C, 88.89; H, 5.18. Found: C, 88.57; H, 5.35.

(16) Melting points were corrected. Elemental analyses were by Dr. Adalbert Elek, Elek Microanalytical Laboratories. Optical rotations were measured with a Rudolf precision polarimeter which read directly to 0.001°.

(17) (a) F. Bodroux, *Compt. rend.*, **136**, 617 (1903); (b) C. Weizmann and E. Bergmann, *J. Chem. Soc.*, 567 (1936).

(±)-2-Hydroxy-1,1'-binaphthyl Phenylglyoxylate.—A solution of 1.7 g. of phenylglyoxyl chloride, 2.7 g. of I and 50 ml. of dry pyridine was allowed to stand at room temperature for 18 hours. The reaction mixture was poured into ice-water, and the precipitated solid was filtered off, washed with dilute hydrochloric acid and water, and dried. The crude pale yellow solid did not dissolve in cold concentrated alkali. Recrystallization from hexane gave 3.0 g. of very pale yellow needles, m.p. 141.5–142.5°. An ethanolic solution of this material gave a precipitate with 2,4-dinitrophenylhydrazine.

Anal. Calcd. for C₂₈H₁₈O₃: C, 83.58; H, 4.48. Found: C, 83.71; H, 4.59.

Preparation and Resolution of 2-Hydroxy-1,1'-binaphthyl Acid Succinate.—A solution of 50 g. of I in 500 ml. of dry pyridine was treated with 18.5 g. of succinic anhydride. The mixture turned green and became warm. After being heated on the steam-bath for 18 hours, the solution was poured into ice-water, and the blackish oil which separated was extracted with ether. The ether solution was thoroughly washed with dilute hydrochloric acid and water and then was extracted with 10% sodium bicarbonate. The aqueous extract was acidified with dilute hydrochloric acid and the resulting precipitate, after being washed with warm (60°) water, was recrystallized from aqueous methanol to give pure white needles, m.p. 221–221.5°.

A solution of 54 g. of the (±)-acid succinate in 2 l. of boiling ethyl acetate was treated with 55.2 g. of quinine trihydrate. A copious crystalline precipitate appeared upon cooling the reaction mixture. After 24 hours at 0–5°, the mixture was filtered to give 100 g. of slightly yellow, coarse crystals, m.p. 193–195°, [α]_D²⁵ 125.5° (in methanol). This material was heated at reflux for 3 hours with 1 l. of acetone, and the mixture was filtered hot. The filtrate was kept at 0–5° for 24 hours, after which time pure white needles m.p. 199–200°, [α]_D²⁵ –85.10° (*c* 5.25 in methanol, *l* 4), were obtained. One further recrystallization from acetone gave material (38 g.) of m.p. 200.5–201° and [α]_D²⁵ –84.22°.

Recrystallization gave material of m.p. 200–201° and [α]_D²⁵ –84.30°. The insoluble material from the original acetone fractionation was recrystallized from acetonitrile, m.p. 181–182°, [α]_D²⁵ –165.4° (in methanol). Further recrystallization gave material of m.p. 181.5–182°, [α]_D²⁵ –165.4°.

The acetone-soluble quinine salt, when shaken with 600 ml. of concentrated ammonia water and 450 ml. of chloroform gave a clear two-phase mixture. The aqueous layer was acidified, the precipitated acid succinate was taken up in chloroform, and the chloroform solution, after being washed with water and dried over magnesium sulfate, was evaporated. Recrystallization of the residue from aqueous methanol gave 15.8 g. of white needles, m.p. 238.5–239°, [α]_D²⁵ +37.65° (*c* 4.50 in methanol, *l* 4). Further recrystallization gave material of m.p. 238–239°, [α]_D²⁵ +37.61°.

Treatment of 14 g. of the acetone-insoluble quinine salt in a similar manner gave 5.9 g. of levorotatory acid succinate, m.p. 238–239°, [α]_D²⁵ –37.38° (*c* 4.55 in methanol, *l* 4). Further recrystallization gave material of m.p. 238–239°, [α]_D²⁵ –37.45°.

Anal. Calcd. for C₂₄H₁₈O₄: C, 78.53; H, 5.08; neut. equiv., 370.4. Found: for (+)-acid succinate: C, 78.40; H, 5.13; neut. equiv., 375. For (–)-acid succinate: C, 78.67; H, 4.90. For (±)-acid succinate: neut. equiv., 367.

(+) and (–)-2-Hydroxy-1,1'-binaphthyl.—A solution of 6.3 g. of lithium aluminum hydride in 400 ml. of dry ether was treated with a solution of 15.8 g. of the dextrorotatory acid succinate at a rate that caused gentle refluxing. After completion of the addition, the reaction mixture was stirred at room temperature for an hour, and the excess hydride was decomposed with ethyl acetate. Hydrochloric acid (2 *N*) was added, the layers were separated and the aqueous layer was extracted with two 250-ml. portions of fresh ether. The combined ether solutions were washed with water and dried over magnesium sulfate. Evaporation of the ether and recrystallization of the residue from aqueous methanol gave 11.1 g. of white crystals, m.p. 199–199.5°, [α]_D²⁵ +21.55° (*c* 3.55 in methanol, *l* 4). Further recrystallization gave material of m.p. 198–199°, [α]_D²⁵ +21.70°.

The (–)-2-hydroxy-1,1'-binaphthyl (1.40 g.) obtained from 1.85 g. of (–)-acid succinate by the same procedure

had m.p. 197–199°, $[\alpha]_{D}^{20} -21.73^{\circ}$ (*c* 3.50 in methanol, *l* 4). Recrystallization gave material of m.p. 198.5–199°, $[\alpha]_{D}^{20} -21.65^{\circ}$.

Anal. Calcd. for $C_{20}H_{14}O$: C, 88.89; H, 5.19. Found: For (–)-isomer: C, 88.88; H, 5.21. For (+)-isomer: C, 88.76; H, 5.33.

Racemization Experiments. A. Acid Succinate.—A solution of 0.75 g. of the acid succinate, $[\alpha]_{D}^{20} -37.45^{\circ}$, in 25 ml. of benzene was heated at reflux for 24 hours. The benzene was evaporated *in vacuo*, leaving 0.70 g. of material, m.p. 237–239°, $[\alpha]_{D}^{20} -35.61^{\circ}$ (4.9% racemization).

B. 2-Hydroxy-1,1'-binaphthyl in Benzene.—A solution of 0.50 g. of I, $[\alpha]_{D}^{20} +21.70^{\circ}$, in 25 ml. of benzene was heated at reflux for 24 hours. The benzene was removed *in vacuo* leaving 0.47 g. of material, m.p. 171–178°, $[\alpha]_{D}^{20} +14.85^{\circ}$ (32% racemization).

C. 2-Hydroxy-1,1'-binaphthyl in *p*-Cymene.—A solution of 1.0 g. of I, $[\alpha]_{D}^{20} +21.70^{\circ}$, in 30 ml. of *p*-cymene was heated at reflux for 3 days. The solution was cooled, extracted with three 30-ml. portions of 25% sodium hydroxide, the aqueous extracts chilled in ice and acidified with hydrochloric acid. The precipitate was filtered off, washed with water and dried. The crude product had m.p. 185–187°. The observed rotation, $\alpha = +0.002 \pm 0.005^{\circ}$ (*c* 5 in methanol, *l* 4), indicated that it was optically inactive. Recrystallization from aqueous methanol gave needles, m.p. 188.5–189.5°, alone or mixed with (±)-I.

Reaction of 2-Hydroxy-1,1'-binaphthyl Phenylglyoxylate with Methylmagnesium Iodide. A. The Racemic Ester.—A solution of 10.0 g. of the racemic phenylglyoxylate in 150 ml. of dry ether was stirred and treated with 31 ml. of a *M* solution of methylmagnesium iodide in ether. The Grignard solution was added in ten equal portions at 3-minute intervals. After completion of the addition, the solution was heated at reflux for 30 minutes. Saturated ammonium chloride solution was added, the layers were separated, and the aqueous layer was extracted with three 75-ml. portions of fresh ether. The combined ether solutions were washed with water, sodium bicarbonate and water, dried over magnesium sulfate and evaporated. The resulting pale yellow oil was saponified with boiling 20% ethanolic potassium hydroxide for 4 hours. The reaction mixture was diluted with four times its volume of water and extracted with four 75-ml. portions of chloroform. The chloroform extracts were dried over magnesium sulfate and evaporated

in vacuo to give 1.2 g. of a pale yellow oil (calculated as 1,1,2-trimethyl-2-phenylethylene glycol, 27%). The aqueous layer was acidified with hydrochloric acid and the precipitated solid was dissolved in ether and the aqueous solution was extracted with more ether. The combined ether extracts were extracted successively with three 50-ml. portions of 10% sodium bicarbonate and then with four 50-ml. portions of 25% sodium hydroxide. Evaporation of the ether left no residue. Acidification of the bicarbonate extract gave a precipitate. Extraction of the resulting mixture with ether, drying, and evaporation of the ether solution gave a crystalline residue, which, after being dried over concentrated sulfuric acid for 18 hours *in vacuo*, weighed 2.7 g. and had m.p. 87–89°, reported¹⁸ for (±)-atrolactic acid, m.p. 93–94°. A mixture with an authentic sample of (±)-atrolactic acid of m.p. 93° melted at 92–93°. The sodium hydroxide extract was acidified with hydrochloric acid and the precipitate was filtered, washed with water and dried at 60° for 18 hours to give 6.3 g. of I, m.p. 185–187.5°.

B. The (+)-Ester.—The phenylglyoxylate of (+)-I, prepared from I of $[\alpha]_{D}^{20} +21.70^{\circ}$ in the same manner as the racemic phenylglyoxylate, had m.p. 154–156°, $[\alpha]_{D}^{20} +32.50^{\circ}$ in methanol when crude. Recrystallization from aqueous methanol and drying *in vacuo*, either at room temperature or at 60° for 48 hours, gave a hemihydrate, m.p. 156–157°, $[\alpha]_{D}^{20} +32.64^{\circ}$ (*c* 3.25 in methanol, *l* 4). The substance sublimed at 80° *in vacuo*. The infrared spectrum in chloroform was identical with that of the racemic phenylglyoxylate. The substance gave an immediate precipitate with 2,4-dinitrophenylhydrazine reagent.

Anal. Calcd. for $C_{23}H_{18}O_3 \cdot 0.5H_2O$: C, 81.74; H, 4.66. Found: C, 81.61, 81.50; H, 5.10, 5.00.

The Grignard reaction procedure was exactly the same as for the racemic ester with the exception that only the bicarbonate-soluble fraction was investigated. From 10.0 g. of (+)-phenylglyoxylate there was obtained 2.55 g. of atrolactic acid, m.p. 95–99°, $[\alpha]_{D}^{20} -48.25^{\circ}$ (*c* 7.05, *l* 4, in *M* sodium hydroxide²⁰). This corresponds to 85% optical purity.

Acknowledgment.—We are indebted to the National Science Foundation for financial support.

(18) R. Fittig and C. Wurster, *Ann.*, **195**, 155 (1879).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

The Lead Tetraacetate Oxidation of *cis*- and *trans*-9,10-Diaryl-9,10-dihydro-9,10-phenanthrenediols. A Kinetic Study

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RECEIVED AUGUST 5, 1957

The rates of oxidation with lead tetraacetate in acetic acid are reported for a series of *cis*- and *trans*-9,10-diaryl-9,10-dihydro-9,10-phenanthrenediols in which the 9,10-diaryl substituents increase in bulk (aryl = 4-methylphenyl, 2,4-dimethylphenyl, 1-naphthyl, 2,4,6-trimethylphenyl, 2,3,5,6-tetramethylphenyl). There was no obvious correlation between rate data and intramolecular hydrogen bonding measurements. Reaction rates and calculated activation energies for both 9,10-dialkyl- and 9,10-diaryl-9,10-dihydrophenanthrenediols are interpreted within the framework of Criegee's cyclic intermediate or a cyclic transition state. The rate acceleration of the lead tetraacetate oxidations of *cis*- and *trans*-9,10-dihydro-9,10-phenanthrenediols and *cis*- and *trans*-9,10-di-(*p*-tolyl)-9,10-dihydrophenanthrenediols in relatively non-polar 99% benzene-1% acetic acid is also indicative of a cyclic process. Arguments against the Cordner-Pausacker mechanism are presented, and Criegee's recently suggested acyclic mechanism is discussed.

Criegee and co-workers^{1–4} have extensively investigated the rate of cleavage of vicinal diols with lead tetraacetate. They have noted the pronounced difference in behavior of *cis*- and *trans*-isomeric diols and have enunciated the empirical rule that the *cis*-diols always show higher oxidation rates than do the isomeric *trans*-diols. Later work

by Criegee,^{5,6} Prelog,⁷ and their co-workers has provided two general exceptions to the rule: (1) In unsubstituted, alicyclic diols, the k_{cis}/k_{trans} ratio is greater than 1 only for those ring systems with seven or less carbon atoms. The ratio is re-

(5) R. Criegee, B. Marchand and H. Wannowius, *Ann.*, **550**, 99 (1942).

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(7) V. Prelog, K. Schenker and H. H. Gunthard, *Helv. Chim. Acta*, **35**, 1598 (1952); V. Prelog, K. Schenker and W. Kung, *ibid.*, **36**, 471 (1953).

(1) R. Criegee, *Ber.*, **64**, 260 (1931).

(2) R. Criegee, L. Kraft and B. Rank, *Ann.*, **507**, 159 (1933).

(3) R. Criegee and E. Buchner, *Ber.*, **73**, 563 (1940).

(4) R. Criegee, E. Buchner and W. Walther, *ibid.*, **73**, 57 (1940).