Anal. Calcd. for $C_{16}H_{21}O_4N$: C, 65.96; H, 7.27; N, 4.81. Found: C, 66.16; H, 7.12; N, 4.98.

The mother liquor of solution A (above) deposited 0.93 g. (32%), m.p. 63.5–65.5°, of the *meso-cis* ester as long needles; recrystallization from 80% methanol gave 0.81 g., m.p. 69.5–70.5°. A mixture of equal parts of the *cis* and *trans* esters melted at 37–60°.

Anal. Calcd. for $C_{16}H_{21}O_4N$: C, 65.96; H, 7.27; N, 4.81. Found: C, 66.17; H, 7.20; N, 4.91.

Hydrolysis of the *meso-cis* ester with 98% sulfuric acid gave 57% of the *meso-cis* acid, m.p. 84–86°; hydrolysis of the *trans* ester gave a 60% of the *meso-trans* acid, m.p. 101.5–102°. The *meso-trans* acid, 1.56 g., also yielded the *meso-trans* ester, 1.85 g. (64%), m.p. 37.7–39.0° (m.p. 47.5–48.5 after two recrystallizations; a mixed melting point with the *meso-trans* ester obtained from the *meso-cis* acid showed no depression). This ester gave *meso-trans* acid by hydrolysis with sulfuric acid.

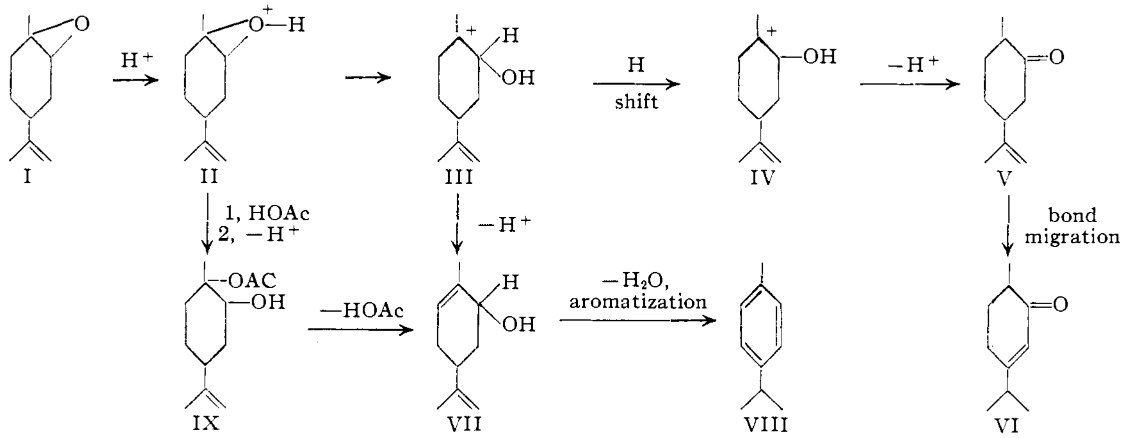
ORGANIC CHEMISTRY BRANCH
CHEMISTRY DIVISION
U. S. NAVAL ORDNANCE TEST STATION
CHINA LAKE, CALIFORNIA

Oxygenated Derivatives of *d*-α-Pinene and *d*-Limonene. Preparation and Use of Monoperphthalic Acid[1]

BY E. EARL ROYALS AND L. L. HARRELL, JR.

RECEIVED OCTOBER 13, 1954

A simplified procedure[2] for the preparation of an ethereal solution of monoperphthalic acid in 65% yield has been developed, and the reagent so prepared has been used to effect the epoxidations of cyclohexene, *d*-limonene and *d*-α-pinene in yields of 64, 71 and 48%, respectively. The low yield of pinene epoxide is probably to be accounted for on the basis of isomerization of the oxide and, perhaps, cleavage of the oxirane ring by phthalic acid produced in the reaction mixture. Appreciable quantities of campholenaldehyde, a known product of isomerization of pinene oxide, were isolated from the epoxidation reaction mixture.



Treatment of limonene monoxide with glacial acetic acid at room temperature for a period of four hours led to the formation of a small amount of dihydrocarvone (V) probably containing some carvenone (VI); 24% of unreacted epoxide was recovered. The dihydrocarvone might conceivably have arisen from direct acid-catalyzed isomerization of limonene monoxide through the intermediates II–IV, or through an initial cleavage of the epoxide ring to the hydroxyacetate, IX, followed by pyrolysis of the acetate during distillation of the product with formation of carveol (VII). Isomerization of carveol in the presence of acetic acid through the intermediates III and IV would lead to dihydrocarvone. In another experiment, limonene monoxide was treated with glacial acetic acid containing 1% of sulfuric acid at 16° for a period of eight hours. The reaction mixture was neutralized and the reaction product distilled under reduced pressure to obviate the possibility of pyrolysis of an intermediately formed hydroxyacetate. Under these conditions, 90% of the reaction product distilled below 100° at 10 mm. indicating the presence of little or no hydroxyacetate. Fractional distillation of the reaction product led to the isolation of *p*-cymene, dihydrocarvone and carvenone in yields of 10, 16 and 35%, respectively. These results indicate that limonene monoxide reacts with acetic acid, particularly in the presence of sulfuric acid, according to the indicated isomerization scheme; *i.e.*, under acid conditions, isomerization of the epoxide is faster than ring cleavage.

In contrast to the above results in acid media, treatment of *d*-limonene monoxide with glacial acetic acid containing sodium acetate led to the formation of a monoacetate of 8-*p*-menthene-1,2-diol in 82% yield. This monoacetate was most probably the 2-acetoxy-1-hydroxy structure, since base-catalyzed cleavage of unsymmetrical epoxides is known[3] to preferentially involve nucleophilic attack at carbon in the order primary > secondary > tertiary. That the product contained at least some of this isomer was shown by boric acid dehydration to give carveyl acetate in 16% yield; *p*-cymene and dihydrocarvone were also isolated in 19 and 21% yields. Dehydration of the hydroxyacetate with *p*-toluenesulfonic acid in benzene led to the isolation of *p*-cymene and carvenone in 31 and 37% yields; no carveyl acetate was isolated.

Reaction of α-pinene oxide with glacial acetic

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(1) Abstracted from a thesis presented by L. L. Harrell, Jr., to the Graduate Faculty of Emory University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 5, 1954.

(2) Compare, H. Böhme, *Ber.*, **70**, 379 (1937); *Org. Syntheses*, **20**, 70 (1940); G. B. Bachman and D. E. Cooper, *J. Org. Chem.*, **9**, 302 (1944).

(3) See S. Winstein and R. B. Henderson in R. C. Elderfield, Editor, "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 32–39.

acid led principally to isomerization with formation of campholenaldehyde (26% yield) whether the reaction was carried out in the presence or absence of sodium acetate. There was produced also, under both conditions, a high boiling fraction which was probably a crude hydroxyacetate; saponification equivalents calcd., 212; found, 255–272. Arbuzow and Mikhailow have reported[4] the formation of a glycol monoacetate on treatment of α-pinene with peracetic acid in chloroform solution, and that a similar product was obtained on treatment of α-pinene oxide with acetic acid. Arbuzow has observed[5] the formation of campholenaldehyde on treatment of α-pinene oxide with the strong acid zinc bromide.

As noted above, isomerization of *d*-limonene monoxide into dihydrocarvone and carvenone was observed during attempted cleavage of the epoxide ring with acetic acid. Several experiments were carried out in an attempt to make this isomerization practical. Attempted pyrolysis of the monoxide by dropping onto glass beads at 415–430° led to 65% recovery of unchanged material; no isomerization products were isolated. Isomerization over alumina at 310–325° led to a mixture from which *p*-cymene, dihydrocarvone and carvenone were isolated, the latter two compounds in combined yield of 30%. Treatment of the monoxide with zinc chloride in benzene at reflux for 20 hours gave dihydrocarvone in 36% yield.

Mugdan and Young[6] have recently investigated the hydroxylation of several alkenes by means of hydrogen peroxide in the presence of tungsten trioxide as catalyst. Hydroxylation of *d*-limonene by this procedure gave a complex reaction product from which 8-*p*-menthene-1,2-diol was isolated in 24% yield. Considerable quantities of high-boiling, water-soluble materials, probably triols and tetrols also were formed. Hydroxylation of α-pinene by a similar procedure gave a complex mixture from which the only product isolated was a small yield of pinol glycol, probably resulting from rearrangement of an initially formed α-pinene glycol to pinol followed by hydroxylation.

Dehydration of 8-*p*-menthene-1,2-diol by refluxing with 5% aqueous oxalic acid led to the formation of *p*-cymene and carvenone in 37 and 26% yields, respectively. An attempted iodine-catalyzed dehydration of the diol was unsuccessful; iodine was steadily consumed during the dehydration and was liberated during distillation of the reaction products with accompanying resinification.

Experimental[7]

Preparation of Monoperphthalic Acid. Böhme Procedure.[2]—A number of attempts were made to duplicate the preparation of monoperphthalic acid by the Böhme procedure before success was achieved. The difficulty was found to lie in the determination of the proper time for acidification of the reaction mixture. It was found in the present work that satisfactory results may be obtained if the phthalic anhydride is added in one portion and the reaction mixture is acidified immediately upon noting a vigorous gas evolution or a sudden temperature rise.

Preparation of Monoperphthalic Acid. Modified Procedure.—Finely-powdered phthalic anhydride, 150 g. (1.0 mole), 250 ml. of 30% hydrogen peroxide and 1000 ml. of ether were stirred together at a moderate rate for 24 hours at room temperature. The aqueous layer was separated and extracted twice with 500-ml. portions of ether, the ethereal extracts being combined with the original ethereal solution. (The extraction of the aqueous layer may be omitted; the yield of monoperphthalic acid is about 10% less, but the concentration in the final solution is greater.) The ethereal solution was washed three times with 175-ml. portions of 40% ammonium sulfate solution, then dried, first, with 80 g. of anhydrous sodium sulfate and, finally, over 75 g. of Drierite. The yield of monoperphthalic acid was determined by adding a 2-ml. aliquot of the ethereal solution to 30 ml. of 20% potassium iodide solution and titrating the liberated iodine after 10 minutes with 0.1 *N* sodium thiosulfate. The yield of monoperphthalic acid was 0.65 mole (65% based on the phthalic anhydride used).

The ethereal solutions of monoperphthalic acid, still over Drierite, were used directly to effect the epoxidations of *d*-limonene, α-pinene and cyclohexene in 71, 49 and 64% yields, respectively. The experimental procedure was to add the alkene dropwise to the monoperphthalic acid solution with stirring at 0° and allow the resulting solution to stand in the refrigerator until reaction was complete as indicated by iodine titration as described above.

Reaction of *d*-Limonene Monoxide with Acetic Acid. (**a**).—*d*-Limonene monoxide, 30.4 g. (0.2 mole), was added during 10 minutes to 10 ml. of glacial acetic acid containing 1.04 g. of concd. sulfuric acid, the temperature being maintained at about 16°. The reaction mixture was then removed from the cooling bath and allowed to stand at room temperature for 7.5 hours. The reaction mixture was neutralized with 20% sodium hydroxide at 20°, extracted four times with 10-ml. portions of ether, and the ether extracts were dried over anhydrous sodium sulfate. The ether was removed by distillation, and the residue was distilled under reduced pressure to give 30 g. of material, b.p. to 100° (10 mm.); only 0.5 g. of material boiled above 100° (10 mm.), and a pot residue of 3.3 g. remained. The material boiling below 100° (10 mm.) was dissolved in ether, washed with 10% sodium carbonate solution, with water, and dried over anhydrous sodium sulfate. The ether was removed by distillation, and the residue was fractionally distilled through a Todd column with monel spiral packing to give 2.8 g. of *p*-cymene, b.p. 64.7–72° (15 mm.), 4.7 g. of dihydrocarvone, b.p. 99–109° (15 mm.), $n^{28}\mathrm{D}$ 1.4691, m.p. of semicarbazone, 190–191° (reported[8] for *d*- and *l*-dihydrocarvone semicarbazones, m.p. 189–191°), and 10.7 g. of carvenone, b.p. 109–111° (15 mm.), $n^{23}\mathrm{D}$ 1.4767, m.p. of semicarbazone, 201–202° (reported[8] for the α-form of carvenone semicarbazone, m.p. 200–201°). The combined yield of dihydrocarvone and carvenone (undoubtedly not completely separated in the distillation) was 51%.

(**b**).—*d*-Limonene monoxide, 22.4 g. (0.15 mole) was treated with 60.84 g. (1.0 mole) of glacial acetic acid at 10–12° for 4.5 hours. The acetic acid was removed by distillation at 15–25 mm., and the pot residue was distilled at atm. pressure to give 11.5 g. of material, b.p. 200–210°; distillation virtually ceased at this point. The pressure was then reduced, and 9.6 g. of material was rather rapidly distilled. These two fractions were combined and fractionally distilled through a Todd column with monel spiral packing to give 5.5 g. (24%) of recovered *d*-limonene monoxide, and 4.1 g. of material, b.p. 98–100° (16 mm.), $n^{22}\mathrm{D}$ 1.4733 which was probably a mixture of dihydrocarvone and carvenone. An oxime and a semicarbazone of m.p.'s corresponding roughly to those of dihydrocarvone were prepared, but could not be completely purified.

(**c**).—*d*-Limonene monoxide, 60.8 g. (0.4 mole), was added dropwise with stirring to 307 g. of glacial acetic acid containing 32.8 g. of sodium acetate. The temperature rose to 36°, and was maintained at this point for a period of five hours. After standing at room temperature for 32 hours, the calculated amount of 20% sodium hydroxide for neutralization was added at 20°. The mixture was extracted four times with 200-ml. portions of ether, the extracts were combined and washed with 10% sodium carbon-

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(4) B. A. Arbuzow and B. M. Mikhailow, *J. prakt. Chem.*, **127**, 1 (1930).

(5) B. A. Arbuzow, *Ber.*, **68**, 1430 (1935).

(6) M. Mugdan and D. P. Young, *J. Chem. Soc.*, 2988 (1949).

(7) Melting points here reported were determined in capillary tubes and are uncorrected.

(8) A. von Baeyer, *Ber.*, **27**, 1923 (1894).

ate, then with water. The ether solution was dried over anhydrous sodium sulfate, the ether was removed, and the residue was distilled from a simple still to give 71 g. of material, b.p. 108–120° (1 mm.). This material was cut into four arbitrary fractions which showed n^{28}D 1.4728–1.4735. Saponification equivalents for the four fractions were 226.1, 215.0, 212.1 and 212.8; theor. sapon. equiv. for 8-*p*-menthene-1,2-diol monoacetate, 212.0.

Dehydration of 8-*p*-Menthene-1,2-diol Monoacetate (**a**).—The monoacetate of 8-*p*-menthene-1,2-diol, 48 g. (0.23 mole), was refluxed in 250 ml. of benzene containing 14 g. (0.23 mole) of boric acid under a water separator. After 3.25 hours, 4.5 ml. of water had collected. The benzene was removed by distillation at atm. pressure, and the residue was distilled at 40 mm., pot temperature 200°. The distillate was dissolved in ether, washed with 10% sodium acetate, and dried over anhydrous sodium sulfate. The ether was removed by distillation, and the residue was fractionally distilled through a Todd column with monel spiral packing to give 5.7 g. of *p*-cymene, b.p. 51–60° (10 mm.), n^{26}D 1.4940–1.4931; 7,3 g. of dihydrocarvone, b.p. 90–92° (10 mm.), n^{26}D 1.4688, m.p. of semicarbazone, 190–191° (reported[8] m.p. 189–191°), m.p, of oxime, 89–89.5° (reported[9] m.p. for *d*- and *l*-dihydrocarvone oximes, 88–89°), 5.4 g. of carveyl acetate, b.p. 106–110° (10 mm.), n^{27}D 1.4742.

(**b**).—*p*-Toluenesulfonic acid monohydrate, 2.2 g., was refluxed under a water separator in 200 ml. of dry benzene until water no longer collected. Monoacetate of 8-*p*-menthene-1,2-diol, 42.4 g. (0.2 mole), was then added, and reflux was continued for 49 hours, at which time 3.4 ml. of water had collected. The benzene solution was cooled and washed with 10% sodium hydroxide solution until acid-free. Benzene was removed by distillation, and the residue was fractionally distilled through a Todd column with monel spiral packing to give 8.5 g. (31%) of *p*-cymene, b.p. 57–60° (10 mm.), n^{25}D 1.4868, and 11.2 g. (37%) of carvenone; b.p. 99.5–101° (10 mm.), n^{25}D 1.4760, m.p. of semicarbazone,[8] 201–202°, m.p. of hydroxyl-amino-oxime, 165–166° (reported[10] m.p. 167–168°).

Isomerization of *d*-Limonene Monoxide. (**a**).—*d*-Limonene monoxide, 27.1 g., was added dropwise at the rate of 12 drops per minute to a 300-ml. flask half filled with glass beads and immersed in a sand-bath at 415–430°. The distillate (24.4 g.) was fractionally distilled through a Todd column with monel spiral packing to give 18.1 g. of unchanged *d*-limonene monoxide (67% recovery). No other product was isolated.

(**b**).—*d*-Limonene monoxide, 33.71 g. (0.22 mole), was added dropwise during 1.3 hours to a vertical glass tube (o.d. 18 mm.) packed to a height of 12 inches with activated alumina and heated to 310–325°. The lower end of the reaction tube was connected to a receiver and condenser. After addition was complete, the tube was allowed to cool and washed with ether. The combined condensate and ether washings were dried over anhydrous sodium sulfate, the ether was removed by distillation, and the residue (27 g.) was fractionally distilled. Four arbitrary fractions, total weight 10.2 g., were collected, b.p. 99–110° (15 mm.). The largest fraction, 4.7 g., b.p. 99–103° (15 mm.), was shown to contain dihydrocarvone by preparation of dihydrocarvone oxime, m.p. 89–89.5° (reported[9] m.p. 88–89°). This material appeared to be dihydrocarvone containing some carvenone (combined yield, 30%).

(**c**).—*d*-Limonene monoxide, 20 g. (0.13 mole), was refluxed for 20 hours in 110 ml. of dry benzene containing 0.5 g. of freshly fused zinc chloride. The solution was cooled, shaken with an equal volume of water, washed with 5% hydrochloric acid, with 10% sodium carbonate, and finally with water. The benzene was removed by distillation, and the residue was fractionally distilled through a Todd column with monel spiral packing. There was obtained 4.1 g. (20%) of unchanged limonene monoxide and 7.2 g. (36%) of dihydrocarvone, b.p. 90–91° (10 mm.), n^{25}D 1.4685, m.p. of oxime, 89–89.5° (reported[9] m.p. 88–89°), m.p. of semicarbazone, 190–191° (reported[8] m.p. 189–191°).

Reaction of α-Pinene Oxide with Acetic Acid. (**a**).—α-Pinene oxide, 30.4 g. (0.2 mole), was added dropwise with stirring to 100 ml. of glacial acetic acid at 18–22°. After addition was complete, the reaction mixture was allowed to stand at room temperature for an additional 18 hours. The acetic acid was neutralized with 20% sodium hydroxide at 15°, and the resulting mixture was extracted four times with 100-ml. portions of ether. The ether extracts were combined, washed with water, dried over anhydrous sodium sulfate, and the ether was removed by distillation. The residual oil, 35,6 g., was distilled from a simple still to give two principal fractions, b.p. 82–95° (12 mm.), and 107–110° (< 1 mm.). These fractions were recombined and fractionally distilled through a Todd column with monel spiral packing to give 8 g. (26%) of campholenaldehyde, b.p. 45–48° (< 1 mm.), n^{32}D 1.4607, m.p. of semicarbazone, 139.5–140.5° (reported[11] m.p. 138–139°). Even at a pressure of < 1 mm. and a pot temperature of 170°, the higher boiling residue did not enter the column.

(**b**),—α-Pinene oxide, 30.4 g. (0.2 mole), was added dropwise with stirring to a solution of 16.4 g. of sodium acetate in 153 g. of glacial acetic acid at 35–37°; 1.25 hours was required for the addition, and the mixture was allowed to stand for 14 hours at room temperature. The mixture was neutralized with 20% sodium hydroxide at 20°, washed with 10% sodium carbonate, with water, and dried over anhydrous sodium sulfate. The ether was removed by distillation, and the residue was distilled from a simple still to give 8.4 g. (28%) of campholenaldehyde, b.p. 50–55° (1–2 mm.), n^{25}D 1.4652, m.p. of semicarbazone,[11] 139.5–140.5°, and a fraction, b.p. 110–125° (1 mm,). This higher boiling fraction showed a sapon. equiv. of 272; theor. sapon. equiv. for the hydroxyacetate, $C_{12}H_{20}O_3$, 212. Hence, this fraction contained a maximum of 78% of the hydroxyacetate.

Hydroxylation of *d*-Limonene.—*d*-Limonene, 224 g. (1.65 moles), in 1200 ml. of acetone was added to a solution prepared by stirring 6 g. of tungsten trioxide for one hour with 146 ml. (1.5 moles) of 30% hydrogen peroxide. The resulting mixture was stirred under reflux for 5 hours. Sixty ml. of 5% sodium carbonate was added, and the mixture was allowed to stand for 12 hours. The acetone was removed by distillation, and the residual solution was extracted with three 100-ml. portions of ether. The ether extracts were combined, washed with 50 ml. of water, and dried over anhydrous sodium sulfate. (Approximately 10 g. of limonene was recovered by dilution of the last 150 ml. of acetone distillate. This was added to the ether extracts.) The ether was removed by distillation, and the residual oil was distilled from a simple still under reduced pressure. The following fractions were collected: (1) to 100° (1 mm.), 82.3 g.; (2) 100–165° (1–2 mm.), 105 g.; (3) pot residue, 28.8 g. Redistillation of fraction 1 gave 69.8 g. of recovered limonene. Fraction 2 and the pot residue from redistillation of fraction 1 were combined and distilled under reduced pressure to give 107 g. of material, b.p. 123–165° (10 mm.). This material was heated with 1200 ml. of water. The undissolved oil was partly removed by means of a separatory funnel, the remainder by gravity filtration. The filtrate on cooling gave crystals of 8-*p*-menthene-1,2-diol hydrate. These were filtered off, and the filtrate was used to extract more of the diol from the undissolved oil. This procedure was used to produce three crops of crystals, total yield, 46.2 g., m.p. 68–68.5° (anhydrous). Further recrystallization from water and dehydration of the hydrate gave pure 8-*p*-menthene-1,2-diol, m.p. 71° (reported[12] m.p. 66.5–67.5° and 72.5–73°). The yield of diol, based on limonene converted, was 24%,

Hydroxylation of α-Pinene.—The hydroxylation of 22.4 g. (1.6 moles) of α-pinene was effected essentially as described above for *d*-limonene, except that the reaction was conducted entirely at room temperature (52 hours). Acetone was removed by distillation, the oil layer was separated, and the aqueous phase was extracted with 400 ml. of ether used in three portions. The combined oil and ether extracts were washed with 100 ml. of 5% sodium carbonate solution, then with water, dried over anhydrous sodium sulfate, and the ether was removed by distillation. The resulting oil was fractionally distilled to give no definite fractions. The highest boiling material, b.p. about 130–165° (2 mm.), set to a glassy mass on cooling. Crystallization from a mixture of methyl acetate and ligroin gave 5.8 g. (3%) of pinol glycol, m.p. 128.5–129° (reported[13] m.p. of *trans*-pinol glycol,

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(9) O. Wallach, *Ann.*, **275**, 117 (1893).

(10) O. Wallach, *Ber.*, **28**, 1963 (1895); *Ann.*, **277**, 126 (1893).

(11) B. A. Arbuzow, *Ber.*, **68B**, 1434 (1935).

(12) N. Prileschaev, *ibid.*, **42**, 4814 (1909); H. Meerwein, A. Ogait, W. Prang and A. Serini, *J. prakt. Chem.*, **113**, 9 (1926).

(13) G. Wagner and K. Slawinski, *Ber.*, **32**, 2067 (1899).

129°). No other definite product was isolated from this reaction.

Dehydration of 8-*p*-Menthene-1,2-diol.—A solution of 34 g. (0.2 mole) of 8-*p*-menthene-1,2-diol in 700 g. of 5% aqueous oxalic acid was refluxed for 16.5 hours. The mixture was then steam distilled until oil ceased to pass over, and the distillate was extracted three times with 100-ml. portions of ether. The combined extracts were washed with 25 ml. of 5% sodium carbonate solution, then with water, and dried over anhydrous sodium sulfate. The ether was removed by distillation, and the residue was fractionally distilled through a Todd column with monel spiral packing to give 6.8 g. (37%) of *p*-cymene, b.p. 57–59° (10 mm.), n^{26}D 1.4873, and 8.7 g. (26%) of carvenone, b.p. 101–101.6° (10 mm.), n^{26}D 1.4797, m.p. of semicarbazone,[8] 201–202°, m.p. of hydroxylaminoöxime,[10] 165–166.5°.

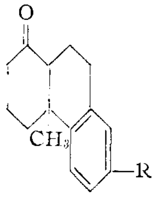
DEPARTMENT OF CHEMISTRY
EMORY UNIVERSITY
EMORY UNIVERSITY, GEORGIA

A New Route to 2-(β-Phenylethyl)-3-methyl-Δ²-cyclohexenones[1]

BY N. N. SAHA, P. N. BAGCHI AND P. C. DUTTA

RECEIVED DECEMBER 28, 1954

With a view to developing a method for the synthesis of diterpenoid resin acids represented by abietic acid and its congeners, we were in need of the tricyclic ketones I (R = H, OCH_3), the synthesis of which has been described briefly by Stork and Burgstahler.[2] While awaiting with interest the details of their experimental findings, we would like to record here a new synthesis of some of the intermediates leading to the synthesis of I (R = H, OCH_3) as our method differs substantially from that of the previous workers. 2-(β-phenylethyl)-cyclohexane-1,3-dione[3] and the corresponding methoxy derivative[4] II (R = OCH_3) have been utilized as our key intermediates for these synthetic attempts. We had some difficulty[5] in preparing the ethyl enol ether from the diketones II (R = H, OCH_3), but have been able to prepare the isobutyl ether[6] in a very good yield. The unsaturated isobutoxy ketones III (R = H, OCH_3) react readily with methylmagnesium iodide in ethereal solution. Decomposition of the reaction mixture with dilute acids leads to the formation of the unsaturated ketones IV (R = H, OCH_3). Measurement of absorption in the ultraviolet region of the ketones IV (R = H) ($\lambda^{\text{alc}}_{\text{max}}$ 242,5 mμ, log ε 4.0) and of the corresponding methoxy ketone IV (R = OMe) ($\lambda^{\text{alc}}_{\text{max}}$ 243.5 mμ, log ε 4.1) reveals a slight but significant hypsochromic shift of their absorption maxima from the values predicted by Woodward's rule.[7] Although no satisfactory explanation can be put forward to explain this shift, it may be of interest to compare a similar value $\lambda^{\text{alc}}_{\text{max}}$ 243 mμ recorded by Tishler, *et al.*,[8] for the compound V



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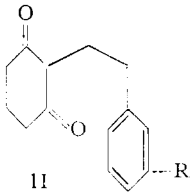

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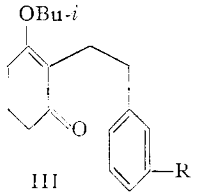

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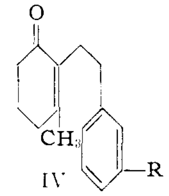
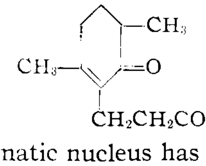


IV



V

where the aromatic nucleus has been replaced by a carboxyl group.

The identity of the ketones IV (R = H, OCH_3) has been established by comparison of the melting points of the solid dinitrophenylhydrazones with those of authentic samples prepared according to the published method. The structure of the unsaturated ketones has been further confirmed by cyclization to the tricyclic ketones I (R = H, OCH_3). It would be interesting to note that attempts at cyclization of the unsaturated ketone IV (R = H) with concentrated phosphoric acid at 165–170°[2] lead to product having a slightly bluish fluorescence and having practically no absorption in the 240–250 mμ region. Moreover, it was noticed that it was particularly difficult to obtain any solid ketonic derivative from this product and it led to an extremely poor yield of the desired condensation product in attempting the condensation of the cyclized ketone with ethyl cyanacetate according to Cragoe[9] in order to push the synthetic scheme further. These results are rather surprising because a closely analogous system, 10-methyldecalin-1-one has been synthesized and been found to undergo reactions with all ketonic reagents quite readily. As a result of further studies we have found that cyclization of IV (R = H) goes better at a lower temperature[10] and on heating for a longer period, and the product thus obtained in a much better yield is characterized readily by the yellow dinitrophenylhydrazone and by the absence of any typical ultraviolet absorption maxima in the 240–250 mμ.

It may be added that new methods[1b] have been successfully explored to build up the 1-methyl-1-carboxyl group in place of 1-carbonyl group as the former grouping is the characteristic of the diterpenoid resin acids.

Acknowledgments.—Ultraviolet measurements have been carried out by Dr. B. Mukherjee of the

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