3,3′,5,5′-Tetra-*t*-butyl-4,4′-diphenoquinone was purified by recrystallization from absolute ethanol; it melted at 242–243° (lit.[5] 246°).

Anal. Calcd for $C_{28}H_{40}O_2$: C, 82.30; H, 9.87. Found: C, 82.3; H, 9.9.

The infrared spectrum was identical with that of the authentic compound[6] and the nmr showed nine *t*-butyl hydrogens for each vinyl hydrogen.

2,6-Di-*t*-butyl-1,4-benzoquinone was purified by recrystallization from absolute ethanol and melted at 66–67° (lit.[7] 67.5–68.5°). Its infrared spectrum matched that of the authentic compound in Sadtler and its nmr showed a 9:1 ratio of *t*-butyl to vinyl hydrogens.

3,5-Di-*t*-butyl-4-hydroxybenzaldehyde was recrystallized from absolute ethanol and melted at 187–188° (lit.[8] 189°). Its 2,4-DNP melted at 231.5–232.5° (lit.[8] 235–236°).

Registry No.—I, 88-26-6.

(5) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1441 (1957).

(6) Courtesy of Dr. G. M. Coppinger.

(7) C. D. Cook, R. C. Woodworth, and P. Fiana, *J. Amer. Chem. Soc.*, **78**, 4159 (1956).

(8) T. W. Campbell and G. M. Coppinger, *ibid.*, **74**, 1469. (1952).

Isomerization of (−)-β-Pinene to High Optical Purity (−)-α-Pinene

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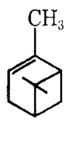
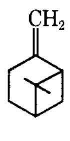
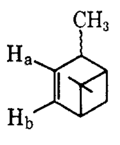
The recent work by Brown and coworkers[1] in the asymmetric synthesis of optically active alcohols has increased the need for a method to conveniently obtain high optical purity (−)-α-pinene[2] (I) in the laboratory. We encountered this need while utilizing Brown's procedure during the course of another investigation which required a rather large quantity of I.


I


II


III

The isomerization of (−)-β-pinene (II) to I has previously been carried out with rosin acid[3] or with palladium black saturated with hydrogen.[4,5] Although the palladium experiment realized nearly quantitative conversion of II to I, the optical yield, *i.e.*, conversion of optical activity to product, was only 82%. In addition, significant quantities of palladium are required to produce large amounts of I.

In view of the recent work in our laboratory and elsewhere in the area of olefin isomerizations with iron pentacarbonyl,[6] it was felt that a similar method might result in an improved synthesis of high optical purity I from II. We wish to report a very convenient method whereby large quantities of high optical purity I can be prepared from II utilizing the relatively inexpensive iron pentacarbonyl.

Isomerization of II, $[\alpha]^{26}\text{D}$ −20.32° (neat) (89.5% optical purity),[7] with 20 mol % iron pentacarbonyl for 32 hr at 135° produces I, $[\alpha]^{26}\text{D}$ −44.45° (neat) (86.7% optical purity),[8] in about 45% yield. This represents an optical yield of 96.9%. Essentially identical results were obtained when the experiment was performed utilizing 10–900 g of II. This is an improvement over the results of Richter and Wolff,[4] who isomerized II, $[\alpha]^{20}\text{D}$ −21.6° (neat) (95.2% optical purity), with palladium black, previously saturated with hydrogen, to I, $[\alpha]^{20}\text{D}$ −40.0° (neat) (78.1% optical purity).

Although smaller amounts of $Fe(CO)_5$ could be used with about equal yields, larger amounts facilitate the isomerization. This preparation allows a considerable amount of less volatile by-products to be produced; however, I is easily purified by distillation. No δ-pinene (III), which might be expected to result from further isomerization of I, could be detected.[9] The nmr spectrum of I exhibited methyl absorptions at τ 9.15 and 8.75 (singlets) and 8.37 (quartet), and a vinyl hydrogen multiplet at τ 4.85. The spectrum shows *no* absorption at τ 4.04, where H_b of III has been reported to absorb,[10] even at high amplitude.

The isomerization was easily followed utilizing gas–liquid partition chromatography (glpc) with a Carbowax column and noting the disappearance and resultant formation of II and I, respectively. Another, but less accurate, method is by observing the disappearance of the characteristic infrared absorption at 11.4 μ (877 cm^{-1}) of II and the corresponding appearance of an absorption at 12.7 μ (787 cm^{-1}) characteristic of I. By such means, it was noted that isomerization began after 20 hr and was complete in less than 32 hr.

Experimental Section

The F & M vapor phase chromatograph, Model 810, equipped with a flame ionization detector, was used for analytical purposes. Helium was used as the carrier gas, with a 3-m Carbowax 20 M on Chromosorb G column. Nuclear magnetic resonance spectra were run on a Varian A-60 and infrared spectra on a Perkin-Elmer Model 137. Melting points were obtained with a Thomas-Hoover capillary apparatus. (−)-β-Pinene was purchased from Aldrich Chemical Co. and iron pentacarbonyl from

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(1) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Amer. Chem. Soc.*, **86**, 397 (1964).

(2) For a recent review of pinenes, see D. V. Banthorpe and D. Whittaker, *Chem. Rev.*, **66**, 643 (1966).

(3) R. N. Moore, C. Golumbic, and G. S. Fisher, *J. Amer. Chem. Soc.*, **78**, 1175 (1956).

(4) F. Richter and W. Wolff, *Chem. Ber.*, **59**, 1733 (1926).

(5) G. Widmark, *Acta Chem. Scand.*, **9**, 938 (1955).

(6) (a) F. G. Cowherd and J. L. von Rosenberg, *J. Amer. Chem. Soc.*, **91**, 2157 (1969); (b) W. T. Hendrix, F. G. Cowherd, and J. L. von Rosenberg, *Chem. Commun.*, 97 (1968); (c) G. F. Emerson and R. Pettit, *J. Amer. Chem. Soc.*, **84**, 4591 (1962); (d) B. Fell, P. Krings, and F. Asinger, *Chem. Ber.*, **99**, 3688 (1966); (e) M. D. Carr, V. V. Kane, and M. C. Whiting, *Proc. Chem. Soc.*, 408 (1964); (f) T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).

(7) The highest reported value for (−)-β-pinene is $[\alpha]^{22}\text{D}$ −22.7° (neat), purified from the silver complex (see ref 2).

(8) (a) The highest reported value for (−)-α-pinene is $[\alpha]^{20}\text{D}$ −51.28°, purified through the nitroso chloride: F. H. Thruber and R. C. Thielke, *J. Amer. Chem. Soc.*, **53**, 1030 (1931); (b) R. N. McDonald and R. N. Steppel, *ibid.*, **91**, 782 (1969), report a new high value for (−)-α-pinene of $[\alpha]^{25}\text{D}$ −54.9° (*c* 2.0, ethanol). The rotation of the α-pinene cited in this work is $[\alpha]^{26}\text{D}$ −47.5° (*c* 2, ethanol), giving an optical purity of 86.5%, which compares well with the value obtained for the neat liquid based on the value reported by Thruber and Thielke for the neat liquid.

(9) Purity is >97% α-pinene, with <3% β-pinene as contaminate, as indicated by gas–liquid partition chromatography.

(10) G. Zweifel and C. C. Whitney, *J. Org. Chem.*, **31**, 4178 (1966). *cis*-δ-Pinene: τ 4.04 (m, H_b) and 4.6 (broad d, H_a); *trans*-δ-pinene: τ 4.04 (m, H_b) and 4.75 (broad d, H_a).

K & K Laboratories. The (−)-β-pinene was distilled under a N_2 atmosphere through a Widmer column before use.

Method of Isomerization.—No attempt has been made to optimize yields, as both reagents are relatively inexpensive.

Into a 3-l., three-neck flask equipped with a magnetic stirrer, condenser, and two septa was placed 780 g (5.73 mol) of freshly distilled (−)-β-pinene, $[\alpha]^{25}\mathrm{D}$ −20.32°. The system was evacuated and N_2 was passed through a T-joint at the top of the condenser. This procedure was repeated several times to ensure a N_2 atmosphere. The liquid was heated to near 150°, and 225 g (115 ml, 1.15 mol, 20 mol %) of iron pentacarbonyl was added *via* a syringe. The temperature of the stirring mixture dropped to 120° owing to the $Fe(CO)_5$ addition and gradually rose; when the solution attained 135° the temperature was held constant. Samples were taken by syringe through a septum and analyzed. After 32 hr [as in the case of 20 mol % $Fe(CO)_5$], the reaction was complete. The black mixture was cooled and volatile material was removed by vacuum distillation using a CO_2-acetone-cooled receiver. The trapped material was then distilled through a Vigreaux column, collecting the 154–157° fraction at atmospheric pressure. Generally, this crude α-pinene occurred in 50–60% yield. Finally, careful fractionation yielded 340.5 g (43.5%) of (−)-α-pinene: bp 155–156°; $n^{25}\mathrm{D}$ 1.4640 (lit.[2] bp 155.9°; $n^{25}\mathrm{D}$ 1.4631); $[\alpha]^{26}\mathrm{D}$ −44.45° (neat).

(+)-Isopinocamphenol.—Hydroboration of the (−)-α-pinene from the isomerization as described by Brown[1] with subsequent oxidation yielded crude (+)-isopinocampheol. The alcohol was recrystallized from a small amount of petroleum ether (bp 60–90°), dried under low vacuum, and sublimed under high vacuum at 30°, giving pure (+)-isopinocampheol: mp 55–55.5°; $[\alpha]^{24}\mathrm{D}$ +28.5° (*c* 3.15, benzene); 88% optical purity [lit.[11] for (−)-isopinocampheol, mp 54–56°; $[\alpha]\mathrm{D}$ −32.4° (*c* 4, benzene)].

Registry No.—I, 7785-26-4; II, 18172-67-3.

Acknowledgment.—The authors are grateful to the National Science Foundation for partial financial support of this work.

[11] H. Schmidt, *Chem. Ber.*, **77**, 544 (1944).

An Unusual Condensation. Ring-Closure Reaction[1]

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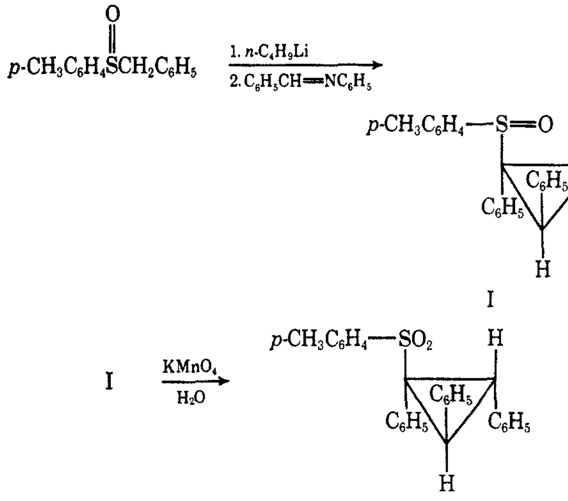
Treatment of benzyl *p*-tolyl sulfoxide with 1 mol of *n*-butyllithium followed by 1 mol of benzalaniline gave a 56% yield of 1,2,3-triphenylcyclopropyl *p*-tolyl sulfoxide (I). The gross and partial configurational structure of I was demonstrated by analytical, nmr, and mass-spectral analysis of I and of its corresponding sulfone, 1,2,3-triphenylcyclopropyl *p*-tolyl sulfone (II). The most prominent peak observed in the mass spectrum of I at 70 eV occurred at *m/e* 191, which is attributed to the 1,2-diphenylcyclopropenium cation fragment.

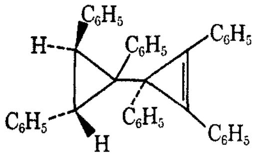
The stereospecific conversion of phosphine oxides to phosphinamides[3a] was used to complete a cycle of transformations that established the stereochemical course of ester–amide interchanges with phosphinate ester as starting material.[3b] In an attempt to complete a similar cycle applied to sulfinate ester–amide interchange, benzyl *p*-tolyl sulfoxide was treated with 1 mol of *n*-butyllithium followed by 1 mol of benzalaniline in tetrahydrofuran. Instead of the anticipated N-phenyl-*p*-toluenesulfinamide, a 56% yield (based on benzalaniline) of a single racemate of I was produced, along with small amounts of hydrazobenzene. Oxidation of sulfoxide I gave sulfone II.



I

II

Evidence for the structure of I was obtained from analytical, nmr, and mass-spectral analysis. Elemental analysis of I and II coupled with a parent peak at *m/e* 408 (70 eV) in the mass spectrum of I established the molecular formula of I. The molecular formulas of I and II demonstrate the presence of a ring in addition to the aryl groups in each of these compounds. The nmr spectrum of I in deuteriochloroform exhibited a singlet at τ 7.78 (3 H) attributed to the methyl group, an AB quartet centered at τ 6.22 (2 H, J_{AB} = 8.0 cps, Δ_{AB} = 0.66 ppm) assigned to the *trans* hydrogens on a saturated cyclopropane ring,[4] a doublet centered at τ 3.62 (2 H), and a multiplet centered at τ 2.9 (17 H) assigned to the other aromatic protons. The nmr spectrum of II in deuteriochloroform gave a singlet at τ 7.62 (3 H), an AB quartet centered at τ 6.1 (2 H, J_{AB} = 9.0 cps, Δ_{AB} = 0.83 ppm), and a multiplet centered at τ 2.9 (19 H). The AB quartet in both of these spectra (2 H) and the chemical shift of the two hydrogens resemble those of the *trans* hydrogens on the cyclopropane compound,[4] III. Sulfone II has the same symmetry properties as III, but sulfoxide I has the additional sulfoxide group as an asymmetric element, and therefore can exist in principle as two racemates, only one of which was obtained. The fact that the two cyclopropane hydrogens split each other in II demonstrates that they possess a *trans* rather than a *cis* arrangement. The sharp



III

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[1] This investigation was supported by U. S. Public Health Service Research Grant GM 12640-04 from the Department of Health, Education and Welfare.

[2] This author wishes to acknowledge gratefully nonresident tuition grants from Dow Chemical Co. and U. S. Rubber Co.

[3] (a) L. Horner and H. Winkler, *Tetrahedron Lett.*, **44**, 3265 (1964); (b) A. Nudelman and D. J. Cram, *J. Amer. Chem. Soc.*, **90**, 3869 (1968).

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