[CONTRIBUTION FROM THE NAVAL STORES STATION[1]]

# Terpene Hydroperoxides. IV. The Thermal Decomposition of Pinane Hydroperoxide. I

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RECEIVED JANUARY 25, 1954

The thermal decomposition of pinane hydroperoxide has been studied. A ketone $C_{10}H_{18}O$ has been obtained in yields of 20% by weight of the hydroperoxide used. The structure of this ketone has been proved by unequivocal syntheses and infrared data to be 2,2-dimethyl-3-ethylacetylcyclobutane. The effects of oxygen and pinane on the ketone formation have been studied. It has been found that the change in the reductive capacity of the decomposition mixture containing the hydroperoxide by the addition of pinane increased the yield of ketone by 100%. The change of the oxidative capacity of the mixture with the addition of oxygen did not alter the yield of ketone when the decomposition was carried out in the absence of pinane. The reaction products are being investigated further with reference to other possible cyclobutane ring containing intermediates.

## Introduction

In recent years there has been considerable interest in the preparation of terpene hydroperoxides.[1a–3] Very little work[4–6] has been reported on the thermal decomposition of these compounds or the varied products that may be obtained by this method of decomposition. This paper is concerned with the thermal decomposition of pinane hydroperoxide at elevated temperatures.[7] The temperature of decomposition was chosen to coincide with the temperature of formation (110°) of the hydroperoxide and to give an efficient decomposition yield in a reasonable period of time.

## Discussion

As might be anticipated, the thermal decomposition of pinane hydroperoxide led to a complex mixture of products. Shochet[6] studied the prolonged oxidation of pinane and reported the isolation of a ketone ($C_{10}H_{18}O$) in low yield. A compound having similar properties was obtained in the present investigation in yields of 10 to 20% depending on the conditions used. On the basis of molecular refraction, elemental analysis and a methyl ketone test, Shochet postulated that this compound was 2,2-dimethyl-3-ethylacetylcyclobutane (III). In view of the well-known tendency of pinane derivatives to isomerize and the rather unusual structure proposed for the ketone, proof of the structure seemed desirable.

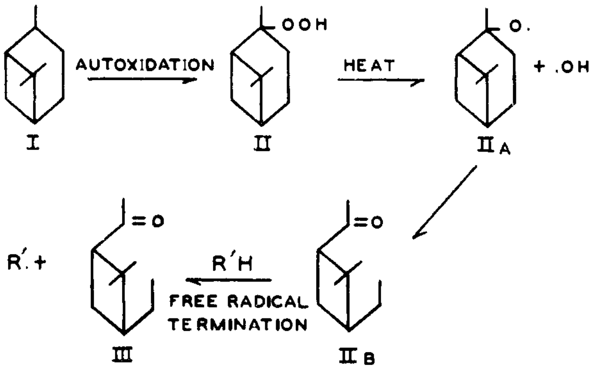

Fig. 1.—Schematic diagram of the preparation and thermal decomposition of pinane hydroperoxide with the formation of 2,2-dimethyl-3-ethylacetylcyclobutane.

Previous work on the oxidation of aliphatic hydrocarbons[8–10] has established the fact that tertiary C–H bonds are attached by oxygen in preference to secondary or primary C–H bonds, and that tertiary hydroperoxides can yield ketones on decomposition. The structure of pinane hydroperoxide also has been established.[4] The over-all reaction of pinane (I) to yield pinane-2-hydroperoxide (II) and subsequent free radical decomposition, rearrangement and reduction to give the ketone III is shown schematically in Fig. 1. The free radical mechanism has not been proven in this case, but such mechanisms have been accepted generally for thermal decomposition of hydroperoxides.[10–12] Furthermore, ionic decomposition with dilute sulfuric acid gives the *cis*-terpin in good yields.[4] The increased yield of the ketone III when the decomposition is carried out in the presence of pinane as a source of hydrogen (R'H) is in accord with this mechanism.

The series of reactions used to establish the structure of the ketone III are indicated in Figure 2. It will be noted that there is an asymmetric carbon atom adjacent to the carbonyl group in III. Degradation of this ketone to the corresponding acid XII results in a change of the sign of the optical rotation. A similar change in rotation has been noted in the degradation of pinonic acid (IV) to pinic acid,[13] and in the degradation of a methyl cyclobutyl ketone derived from caryophyllene.[14,15]

The fact that most of the compounds involved in this work can exist in *cis-d* and *-l* and *trans-d* and *-l* forms as well as the *cis* and *trans* racemates complicates the comparison of products obtained from different starting materials. In Fig. 2 all compounds

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[1] (a) One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture; (b) G. S. Fisher, L. A. Goldblatt, I. Kniel and A. D. Snyder, *Ind. Eng. Chem.*, **43**, 671 (1951).

[2] K. Suzuki, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **14**, 179 (1935).

[3] E. J. Lorand and J. E. Reese, U. S. Patent 2,438,125 (1948).

[4] G. S. Fisher, J. S. Stinson and L. A. Goldblatt, THIS JOURNAL, **75**, 3675 (1953).

[5] K. Suzuki, *J. Soc. Chm. Ind. (Japan) Suppl. Binding*, **39**, 189 (1936).

[6] D. Shochet, *Bull. soc. chim. Belg.*, 387 (1935).

[7] Most hydroperoxides explode when heated at elevated temperatures. Care should be exercised in carrying out such decompositions.

[8] A. D. Walsh, *Trans. Faraday Soc.*, **42**, 99 (1946).

[9] A. D. Walsh, *ibid.*, **43**, 297 (1947).

[10] N. A. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 205 (1946).

[11] E. J. Gasson, E. G. E. Hawkins, A. F. Millidge and D. C. Quin, *J. Chem. Soc.*, 2798 (1950).

[12] C. E. Frank, *Chem. Revs.*, **46**, 155 (1950).

[13] Barbier and Grignard, *Bull. soc. chim.*, [IV] **7**, 548 (1910).

[14] F. W. Semmler and E. W. Mayer, *Ber.*, **44**, 3657 (1912).

[15] L. Ruzicka, W. Zimmermann and D. Huber, *Helv. Chim. Acta*, **19**, 343 (1936).

are shown as being in the *cis* form for convenience although, as will be discussed later, some of the products obtained are undoubtedly *trans* compounds or mixtures of the two forms. In the present investigation the ketone used for the proof of structure was derived from a sample of pinane containing about 3 parts of *l*-pinane and 1 part of *d*-pinane. The compounds derived from this pinane mixture will be referred to as "*l* and *d*" compounds to distinguish them from the compounds obtained from optically homogeneous starting materials.

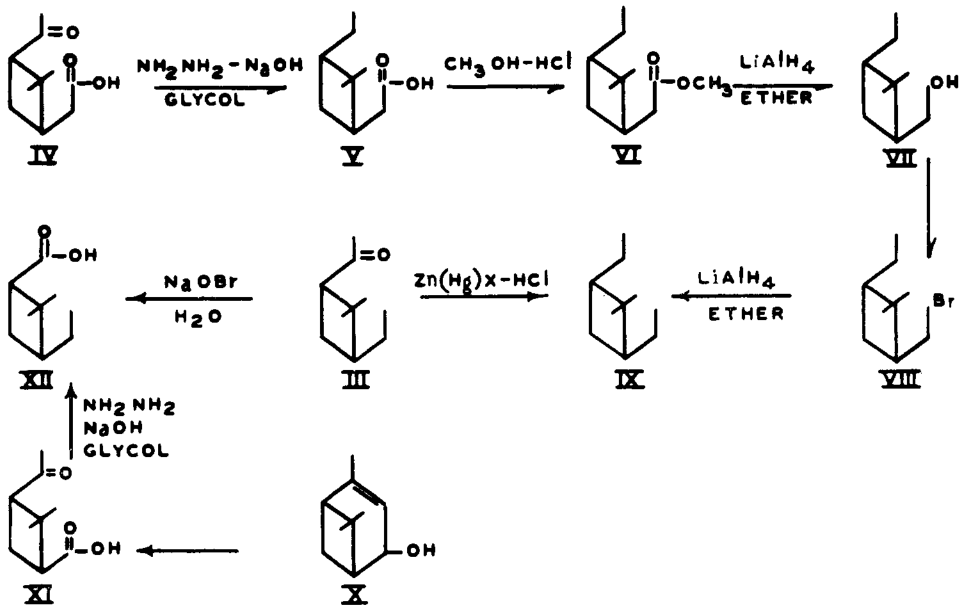

Fig. 2.—Schematic diagram of the syntheses of 2,2-dimethyl-1,3-diethylcyclobutane and 2,2-dimethyl-3-ethylcyclobutane-carboxylic acid.

On the assumption that the acid XII had the indicated structure, this acid was synthesized for comparison. The acid obtained by hypobromite degradation of the mixed *l*- and *d*-ketone was a liquid, $\alpha^{28}$D +4.3° (1 dcm., neat). When the acid was cooled for several days a small amount of solid separated. After recrystallization, this acid melted at 47.5 to 49° and was optically inactive. An authentic sample of the acid was prepared by Wolff-Kishner reduction of optically pure *cis*-*d*-2,2-dimethyl-3-acetylcyclobutanecarboxylic acid (pinononic acid) (XI). The acid obtained was a liquid [$\alpha$]D +2.0 (*c* 3.6% in chloroform). The infrared spectra[16] of the synthetic acid, the crude *d*- and *l*-acid obtained from the ketone III, and the solid *dl*-acid were all substantially identical. This indicates that all the samples are similar mixtures of *cis*- and *trans*-acids. Although optically pure acid XI was used in the synthesis, a *dl*-*p*-phenylphenacyl ester was obtained from the synthetic acid XII. Its melting point was not depressed by admixture with the corresponding ester prepared from the solid *dl*-acid. This indicates that partial inversion occurred at both active carbon atoms during the reduction. Delépine and Badoche[17] have shown that even under mild alkaline conditions *cis*-*l*-pinononic acid mutarotates to an equilibrium mixture of *cis*-*l*- and *trans*-*d*-pinononic acids containing about 25% of the *trans* form. As pointed out by Alexander[18] under such strongly basic conditions as are used in the reduction even carboxylic acids may be expected to undergo carbanion formation at the $\alpha$-carbon atom, with attendant mutarotation if this is an asymmetric carbon atom. Mutarotation at both carbon atoms would, of course, result in a complex mixture of *d*- and *l*-, *cis*- and *trans*-acids similar to that obtained by basic hypobromite oxidation of the mixed *l*- and *d*-ketone III. It will be noted that the crude acid mixture is dextrorotatory in both cases, *i.e.*, *d*-$\alpha$-pinene → *d*-verbenol → *d*-acid XII and *l*-$\alpha$-pinene → *l*-pinane → *l*-ketone III → *d*-acid XII. This is to be expected since in the first series of reactions the ethyl group in acid XII is attached to the 1-carbon atom of the original pinene while in the second series it is attached to the 5-carbon atom. Hence, if *d*-$\alpha$-pinene yields *d*-*cis*-XII by the first route it will yield *l*-*cis*-XII by the second route. The higher rotation of the acid obtained from the ketone III is due probably to the fact that only one asymmetric carbon atom is susceptible to mutarotation so racemization does not occur.

The proposed structure of the ketone III was also confined by reduction to the hydrocarbon IX. An authentic sample of this hydrocarbon was prepared by stepwise reduction of *dl*-2,2-dimethyl-3-acetylcyclobutaneacetic acid (IV) (pinonic acid). Except for optical rotation, the physical properties and infrared spectra of the two hydrocarbon samples were substantially identical. The observed optical activity of the hydrocarbon IX obtained from the mixed *l*- and *d*-ketone III indicates that it is at least partially in the *trans* form since the *cis* form would be *meso*. Although it is possible that the ketone III is not entirely in the *cis* form, it appears more probable that under the acidic conditions of the Clemmensen reduction a carbonium ion is formed at the asymmetric carbon atom and the reduction is accompanied by mutarotation. The slight differences in refractive index and infrared spectra observed for the two samples is due probably to different ratios of *cis* and *trans* forms.

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[16] The infrared analysis were obtained from the Chemistry Department of the University of Florida, Gainesville, Fla., using a Perkin-Elmer 21 recording infrared spectrophotometer with rock salt optics. All liquid samples were measured as liquids between plates (0.038 mm). The solid *dl*-acid was measured in a carbon tetrachloride solution between plates (0.2 mm.).

[17] M. Delépine and M. Badoche, *Ann. chim.*, **6**, 777 (1951).

[18] E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 126.

## Experimental[19]

*cis-l*-**Pinane (I).**—The *cis-l*-pinane used had been prepared previously[4] by hydrogenation of *β*-pinene and after a bulb-to-bulb distillation at 20 mm. had the following physical constants: $n^{20}\mathrm{D}$ 1.4626, $d^{20}_{4}$ 0.8575 and $[\alpha]^{20}\mathrm{D}$ −23.60° (neat).

*cis-l*-**Pinane Hydroperoxide (II).**[4,20]—To a 2-liter three-neck flask equipped with oxygen bubbler, thermometer, stirrer, Dean–Stark trap, condenser and Dry Ice trap was charged 1,008 g. (7.25 moles) of *l*-pinane. The temperature of the liquid was raised to 120°. Oxygen was bubbled into the liquid at such a rate to afford an excess of oxygen. After 30 minutes the temperature was lowered to 110°. The total reaction time was 4.5 hours. At the end of this time the peroxide number of the solution was 5,400 and the trap contained 0.1 ml. of water. The excess pinane was removed by simple distillation at 1 mm. pressure until the head temperature reached 80°. There was obtained 434 g. of *l*-pinane hydroperoxide having a peroxide number of 8,500. This corresponds to a 72% yield, based on the pure hydroxide having a peroxide number of 11,760 meq. of peroxide per kilogram.

**Thermal Decomposition of *l*- and *d*-Pinane Hydroperoxide (II).**—The hydroperoxide used was prepared[20] from a mixture of approximately two parts of *l*- and one part *d*-pinane. Eight hundred and fifteen grams (peroxide number 9,200) was decomposed in two separate portions at 117°.

To a false-bottom reactor immersed in a constant temperature bath, equipped with thermoregulated inner cooling coils, Dean–Stark trap, condenser and nitrogen inlet tube, was added 335 g. of the hydroperoxide. Nitrogen gas was bubbled at about 20 liters/hr. to remove water and other volatile products. The material was decomposed for 37 hours and had a final peroxide number of 150. The material weighed 295 g. and was a yellow viscous liquid. Another portion (480 g.) decomposed under the same conditions gave after 31 hours, 436 g. of a viscous light yellow liquid having a peroxide number of 300. The combined products were distilled bulb-to-bulb at 0.5 mm. until the flask temperature reached 220°. At this temperature decompositions of the residue began. The water-white distillate was charged to a micro Podbielniak[21] column and carefully fractionated over a period of five days. From the complex mixture there was obtained a fraction which when refractionated through the micro Podbielniak column gave 86 g. of a colorless liquid with a strong Kummel odor. The liquid[22] boiled at 86° and 20 mm., $n^{20}\mathrm{D}$ 1.4416, $d^{20}_{4}$ 0.8728, $[\alpha]\mathrm{D}$ −25.30° (neat). The liquid gave an iodoform test indicating a methyl ketone.

*Anal.* Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.74; H, 11.69.

**Decomposition of *cis-l*-Pinane Hydroperoxide (II) in the Presence of Oxygen.**—To a ground-glass test-tube with a fritted glass oxygen bubble and condenser was added 38.3 g. of *l*-pinane hydroperoxide (peroxide number 8,500). The apparatus was immersed in a constant temperature bath at 117°. Oxygen was bubbled in at such a rate (*ca.* 28 liters/hr.) as to leave an excess of oxygen as a carrier gas at all times. Heating for 13 hours gave 35.2 g. of a viscous liquid with a peroxide number of 400. The product was distilled bulb-to-bulb at 4 mm. pressure, until a flask temperature of 212° and a head temperature of 160° was reached. At this temperature no more distillate was obtained and decomposition of the residue began. There was obtained 16.7 g. of distillate and 17.0 g. of residue. The distillate was carefully fractionated through a spinning band column[23] to give 4.7 g. (12.5% based on total weight of material used) of ketone boiling at 86° and 20 mm., $n^{20}\mathrm{D}$ 1.4418, $d^{20}_{4}$ 0.8742, $[\alpha]^{20}\mathrm{D}$ −58.9 (neat), $[\alpha]^{28}\mathrm{D}$ −76° (*c* 4.6% chloroform); $[R]\mathrm{D}$ calcd. 46.63, found 46.58.

**Decomposition of *cis-l*-Pinane Hydroperoxide (II) in an Equal Mixture by Weight of *cis-l*-Pinane.**—A solution of 50 g. of the same *cis-l*-pinane hydroperoxide in 50 g. of *l*-pinane was decomposed at 117° using nitrogen as a carrier gas. After 28 hours the peroxide number was 220. The mixture (92 g.) was distilled bulb-to-bulb at 1 mm. pressure to give 72.2 g. of liquid boiling from 32 to 140°. The residue weighed 14.0 g. The loss of weight was due to low molecular weight material that was obtained in the Dry Ice trap. It was noted that the distillation residue was not as viscous as the residue obtained when the decomposition was carried out in the presence of oxygen or with pinane hydroperoxide alone. The complex distillate mixture was distilled carefully through a spinning band column. There was obtained 10.1 g. (20%) of the ketone boiling at 86° and 20 mm. pressure.

***l*-2,2-Dimethyl-3-ethylacetylcyclobutane Semicarbazone.**[24]—To a 50-ml. erlenmeyer was added 0.4 g. (0.0026 mole) of *l*-ketone, 0.7 g. of semicarbazide hydrochloride in 15 ml. of ethanol and 10 ml. of water. The mixture was heated for 15 minutes. One gram of sodium acetate was added and the solution refluxed for 15 minutes. Subsequent processing of the mixture gave 0.5 g. (91%) of solid melting at 180–181° dec. Two recrystallizations of the solid from ethyl acetate and two from 30% methanol gave 0.05 g., melting at 188–189° dec. The combined residues gave a more soluble form, m.p. 180–181° dec.

*Anal.* Calcd. for $C_{11}H_{21}ON_3$: N, 19.89. Found: N, 19.80.

***l*-2,3-Dimethyl-3-ethylacetylcyclobutane 2,4-Dinitrophenylhydrazone.**—The 2,4-dinitrophenylhydrazone was prepared in the normal manner.[25] From 1.0 g. (0.0065 mole) of the ketone there was obtained 1.4 g. of yellow plates melting at 152–154°. Two subsequent recrystallization from ethanol gave 1.0 g. (46%) melting at 160–161°. A mixed melting point with a sample prepared from the *l*- and *d*-ketone gave no depression.

*Anal.* Calcd. for $C_{16}H_{22}O_4N_4$: N, 16.76. Found: N. 16.51.

***d*- and *dl*-2,2-Dimethyl-3-ethylcyclobutanecarboxylic Acid.**—In a 150-ml. erlenmeyer flask equipped with a magnetic stirrer 6.0 g. (0.039 mole) of the *l*- and *d*-ketone was added to 75 ml. of sodium hypobromite (21.8 g. of $Br_2$ and 12 g. of NaOH). After stirring for 18 hours, the mixture was extracted with ether and the aqueous layer acidified and extracted with ether. The acidic ether extract was dried and distilled to give 5.2 g. of clear liquid boiling at 88° and 0.8 mm., $[\alpha]\mathrm{D}$ +4.2° (neat). When a solution of the acid in 20 cc. of pentane was cooled to −20° and seeded, a solid form separated. The pentane mother-liquor was decanted and the solid residue, which weighed 1.3 g., was taken up in 50% ethanol and recrystallized to give 1.1 g. melting at 45–47°. Two additional recrystallizations from pentane gave a solid which melted at 47.5–49°, $[\alpha]\mathrm{D}$ +0.01° (*c* 4.0% in chloroform).

*Anal.* Calcd. for $C_9H_{16}O_2$: C, 69.15; H, 10.32. Found: C, 68.86; H, 10.25.

***l*- and *d*-Methyl Bromo-2,2-dimethyl-3-ethylcyclobutanecarboxylate.**—Two grams (0.012 mole) of the crude acid mixture above was refluxed with thionyl chloride for one hour in a steam-bath. The excess thionyl chloride was removed and 1.5 g. of bromine was added to the cooled acid chloride. No hydrogen bromide was given off on standing one hour. The solution was heated to 70° for one hour. This failed to decolorize the bromine solution. To the cooled mixture was added 0.1 g. of phosphorus pentachloride. The mixture was refluxed for 30 minutes and the bromine solution was decolorized. An additional 1.5 g. of bromine was added and the mixture refluxed for 30 minutes longer. Almost all the bromine was utilized. Ten ml. of methanol was added to the cooled solution and the mixture was refluxed for 30 minutes. The solution was poured into

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(19) All melting points were taken in an air-bath and are uncorrected; all neat rotations were taken in a 1.0 dcm. micro tube.

(20) The procedure used for the preparation of the hydroperoxide was previously described in a paper by G. S. Fisher, J. S. Stinson, R. Moore and L. A. Goldblatt, submitted for publication in the *Ind. Eng. Chem.*

(21) The micro Podbielniak heligrid column (1.27 × 101.6 cm.) was equipped with a total condensation partial take-off head and was rated at 100 theoretical plates.

(22) Shochet[6] reported the following physical constants for the *l* ketone 80–82° at 16 mm., $n^{20}\mathrm{D}$ 1.4412, $d^{20}_{4}$ 0.8716, $[\alpha]^{20}\mathrm{D}$ −57.40°.

(23) The vacuum jacketed spinning band column (6 mm. × 60 cm.) was equipped with partial take off head and rated at 100 theoretical plates.

(24) D. Shochet[6] reported 196 ± 1° in 20 seconds, for the semicarbazone.

(25) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd. ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

water and extracted with ether. The ether solution was washed with sodium bicarbonate, followed with water and dried over sodium sulfate. The ether was removed at atmospheric pressure and 1 g. (33%) of a colorless liquid distilled at 63–66° and 0.5 mm., $n^{20}\mathrm{D}$ 1.4708.

*Anal.* Calcd. for $C_{10}H_{17}O_2Br$: C, 50.22; H, 7.16; Br, 33.42. Found: C, 50.10; H, 7.37; Br, 33.04.

*d*-**2,2-Dimethyl-3-acetylcyclobutanecarboxylic Acid (XI).**[14]—Verbenol (X) (40.0 g., $[\alpha]\mathrm{D}$ 72°) was oxidized with potassium permanganate in the presence of ammonium sulfate, essentially under the conditions used by Delépine[26] for the oxidation of α-pinene to pinonic acid. The crude acid mixture (28 g.) was recrystallized twice from water to give 4.8 g. of *d*-2,2-dimethyl-3-acetylcyclobutanecarboxylic acid, m.p. 130–131°, [α] +73° (*c* 4.8% in chloroform).

*d*- **and** *l*-**2,2-Dimethyl-3-ethylcyclobutanecarboxylic Acid (XII).**—To a 200-ml. round-bottom flask was added a solution of 60 ml. of ethylene glycol, 2.8 g. of sodium, 6.0 g. of hydrazine hydrate and 6.6 g. (0.039 mole) of *d*-2,2-dimethyl-3-acetylcyclobutanecarboxylic acid. The mixture was heated at 100° for two hours. The solution was distilled until the head temperature reached 197° and then refluxed for 18 hours. Work-up of the reaction mixture was essentially the same as that for the preparation of 2,2-dimethyl-3-ethylcyclobutaneacetic acid. There was obtained 4.3 g. (70%) of colorless liquid boiling 100° and 1.5 mm., $n^{25}\mathrm{D}$ 1.4458, $\alpha^{28}\mathrm{D}$ 2.2° (neat), $[\alpha]\mathrm{D}$ 2.0° (*c* 3.6% in chloroform).

*Anal.* Calcd. for $C_9H_{16}O_2$: C, 69.15; H, 10.32. Found: C, 68.97; H, 10.34.

*dl*-*p*-**Phenylphenacyl 2,2-Dimethyl-3-ethylcyclobutanecarboxylate.**—A solution of 1 g. (0.0065 mole) of the acid XII obtained by the Wolf–Kishner reduction of 2,2-dimethyl-3-acetylcyclobutanecarboxylic acid and 1.75 g. (0.0065 mole) of *p*-phenylphenacyl bromide in 100 ml. of alcohol was refluxed for 1.5 hours. The solid, which separated on cooling, was taken up in alcohol, treated with Norite and recrystallized to give 1.1 g. (68%) of plates melting at 57–59°.

Two additional recrystallizations from alcohol gave 0.6 g. melting 60–61°. Another recrystallization from a solution of alcohol and ethyl acetate gave 0.5 g. of solid melting at 60–61°, $[\alpha]\mathrm{D}$ 0.0° (*c* 4.0% in chloroform). The ester was allowed to crystallize slowly over a period of five days from ethanol to give plates melting at 61–62.2°.

*Anal.* Calcd. for $C_{23}H_{26}O_2$: C, 78.73; H, 7.48. Found: C, 78.61; H, 7.49.

To a neutral alcoholic solution of 0.35 g. (0.0022 mole) of the solid acid (m.p. 47.5°–49°) was added 0.6 g. of *p*-phenylphenacyl bromide. The solution was refluxed for one hour. There was obtained upon cooling a solid, which was purified as described above to give 0.35 g. of ester melting at 65–66°. An equal mixture with the ester prepared from reduced 2,2-dimethyl-3-acetylcyclobutanecarboxylic acid melted from 63.5–65°.

*Anal.* Calcd. for $C_{23}H_{26}O_2$: C, 78.73; H, 7.48. Found: C, 79.02; H, 7.48.

*dl*-**2,2-Dimethyl-3-ethylcyclobutaneacetic Acid (V).**—To a 1-liter flask equipped with reflux condenser was added 18.4 g. (0.1 mole) of *cis*-*dl*-2,2-dimethyl-3-acetylcyclobutaneacetic acid (IV), 50 g. (1.0 mole) of hydrazine hydrate and a solution of 21 g. of sodium metal in a mixture of ethylene glycol and 110 ml. of diethylene glycol. The contents were heated and the excess hydrazine and water were removed by distillation, until the flask temperature reached 190°. The reflux was continued for seven hours at 190°. The mixture was cooled, acidified to *p*H 2 with concentrated hydrochloric acid and extracted with three 100-ml. portions of benzene. The benzene solution was washed with water, dried over sodium sulfate and the benzene removed at atmospheric pressure. Distillation of the residue at reduced pressure gave 15.7 g. (92%) of a liquid boiling at 110° and 1 mm., $n^{25}\mathrm{D}$ 1.4472. The acid had a rotation of $\alpha^{30}\mathrm{D}$ −0.10° (neat).

*Anal.* Calcd. for $C_{10}H_{20}O_2$: C, 70.55; H, 10.67. Found: C, 70.34; H, 10.60.

*dl*-*p*-**Phenylphenacyl 2,2-Dimethyl-3-ethylcyclobutylacetate.**—The ester was prepared in the usual manner.[27] To the sodium salt of 0.65 g. (0.0038 mole) of the acid in 100 ml. of alcohol was added 1.0 g. (0.037 mole) of *p*-phenylphenacyl bromide. The mixture was refluxed for one hour. There was obtained 0.8 g. (62%) of platelets melting at 46.5–48.5°. Another recrystallization from ethanol gave 0.4 g. of platelets melting at 48.5–49.5°.

*Anal.* Calcd. for $C_{24}H_{28}O_2$: C, 79.06; H, 7.77. Found: C, 78.87; H, 7.76.

*dl*-**Methyl 2,2-Dimethyl-3-ethylcyclobutylacetate (VI).**—A mixture of 14.5 g. (0.086 mole) of the acid and 17 g. of thionyl chloride was refluxed for three hours. The excess thionyl chloride was removed by azeotrope distillation using benzene. A large excess of methanol was added cautiously down the condenser. The mixture was refluxed for 30 minutes. There was obtained 13.0 g. (83%) of a colorless liquid boiling 51° and 0.8 mm., $n^{25}\mathrm{D}$ 1.4357.

*Anal.* Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.50; H, 11.01.

*dl*-**2,2-Dimethyl-3-ethylcyclobutane-ethanol (VII).**—To a stirred solution of 11.4 g. (0.3 mole) of lithium aluminum hydride[28] in 100 ml. of ether at 0° was added slowly 12 g. (0.065 mole) of the ester VI in 50 ml. of ether. The slurry was stirred for three hours at 0° and allowed to come slowly to room temperature. The excess hydride was destroyed with water. The mixture was acidified with sulfuric acid and extracted with additional ether. The ether solution was washed and dried over sodium sulfate. Removal of the ether at atmospheric pressure and distillation of the residue under vacuum gave 8.2 g. (80%) of a colorless liquid boiling at 80° and 2 mm. pressure, $n^{25}\mathrm{D}$ 1.4492.

*Anal.* Calcd. for $C_{10}H_{20}O$: C, 76.85; H, 12.91. Found: C, 76.55; H, 12.77.

*dl*-**2,2-Dimethyl-3-ethylbromoethylcyclobutane (VIII).**—The bromide was prepared in the usual manner[29] by treating 6.3 g. (0.04 mole) of the alcohol with 8.0 g. of phosphorus tribromide at 0°. After addition of the tribromide the mixture was allowed slowly to come to room temperature. The excess phosphorus tribromide was decomposed with water. The bromide was washed with water, taken up in ether and dried over sodium sulfate. The ether was removed at atmospheric pressure and the bromide was distilled under vacuum to give 5.8 g. (65% yield) of a colorless liquid boiling at 80° and 4 mm. pressure, $n^{25}\mathrm{D}$ 1.4687.

*Anal.* Calcd. for $C_{10}H_{19}Br$: C, 54.84; H, 8.74. Found: C, 55.23; H, 8.88.

*dl*-**2,2-Dimethyl-1,3-diethylcyclobutane (IX).**—The reaction was carried out as described for the preparation of *dl*-2,2-dimethyl-3-ethylcyclobutane-ethanol. To 5 g. of lithium aluminum hydride in 50 ml. of ether was added 5.0 g. (0.022 mole) of the bromide in 50 ml. of ether. There was obtained 2.3 g. (75%) of a colorless liquid boiling at 155°, $n^{25}\mathrm{D}$ 1.4243.

*Anal.* Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.24; H, 14.34.

The infrared spectra gave a weak carbonyl band. The combined distillate was taken up in 20 ml. of pentane, washed with concentrated sulfuric acid and water and distilled at 153° to give 2.2 g. of colorless liquid, $n^{25}\mathrm{D}$ 1.4243.

*l*- **and** *d*-**2,2-Dimethyl-1,3-diethylcyclobutane.**—The Clemmensen reduction of the ketone (5.5 g.) was carried out according to the general procedure[30] using 43 g. of zinc amalgam, 100 ml. of ethanol and 110 ml. of hydrochloric acid (33%) which was added in three portions. The mixture was refluxed for 20 hours and the product was recovered by ether extraction. Removal of the ether and distillation of the residue gave 2.4 g. of a colorless liquid boiling 159–163°. A solution of this material in 30 ml. of pentane was washed well with sulfuric acid (sp. gr. 1.80) and water. The pentane was removed and the residue distilled to give 1.0 g. (20%) of a colorless liquid boiling 152–156°, $n^{25}\mathrm{D}$ 1.4257. This material had a rotation $[\alpha]^{28}\mathrm{D}$ +6.90° (neat).

*Anal.* Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.79; H, 14.31.

**Acknowledgment.**—The authors wish to express their thanks to Mr. Lawrence Brown of the

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(26) M. Delépine, *Bull. soc. chim.*, [5] **3**, 1369 (1936).

(27) R. L. Shriner and R. C. Fuson, ref. 25, p. 157.

(28) R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197 (1947).

(29) C. Hsueh and C. S. Marvel, *ibid.*, **50**, 855 (1928).

(30) R. Adams, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y.

Southern Regional Research Laboratory for all the micro analyses and Miss Mary Louise Van Natta of the University of Florida for the infrared analysis. The authors also wish to thank Mr. Richard Moore of this Laboratory for the generous supply of verbenol used in the preparations of *d*-2,2-dimethyl-3-acetylcyclobutanecarboxylic acid.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

# The Acid-catalyzed Conversion of β-Arylketones to Tetrahydroindeno[1.2-a]indenes[1]

BY RODERICK A. BARNES AND BURTON D. BEITCHMAN[2]

RECEIVED MAY 20, 1954

Some reactions of the hydrocarbon which results from the action of acids on 4-methyl-4-(*p*-tolyl)-2-pentanone have indicated it to be a tetrahydroindeno[1.2-a]indene. Although hydrocarbons with this ring system have not been previously described, the synthetic experiments which have been carried out confirm the structural assignment.

Four years ago in our laboratory it was observed that 4-methyl-4-(*p*-tolyl)-2-pentanone (I) was converted by boiling 50% sulfuric acid to a hydrocarbon II of unknown structure.[3] A similar result from the reaction of zinc chloride with 4-methyl-4-phenyl-2-pentanone (III) had been reported previously by Hoffmann.[4]

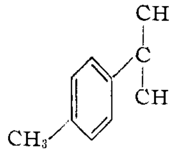
These facts suggested the possibility that an unusual ketone reaction of some generality might be involved. For this reason an investigation of the structure and mechanism of formation of these unknown hydrocarbons was initiated.

On the basis of an analysis and a molecular weight determination by the Rast procedure, Hoffmann assigned to his hydrocarbon IV the molecular formula $C_{24}H_{28}$. This formula would result if two molecules of ketone III reacted with the elimination of two water molecules. A cryoscopically determined molecular weight for our hydrocarbon II and the analysis of nitro and bromo derivatives were in best agreement with the formula $C_{23}H_{28}$; a hydrocarbon of this formula could result from two molecules of ketone I only by elimination of a three-carbon fragment. A similar process would lead to the formula $C_{21}H_{24}$ for Hoffmann's hydrocarbon.

Hydrocarbon II was inert toward potassium permanganate in acetone and reacted with bromine only slowly and with evolution of hydrogen bromide. This evidence for the absence of aliphatic double bonds in II requires the presence of two rings in addition to the two benzene rings. The failure of selenium at 400° to produce a dehydrogenation product suggested that these two rings were probably not six membered.

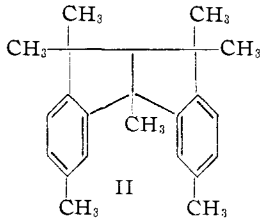
Hydrocarbon IV was not brominated by N-bromosuccinimide nor oxidized by chromic acid; however, both of these reagents attacked hydrocarbon II to yield a dibromide and a dibasic acid, respectively. When the carboxyl groups of the acid were reduced and the resulting glycol treated with phosphorus tribromide, a dibromide identical with that from the N-bromosuccinimide reaction was formed. Lithium aluminum hydride reduction of the dibromide regenerated hydrocarbon II. These transformations furnished definite evidence that except for the two methyl groups in hydrocarbon II only quaternary carbons[5] were joined directly to the benzene rings of these compounds.

This situation would result if the $C_{10}$-fragment (V) from ketone I remained essentially intact during the transformation to the hydrocarbon.



V

If two such fragments are present then only three more carbon atoms are available for constructing a system of two aliphatic rings. Five reasonable structures resulted from such constructions but only one fitted all of the experimental data.



II

The only previous example of a substance having four carbocyclic rings fused in this manner[6] is 9-keto-10-phenyl-9,10-dihydroindeno[1,2-a]indene[7] which was prepared by Kohler.[8]

The synthesis of a simpler homolog of structure II was planned in order to find out if this somewhat strained[9] ring system could be formed by an acid-catalyzed cyclization.

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[1] Presented at the 125th Meeting of the A.C.S., Kansas City, Missouri, March 27, 1954.

[2] Abstracted from a thesis presented by B. D. Beitchman to the Graduate School for the Ph.D. degree, December, 1953.

[3] This observation was made by Dr. G. R. Buckwalter, Ph.D. thesis, Rutgers University, 1950.

[4] A. Hoffmann, THIS JOURNAL, **51**, 2542 (1929).

[5] For examples illustrating the fact that N-bromosuccinimide will attack preferentially secondary or tertiary carbon atoms adjacent to a benzene ring rather than a methyl group see R. A. Barnes and G. R. Buckwalter, THIS JOURNAL, **73**, 3959 (1951).

[6] A hydrocarbon, diphensuccindan, having two benzene rings fused in a different manner to the pentalene system was prepared by W. Roser, *Ann.*, **247**, 156 (1888).

[7] The numbering system used is that of A. M. Patterson and L. T. Capell, "The Ring Index," Reinhold Publ. Corp., New York, N. Y., 1940, p. 314.

[8] E. P. Kohler, *Am. Chem. J.*, **37**, 369 (1907).

[9] The five-membered ring of indane itself is distorted because the angle between a substituent group and the benzene ring tends to be near 120°. In structure II two such distorted rings are fused; however, the successful preparation of diphensuccindan, ref. 6, indicates that this kind of structure is possible.