centrated and the residue was distilled under vacuum to yield 19.0 g. (50%) of the disilacycloheptane, b.p. 79–80° (3.2 mm.), $n^{24}\text{D}$ 1.4822. An analytical sample ($n^{24}\text{D}$ 1.4850) was obtained using the preparative gas chromatographic column.

Anal. Calcd. for $C_7H_{16}Cl_2Si_2$: C, 37.00; H, 7.05. Found: C, 36.93; H, 6.94.

1-Butyl-3,3-dimethyl-3-sila-1-azacycloheptane.—A mixture of 31.7 g. (0.11 mole) of δ-bromobutyl(bromomethyl)dimethylsilane and 17.1 g. (0.22 mole) of *n*-butylamine was placed in a 100-ml. round-bottomed flask. A thermometer was placed through the condenser into the reaction mixture. Reaction was initiated by warming the mixture to 40°, at which temperature a slow but spontaneous exothermic reaction raised the temperature of the mixture to 183°. After completion of the spontaneous reaction, the mixture was heated to a temperature of 215° for 5 min., then allowed to cool to room temperature. The semisolid material was transferred to a beaker and an equal volume of ethanol (95%) was added. After chilling in an ice bath, crystals formed. Filtration and recrystallization from ethanol (95%) yielded 4.5 g. of the amine hydrobromide, m.p. 166.5–168°.

Anal. Calcd. for $C_{11}N_{26}BrNSi$: C, 47.14; H, 9.28; N, 5.00; Si, 10.00. Found: C, 47.02; H, 9.22; N, 4.91; Si, 10.05.

The filtrate was made basic with 8 *N* sodium hydroxide, and organic material was extracted with two 25-ml. portions of ether. After drying with magnesium sulfate, fractional distillation yielded 7.2 g. of the free amine, b.p. 72–75° (3.8 mm.), $n^{23.5}\text{D}$ 1.4600. The infrared spectrum of the free amine was in agreement with the assigned structure and showed bands at 3.45 and 3.60 (C–H), 7.85, 8.0 (Si–CH_3), 8.45 (C–N), 11.45, 11.90, and 12.55 μ. No band was observed in the N–H region of the spectrum. The over-all yield of the amine and amine hydrobromide was 43%.

3,3-Dimethyl-3-sila-1-thiacycloheptane.—In a 500-ml. round-bottomed flask were placed 27.2 g. (0.11 mole) of sodium sulfide (dissolved in 50 ml. of water), 200 ml. of ethanol (95%), and 21.7 g. (0.11 mole) of δ-chlorobutyl(chloromethyl)dimethylsilane. The mixture was heated at reflux for 20 hr., then distilled to dryness. A saturated solution of mercuric chloride (about 600 ml.) was added to the distillate until no further precipitation was noted. The precipitate was filtered using suction and transferred to a 2-l. flask, and 1 l. of water was added. The mixture was steam distilled and *ca.* 600 ml. of distillate was collected. The distillate was extracted with three 100-ml. portions of petroleum ether (b.p. 30–60°). Fractional distillation yielded 2.0 g. (11.6%) of the silathiacycloheptane, b.p. 82–83° (13.0 mm.), $n^{24.5}\text{D}$ 1.5054. In one run an attempted atmospheric distillation resulted in decomposition. The infrared spectrum showed bands at 3.45, 7.2, 8.0, 9.3, and 12.0 μ.

Anal. Calcd. for $C_7H_{16}SSi$: C, 52.50; H, 10.00; S, 20.00. Found C, 52.20; H, 9.90; S, 19.85.

Attempted Preparation of β-Hydroxyethyl(chloromethyl)dimethylsilane.—In a 1-l. three-necked round-bottomed flask were placed 27.3 g. (1.1 g.-atoms) of magnesium turnings and 75 ml. of ether. To this mixture was added over a period of 2 hr. 175 g. (1.1 moles) of 2-trimethylsiloxy-1-chloroethane.[14] After the addition had been completed, the reaction mixture was heated at reflux overnight. Then was added 156 g. (1.1 moles) of (chloromethyl)dimethylchlorosilane over a period of 5 min., and the mixture was heated at reflux for 24 hr. The mixture was then filtered and the filtrate was treated with water, then extracted with three 100-ml. portions of ether. Fractional distillation of the organic material yielded 95.3 g. (48.5%) of pentamethyl(chloromethyl)disiloxane, b.p. 150–153°, $n^{22}\text{D}$ 1.4114 (lit.[15] b.p. 151.7–151.8°, $n^{20}\text{D}$ 1.4106).

Acknowledgment.—The authors wish to acknowledge the aid rendered by Mr. Charles Bowen during the course of this synthetic investigation.

(14) R. O. Sauer and W. I. Patnode, *J. Am. Chem. Soc.*, **67**, 1548 (1945).

(15) R. H. Krieble and J. R. Elliott, *ibid.*, **67**, 1810 (1945).

The Synthesis of Bicyclic Ketols from Cyclohexanones

JAMES A. MARSHALL AND WAYNE I. FANTA

Department of Chemistry, Northwestern University, Evanston, Illinois

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Reaction conditions are defined for the preparation of ketols by Robinson annelation of cyclohexanones. The *cis*-ketol II and the *trans*-ketol III are formed stereoselectively from 2-methylcyclohexanone and cyclohexanone using an equimolar quantity of methyl vinyl ketone. The ketol II is a convenient source of 10-methyl-1(9)-octalone-2 (I). The scope and stereochemistry of the Michael–aldol reaction sequence is discussed.

In the course of synthetic work we required various homologs of octalone I. Although the Robinson annelation reaction[1,2] provides a direct route to fused ring ketones, the application of this method to cyclohexanones such as 2-methylcyclohexanone[3] has proved generally unsatisfactory.[4] For example, the Robinson synthesis of 10-methyl-1(9)-octalone-2 (I),[3a] and variations thereof,[3b–g] proceeds in low yield, requires a two- or threefold excess of 2-methylcyclohexanone,[3] and affords a product of questionable purity.[3h,5] We undertook a study of this reaction in an effort to discover a reasonable correlation between yield and reaction conditions. Numerous attempts to improve the yield of octalone I by varying the solvent, temperature, ratio of reactants, and nature and quantity of the basic catalyst proved unsuccessful. We then investigated the possibility of effecting the condensation between 2-methylcyclohexanone and methyl vinyl ketone under conditions which might allow the isolation of a ketol intermediate.[2] We eventually found that slow addition of methyl vinyl ketone to an equimolar quantity of 2-methylcyclohexanone at −10° in the presence of a catalytic amount of ethanolic sodium ethoxide gave crystalline ketol II, in 50–55% yield. Under the same conditions cyclohexanone was converted to the ketol III (17% yield), dihydrocarvone gave an epimeric mixture of ketols IV and V (49% yield), and 2,6-dimethylcyclohexanone afforded an impure product (11%) containing ketol VI which was characterized by conversion to octalone VII.

Crude ketol III was accompanied by impurities which, on the basis of infrared and p.m.r. spectra, appeared to consist of diketone VIII and bridged ketol IX. These contaminants could be separated from ketol III,

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(1) W. S. Rapson and R. Robinson, *J. Chem. Soc.*, 1285 (1935).

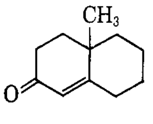
(2) W. S. Johnson, J. J. Korst, R. A. Clement, and J. Dutta, *J. Am. Chem. Soc.*, **82**, 614 (1960).

(3) (a) E. C. du Feu, F. J. McQuillin, and R. Robinson, *J. Chem. Soc.*, 53 (1937); (b) F. D. Gunstone and R. M. Heggie, *ibid.*, 1437 (1952); (c) A. S. Hussey, H. P. Liao, and R. H. Baker, *J. Am. Chem. Soc.*, **75**, 4727 (1953); (d) W. G. Dauben, J. B. Rogan, and E. J. Blanz, *ibid.*, **76**, 6384 (1954); (e) A. L. Wilds, C. H. Hoffman, and T. H. Pearson, *ibid.*, **77**, 647 (1955); (f) M. Yanagtia and K. Yamakawa, *J. Org. Chem.*, **22**, 291 (1957); (g) B. Gaspert, T. G. Halsall, and D. Willis, *J. Chem. Soc.*, 624 (1958); (h) F. Sondheimer and D. Rosenthal, *J. Am. Chem. Soc.*, **80**, 3995 (1958).

(4) E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. Reactions*, **10**, 179 (1959).

(5) The following refractive index values have been recorded for octalone I: $n^{16}\text{D}$ 1.5341,[3a] $n^{19}\text{D}$ 1.5154,[3b] $n^{28}\text{D}$ 1.5060,[3c] $n^{25}\text{D}$ 1.5203,[3d] $n^{19}\text{D}$ 1.5190.[3g]

but not from each other, by chromatography. A large portion (50–70%) of 2,6-dimethylcyclohexanone was recovered from attempts to prepare ketol VI. The spectral properties of material isolated in low yield from one such attempt were suggestive of the diketone X, but a crystalline derivative could not be prepared.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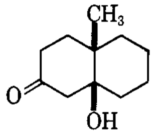
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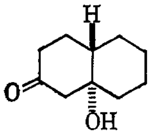
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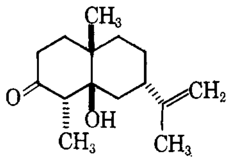
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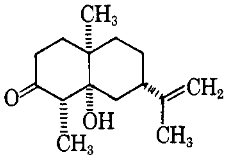
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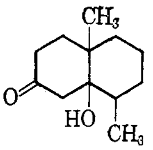
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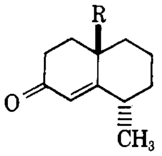
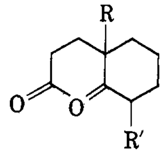
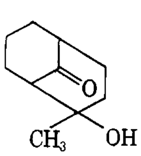

VII, R = CH_3


VIII, R = R′ = H
X, R = R′ = CH_3

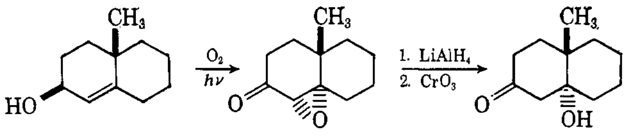

IX

The yield of ketols obtained by this method is largely determined by the insolubility of these products in the reaction media and the ease with which the diketone intermediates (for example VIII) undergo aldol cyclization. Evidently diketones VIII and X prefer condensation with methyl vinyl ketone instead of intramolecular aldolization.

Ketol Stereochemistry.—Ketols have been isolated previously from the Robinson annelation reaction,[2,4,6,7] but the structure[2] and stereochemistry[6,7] of these intermediates have only recently been investigated.

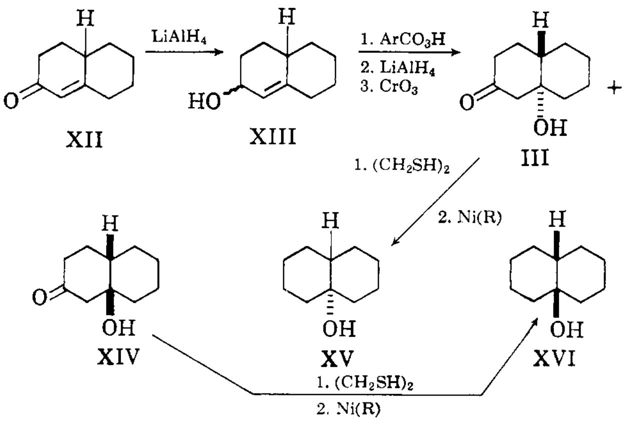
Henbest and McEntee[8] prepared a mixture of the *cis*- and *trans*-ketols II and XI from octalone I by a route based on steroid analogy. We repeated this sequence and found that the ketol assigned structure II[8] was identical with the ketol which we isolated from annelation of 2-methylcyclohexanone. We subsequently prepared the *trans*-ketol XI by a stereoselective route (Scheme I) thereby confirming Henbest and McEntee's[8] stereochemical assignments.

SCHEME I


XI

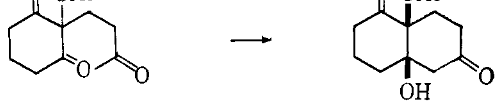
The ketol III was prepared by Tsatsos[9] but its stereochemistry was not investigated. We attempted a synthesis of authentic *cis*-ketol XIV along the lines of Henbest and McEntee[8] (Scheme II). This sequence unexpectedly afforded a nearly 1:1 mixture of the isomeric ketols III and XIV. Apparently, reduction of the octalone XII and epoxidation of the resulting octalol XIII are less stereoselective[10] than corresponding steps in the homologous example where *cis*-ketol II is the predominant eventual product.[8] We succeeded in unambiguously defining the stereochemistry of ketol III by converting it, through the thioketal derivative, to *trans*-9-decalol XV. The isomeric *cis*-ketol furnished *cis*-9-decalol XVI by the same route (Scheme II).

SCHEME II



A careful product analysis of the material obtained from annelation of 2-methylcyclohexanone failed to uncover the *trans*-ketol XI. Likewise, the *cis*-ketol XIV was undetected in the products derived from cyclohexanone. Apparently aldol cyclization leading to ketols II and III is remarkably stereoselective. If this stereoselectivity is determined by ketol stability, then equilibration (*via* retroaldolization) of the undetected ketols XI and XIV with their stereoisomers II and III should be observed in alkaline solution. However, this was not the case. Instead, ketols II, XI, and XIV were readily dehydrated by alkali, and mixtures of octalone I or XII and unchanged ketol were obtained. Therefore, stereoselective formation of ketols II and III must result from kinetic control of aldol cyclization.

While this work was in progress, Spencer and coworkers[7] reported the stereoselective aldol cyclization of acetoxytrione XVII. The selective formation of *cis*-ketol XVIII was attributed to the steric effect of the acetoxyl group which blocks equatorial attack of the butanone side chain. Our findings support this explanation and suggest that equatorial attack on the cyclohexanone is preferred in the absence of α-substituents.[11]


XVII XVIII

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[6] R. Howe, F. J. McQuillin, and R. Temple, *J. Chem. Soc.*, 363 (1959), and references therein to previous papers.

[7] T. A. Spencer, K. K. Schmiegel, and K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 3785 (1963).

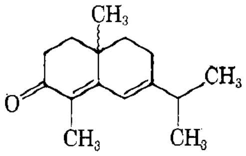
[8] H. B. Henbest and J. McEntee, *J. Chem. Soc.*, 4478 (1961).

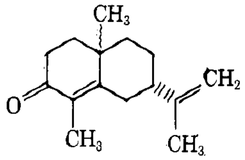
[9] Footnote 17 of ref. 2.

[10] H. B. Henbest and R. A. L. Wilson [*J. Chem. Soc.*, 1958 (1957)] discuss the steric course of allylic alcohol epoxidation.

[11] Contrast the preferred axial attack of cyanide and acetylide anions on 2-methylcyclohexanone: A. V. Kamernitzky and A. A. Akhrem, *Tetrahedron*, **18**, 705 (1962).

Ketol Dehydration.—Ketol II was conveniently dehydrated by steam distillation from aqueous oxalic acid or potassium hydroxide. The octalone I, thus obtained in 90% yield, was identical with a sample generated from the purified semicarbazone derivative.[3h] The ketol mixture IV and V afforded the epimeric diones XIX with refluxing aqueous oxalic acid whereas steam distillation from aqueous potassium hydroxide yielded an epimeric mixture of cyperones XX.


XIX


XX

Experimental[12]

cis-**10-Methyl-2-decalon-9-ol** (II).—A solution of 3 ml. of 3 *N* ethanolic sodium ethoxide in 56 g. of 2-methylcyclohexanone maintained at −10° was efficiently stirred under a nitrogen atmosphere[13] and 35 g. of methyl vinyl ketone was added over a 6-hr. interval. As the addition was completed, the reaction mixture became very thick (almost solid) and stirring was continued with difficulty. The reaction mixture was allowed to stand at −10° for an additional 6 hr. and the cold mass was transferred with ether and brine to a separatory funnel and thoroughly extracted with ether. The combined extracts were washed with saturated brine, dried over anhydrous sodium sulfate, and concentrated to a volume of 0.7 l. This volume was maintained by adding hexane as the ether was removed by evaporation on a steam bath until crystallization commenced. The first crop afforded 35 g. (39%) of white needles, m.p. 120–121°. A second crop gave 13 g. (15%), m.p. 104–112°. The analytical sample, m.p. 120–121° (lit.[8] m.p. 124–125°), was obtained by recrystallization from ether–hexane and sublimination at 60° (20 mm.); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.87 (OH), 5.87 (C=O), 9.59, 9.69 μ (C—O); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 2.35–2.50 (O*H*), 1.13 p.p.m. (C*H*$_3$).[14]

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.4; H, 10.0.

This material was identical (infrared, p.m.r., melting point, and mixture melting point) with a sample prepared according to Henbest and McEntee.[8]

The filtrate was distilled affording 6.5 g. (12%) of 2-methylcyclohexanone, b.p. 65° (24 mm.), and 0.4 g. (0.5%) of octalone I, b.p. 70° (0.3 mm.), identified by comparison of their infrared spectra with those of authentic specimens. The distillation residue consisted of 24 g. (26%) of viscous orange oil. A 1.0-g. sample of this material was chromatographed on 50 g. of Florisil. Elution with 5% ether in benzene afforded 0.3 g. of a mixture containing octalone I and ketol II. The 10–25% ether in benzene fractions contained an additional 0.2 g. of ketol II. Infrared spectra of these fractions showed no absorption at 8.57 μ. This band is characteristic of the *trans*-ketol XI and is apparent in a 1:9 synthetic mixture of *trans*-ketol XI and *cis*-ketol II. The *trans*-ketol XI in a mixture of XI and II was eluted from Florisil in the early 10% ether in benzene fractions and the *cis*-ketol II was found in the late 10% ether in benzene to 25% ether in benzene fractions.

trans-**10-Methyl-2-decalon-9-ol** (**XI**).—The procedure of Nickon[15] was applied. A 25-mm. Pyrex tube surrounded by four 15-w. fluorescent lamps placed about 5 cm. from its walls was charged with a solution of 7.0 g. of 10β-methyl-1(9)-octalin-2β-ol[16] and 56 mg. of hematoporphorin in 140 ml. of anhydrous pyridine. Oxygen was admitted through a gas dispersion tube while the solution was irradiated during 5 days. The pyridine was removed under reduced pressure with the aid of the toluene azeotrope affording 6.34 g. (85%) of an oil containing the desired oxidodecalone (60%), octalone I (20%), and starting octalol (20%). The composition of this mixture was estimated from the integrated p.m.r. spectrum.

A solution of 5.97 g. of crude oxide mixture in 300 ml. of anhydrous ether was stirred with 3.7 g. of lithium aluminum hydride at room temperature for 5 hr. The mixture was treated with 7.9 ml. of water and 6.35 ml. of 10% aqueous sodium hydroxide and allowed to stir overnight. The insoluble salts were removed by filtration and the filtrate was evaporated to give 6.0 g. of viscous oil.

The crude reduction product was dissolved in 160 ml. of acetone, cooled to 0°, and treated with 9.0 ml. of Jones reagent[17] with stirring over a 0.5-hr. period. The mixture was filtered, and the filtrate was diluted with saturated aqueous sodium bicarbonate and extracted with ether. The combined extracts were washed with saturated brine and dried over anhydrous sodium sulfate. The solvent was removed and residue was crystallized from ether–hexane to give 1.32 g. of ketol XI, m.p. 155–156°, undepressed on admixture with a sample prepared according to Henbest and McEntee[8] (lit.[8] m.p. 162–163°); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.91 (OH), 5.87 (C=O), 8.57 μ (C—O); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 2.22 (O*H*), 1.20 p.p.m. (C*H*$_3$).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.4; H, 9.9.

The mother liquor afforded 1.81 g. of octalone I, b.p. 76–83° (0.4 mm.). The distillation residue was comprised mainly of *trans*-ketol XI as evidenced by the infrared spectrum. The infrared and p.m.r. spectra of the *cis*- and *trans*-ketols II and XI exhibited major differences. The mixture melting point of these ketols was depressed to 103–116°.

trans-**2-Decalon-9-ol** (III).—The ketol was prepared from 2.5 ml. of 3 *N* ethanolic sodium ethoxide in 39.2 g. of cyclohexanone and 28.0 g. of methyl vinyl ketone according to the procedure described for ketol II. The product was distilled affording 4.9 g. (12%) of recovered cyclohexanone and 31.7 g. (47%) of impure ketol III, b.p. 100–140° (0.05 mm.), as a semisolid mass. The high-boiling fraction was distilled rapidly with superheating to avoid formation of solid plugs in the condenser. A 3.2-g. sample was removed from this fraction and the remainder was crystallized from hexane–ether to give 9.37 g., m.p. 143–145°. A second crop yielded 1.01 g., m.p. 145–147° (lit.[2] m.p. 147–148.5°); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.8 (OH), 5.88 (C=O), 10.42 μ (C—O).

The infrared spectrum of the concentrated mother liquor exhibited strong bands at 2.88 (OH), and 5.88 μ (C=O) but lacked the band at 9.73 μ characteristic of the *cis*-ketol XIV (see below). Furthermore, this spectrum contained a barely perceptible band at 10.42 μ, whereas the *trans*-ketol III displays a strong sharp band at this wave length.

A 1.00-g. sample representing the crude distilled ketol mixture, b.p. 100–140° (0.05 mm.), was chromatographed on 120 g. of silica.[18] The early 10% ether in benzene fractions (0.05 g.) consisted mainly of 1(9)-octalone-2 identified by its infrared spectrum. Further elution with 10% ether in benzene to 15% ether in benzene afforded 0.14 g. of oil, $\lambda_{\max}^{\mathrm{film}}$ 2.88 (OH) and 5.88 μ (C=O), which lacked both the band at 9.73 μ characteristic of *cis*-ketol XIV, and the band at 10.42 μ characteristic of the *trans*-ketol III (see below). The p.m.r. spectrum of this material showed strong sharp peaks at δ = 2.12 (CH_3C=O) and 1.00 p.p.m. (CH_3—C—)[19] suggestive of the diketone VIII and bridged ketols IX. Continued elution with 15–20% ether in benzene afforded 0.55 g. of solid ketol III. Recrystallization from ether–hexane gave 0.32 g., m.p. 147–148°. A second crop afforded 0.05 g., m.p. 138–145°. Further elution with 20–50% ether in benzene afforded 0.15 g. of oil which showed a weak band at 10.42 μ indicative of *trans*-ketol III, but lacked a band at 9.73 μ. The remaining major infrared peaks appeared at 2.92 (OH), 5.88 (C=O), 6.05 (conj. C=O), and 6.18 μ (conj. C=C).

cis **and** *trans*-**2-Decalon-9-ol** (**XIV and III**).—A solution of 12.0 g. of 1(9)-octalone-2[7,20] in 330 ml. of anhydrous ether

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[12] Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., and Microtech Laboratories, Skokie, Ill. Melting points were taken on a Fisher-Johns hot stage and are corrected. P.m.r. spectra were determined with a Varian A-60 spectrometer.

[13] W. S. Johnson and W. P. Schneider, *Org. Syn.*, **30**, 18 (1950).

[14] We prefer the notation $\delta_{\text{internal standard}}^{\text{solvent}}$ to express chemical shift data.

[15] A. Nickon and W. Mendelson, *J. Am. Chem. Soc.*, **85**, 1894 (1963).

[16] (a) W. J. Vandenheuvel and E. S. Wallis, *J. Org. Chem.*, **27**, 1233 (1962). (b) the prefixed "α" and "β" are used to designate the relative stereochemistry of racemic compounds.

[17] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

[18] Davison Chemical, Baltimore, Md.

[19] H. Conroy, "Advances in Organic Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1960, p. 287.

[20] Purified by crystallization at −40°.

containing 3.1 g. of lithium aluminum hydride was stirred for 4 hr. The mixture was cautiously treated with 6.7 ml. of water and 5.3 ml. of 10% aqueous sodium hydroxide, stirred for 8 hr., and filtered. The filtrate was evaporated and distilled affording 11.6 g. (95%) of a 4:1 mixture (by gas–liquid chromatography) of *cis* and *trans*-1(9)-octalol-2, b.p. 60–67° (0.15 mm.). The analytical sample, b.p. 68° (0.3 mm.), was obtained by redistillation.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.83; H, 10.59. Found: C, 78.7; H, 10.6.

A 3.14-g. portion of the octalol mixture in 125 ml. of benzene containing 4.6 g. of *m*-chloroperbenzoic acid[21] was allowed to stand protected from light for 45 min.; 95% of the theoretical amount of peracid was consumed. The solution was washed with 10% aqueous sodium hydroxide and saturated brine, and dried over anhydrous sodium sulfate. The material was evaporatively distilled affording 2.6 g. of colorless oil, b.p. 50–75° (bath temp.) at 0.1 mm.

A 1.90-g. sample of this oil was reduced with 0.86 g. of lithium aluminum hydride in 85 ml. of ether for 4 hr. Work-up with water and 10% aqueous sodium hydroxide gave 2.0 g. of a viscous oil.

A 0.42-g. sample of this oil in 15 ml. of acetone was stirred at 0° while 0.70 ml. of Jones reagent[22] was added dropwise. The mixture was diluted with aqueous sodium bicarbonate and thoroughly extracted with ether. The combined extracts were washed with saturated brine, dried over anhydrous sodium sulfate, and distilled leaving 0.38 g. of solid residue. This residue was chromatographed on 50 g. of silica.[18] Elution with 15% ether in benzene afforded 0.21 g. of solid which showed a single spot on a silica gel thin layer chromatogram. This material was recrystallized from ether–hexane to give 0.12 g. of *trans*-ketol III, m.p. 145–146° alone or on admixture with material obtained previously from the Robinson annelation reaction. Elution with 20% ether in benzene afforded 0.07 g. of a mixture of *cis*- and *trans*-ketols XIV and III followed by 0.12 g. of material comprised mainly of *cis*-ketol XIV. This material was recrystallized from hexane to give 0.08 g. of *cis*-ketol XIV, m.p. 130–131°; $\lambda_{max}^{CHCl_3}$ 2.88 (OH), 5.88 (C═O), 9.73 μ (C—O).

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.5; H, 9.5.

The intermediate chromatographic fractions afforded material, m.p. 109–112°, after combination and crystallization from ether–hexane. The same substance could be isolated in 60% yield by direct crystallization of the crude oxidation mixture. The infrared spectrum of this material was superimposable with that of a synthetic 1:1 mixture of the *cis*- and *trans*-ketols XIV and III. The band at 9.73 μ is apparent in the spectrum of a synthetic mixture containing 10% *cis*-ketol XIV and 90% *trans*-ketol III.

1,10-Dimethyl-7-isopropenyl-2-decalon-9-ol (IV and V).—The ketol was prepared from 0.3 ml. of 3 *N* sodium ethoxide in 7.6 g. of dihydrocarvone and 4.6 g. of ethyl vinyl ketone according to the procedure described for ketol II. A forerun of dihydrocarvone followed by 5.8 g. (49%) of the ketol, b.p. 120–130° (0.3 mm.),[22, 22a] was obtained by distillation; λ_{max}^{film} 2.84 (OH), 5.85 (C═O), 6.07 μ (C═CH₂); $\delta_{TMS}^{CCl_4}$ 4.57–4.68 (═CH_2) 2H, 2.48 (OH) 1H, 1.22 (CH_3) 3H, 0.96 p.p.m. (CHCH_3, J = 7 c.p.s.) 3H.

Gas–liquid chromatography on a 10-ft. 8% silicone gum rubber column showed two peaks in the ratio of 7:3.[22]

8,10-Dimethyl-1(9)-octalone-2 (VII).—The procedure described for ketol II was employed using 12.6 g. of 2,6-dimethylcyclohexanone, 0.6 ml. of 3 *N* ethanolic sodium ethoxide, and 7.7 g. of methyl vinyl ketone. In this case, however, the reaction mixture remained homogeneous. After the usual work-up the product was distilled affording 6.0 g. (48%) of recovered 2,6-dimethylcyclohexanone, b.p. 45–50° (5 mm.), and 2.2 g. of material, b.p. 85 (0.3 mm.) to 155° (0.2 mm.), λ_{max}^{film} 2.88 (OH), 5.88 μ (C═O).

The 2.2 g. of higher boiling material was refluxed[13] with a solution of 1.25 g. of sodium hydroxide in 25 ml. of 95% ethanol for 4 hr. The cooled mixture was diluted with saturated brine and extracted with ether. The extracts were washed, dried, and distilled affording 1 g. of orange oil, b.p. 65–135° (bath temp.) at 0.08 mm. The infrared spectrum displayed medium intensity bands at 2.88 (OH) and 5.88 (C═O) and strong bands at 6.0 (conj. C═O) and 6.20 μ (conj. C═C). A 0.2-g. sample was redistilled affording 0.1 g., b.p. 50–60° (bath temp.) at 0.03 mm., which still contained hydroxyl and saturated ketone bands in the infrared spectrum. A 0.07-g. sample was converted to the 2,4-dinitrophenylhydrazone, m.p. 170–172°. The over-all yield of octalone VII, calculated on the basis of 2,4-dinitrophenylhydrazone, was 4%. An authentic sample of this derivative, m.p. 172.5–174°, was obtained from octalone VII prepared by the conventional method[3a] in 12% over-all yield.[23] The melting point of a mixture of the derivatives was undepressed.

Anal. Calcd. for $C_{18}H_{22}N_4O_4$: C, 60.31; H, 6.20; N, 15.63. Found: C, 60.4; H, 6.3; N, 15.6.

After several distillations the octalone VII, b.p. 88° (0.3 mm.), displayed λ_{max}^{EtOH} 240 mμ (ε 13,500).[23]

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.83; H, 10.20. Found: C, 80.24; H, 9.99.

Satisfactory analytical values could not be obtained because of a tenacious alcoholic impurity (λ_{max} 2.9 μ). A semicarbazone derivative, m.p. 209–210°, was prepared.

Anal. Calcd. for $C_{13}H_{21}N_3O$: C, 66.35; H, 9.00; N, 17.86. Found: C, 66.4; H, 8.6; N, 17.6.

When the amount of 3 *N* ethanolic sodium ethoxide was doubled and the vinyl ketone was added over a 9-hr. period, 72% of the 2,6-dimethylcyclohexanone was recovered and a colorless liquid, b.p. 75–120° (0.04 mm.), was obtained in 13% yield. The infrared spectrum exhibited weak bands at 2.86 (O—H) and 5.98 (conj. C═O) and a strong band at 5.86 μ (C═O). The p.m.r. spectrum had strong bands at δ_{TMS}^{neat} 1.98 (CH_3CO), 0.81 (CH_3—C<), and 0.82 p.p.m. (CH_3—CH, J = 7 c.p.s.) according to expectation for the diketone X.[19]

A semicarbazone derivative prepared by the method of Fieser[24] had m.p. 209–210° after several recrystallizations from methanol. Infrared comparison and mixture melting point determination established the identity of this derivative with the semicarbazone of the octalone VII.

***trans*-9-Decalol (XV).**—A solution of 3.50 g. of *trans*-ketol III in 60 ml. of glacial acetic acid, 6 ml. of 1,2-ethanedithiol, and 6 ml. of boron trifluoride etherate[25] was allowed to stand at room temperature for 1 hr. The solution was diluted with saturated brine and extracted with ether. The combined extracts were washed with dilute sodium hydroxide and saturated brine, and dried over anhydrous sodium sulfate. The ether was distilled and the residue was crystallized from hexane affording 2.47 g. (49%) of the thioketal, m.p. 93–95°. The analytical sample, m.p. 94–95°, was obtained by recrystallization from hexane.

Anal. Calcd. for $C_{12}H_{20}OS_2$: C, 58.97; H, 8.25; S, 26.24. Found: C, 59.0; H, 8.2; S, 26.1.

A solution of 1.00 g. of this thioketal in 50 ml. of absolute ethanol was stirred with 30 g. of freshly prepared W-2 Raney nickel[26] at room temperature for 2 hr. and at reflux for 4 hr. The cooled mixture was filtered and the ethanol was distilled from the filtrate at atmospheric pressure. The residue was dissolved in ether, washed with brine, and dried. The ether was removed by distillation affording 0.53 g. (84%) of solid material. A 0.27-g. sample of this solid was recrystallized from pentane at −70° affording 0.12 g., m.p. 51–52°.[27a] A second crop yielded 0.07 g., m.p. 50.5–51.5°. The analytical sample sublimed at 25° (0.04 mm.) as hexagonal plates, m.p. 51.5–52.5° (lit.[27b] m.p. 50–51.5°).

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.77. Found: C, 77.7; H, 11.7.

***cis*-9-Decalol (XVI).**—Preparation of the thioketal derivative from 0.25 g. of *cis*-ketol XIV afforded 0.36 g. (99%) of crude solid. Recrystallization from hexane gave 0.26 g. (70%), m.p. 120–122°. A second crop afforded 0.01 g. (5%), m.p. 117–120°. The analytical sample, m.p. 121–122°, was obtained by recrystallization of the first crop from hexane.

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(21) FMC Corporation, Carteret, N. J.

(22) F. J. McQuillin [*J. Chem. Soc.*, 528 (1955)] reported b.p. 110–120° (0.1 mm.) and 140–150° (0.5 mm.).

(22a) NOTE ADDED IN PROOF.—This ketol crystallized after refrigeration for 1 year. Recrystallization from hexane afforded material with the reported[22] m.p. 106–108°.

(23) We are indebted to Mr. Noal Cohen, Northwestern University, for this sample.

(24) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath, Boston, Mass., 1957, p. 339.

(25) The procedure of L. F. Fieser, *J. Am. Chem. Soc.*, **76**, 1945 (1954).

(26) R. Mozingo, *Org. Syn.*, **21**, 15 (1941).

(27) (a) The infrared spectrum of this material was identical with a *trans*-9-decalol spectrum kindly provided by Professor W. G. Dauben; (b) W. G. Dauben, R. C. Tweit, and R. L. MacLean, *J. Am. Chem. Soc.*, **77**, 48 (1955).

Anal. Calcd. for $C_{12}H_{20}OS_2$: C, 58.97; H, 8.25; S, 26.24. Found: C, 59.2; H, 8.3; S, 26.1.

A 0.20-g. sample of this thioketal was desulfurized by the procedure described for the *trans* isomer. The decalol, m.p. 57–64°, was obtained in quantitative yield.[28] The solid was sublimed at 25° (0.05 mm.) to give 89 mg. (71%), m.p. 65–66.5°.[29]

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.77. Found: C, 78.1; H, 11.8.

10-Methyl-1(9)-octalone-2 (I).—A 7.50-g. sample of the ketol II was distilled with steam from 100 ml. of 10% aqueous potassium hydroxide. The distillate (1 l.) was saturated with sodium chloride and thoroughly extracted with ether. The extracts were dried over anhydrous sodium sulfate and distilled affording 5.83 g. (86.3%) of colorless octalone I, b.p. 82–83° (0.7 mm.); $\lambda_{\max}^{\text{film}}$ 5.99 (conj. C=O), 6.18 μ (conj. C=C); $\lambda_{\max}^{\text{EtOH}}$ 239 mμ (ϵ 14,400), lit.[3h] 239 mμ (ϵ 14,800).

Comparable yields were obtained when 100 ml. of 10% aqueous oxalic acid was used in the dehydration either with or without steam distillation of the product. Material from typical experiments gave the following refractive index values[5]: $n^{25}\text{D}$ 1.5230,[30a] 1.5228,[30b] $n^{30}\text{D}$ 1.5215.[30c] A single peak was observed from gas–liquid chromatography using a 10-ft. 8% silicone gum rubber column at 160°.

The *trans*-ketol XI afforded octalone I in 90% yield by steam distillation from aqueous potassium hydroxide.

1,10-Dimethyl-7-isopropyl-1(9)-hexalin-2-one (**XIX**).—A mixture of 1.00 g. of the ketols IV and V in 10 ml. of 10% aqueous oxalic acid was stirred at reflux for 8 hr.[13] The cooled mixture was extracted with ether and the combined extracts were washed with aqueous sodium bicarbonate and saturated brine, and dried over anhydrous sodium sulfate. The residue was distilled affording 0.85 g. (92%), b.p. 70–110° (bath temp.) at 0.2 mm.; $\lambda_{\max}^{\text{film}}$ 6.06 (conj. C=O), 6.21, 6.35 μ (conj. C=C); $\delta_{\text{TMS}}^{\text{CCl}_4}$ 6.28 (C=C*H*), 1.75 (C*H*₃), 1.11 (CHC*H*₃, J = 7 c.p.s.), 1.09 p.p.m. (angular C*H*₃); $\lambda_{\max}^{\text{EtOH}}$ 300 mμ (ϵ 19,100), lit.[22] 301 mμ (ϵ 27,600).

Both the p.m.r. and ultraviolet spectral data indicate the presence of about 70% of the dienone XIX in this material. Attempts to purify the semicarbazone to constant melting point by successive recrystallization failed. Undoubtedly, purification is hampered by the presence of a substantial amount (60% *assuming an initial* 70:30 *mixture)* of racemic dienone XIX resulting from the original mixture of ketols IV and V.

1,10-Dimethyl-7-isopropenyl-1(9)-octalone-2 (**XX**).—A mixture of 0.50 g. of ketols IV and V in 50 ml. of 10% aqueous potassium hydroxide was distilled with steam until 500 ml. of distillate was collected. The distillate was extracted with ether and the extracts were dried over anhydrous sodium sulfate. The ether was distilled and the residue was converted to the 2,4-dinitrophenylhydrazone derivative which after several recrystallizations from ethyl acetate–ethanol had m.p. 199–200° (lit.[22] m.p. 202°).

Anal. Calcd. for $C_{21}H_{26}N_4O_4$: C, 63.30; H, 6.58. Found: C, 63.2; H, 6.6.

Attempted Equilibration of the Ketols II and XI.—The following procedure was employed. A solution of 50 mg. of the pure ketol in 4 ml. of absolute ethanol was cooled to −10° and varying amounts of 3 *N* ethanolic potassium hydroxide[31] were added. The alkaline solution was maintained at −10° for 3 hr., diluted with saturated brine, and extracted with ether. The extracts were dried and solvent was evaporated. The residue was crystallized, the mother liquor was concentrated, and an infrared spectrum was determined. The band at 8.57 μ was used to estimate the *trans*-ketol XI and the bands of 9.59 and 9.69 μ were employed to estimate *cis*-ketol II (see Table I). These bands were apparent in synthetic 1:9 mixtures of the ketols.

TABLE I

Ketol	3 *N* KOH, ml.	Crystalline product, mg. (m.p., °C.)	Mother liquor
II (m.p. 120–122°)	0.01	45 (118–120)	. . .
	0.17	26 (114–118)	Octalone I plus *cis*-ketol II, no 8.57-μ band
XI (m.p. 156–157°)	0.01	48 (157–158)	. . .
	0.02	48 (154–156)	. . .
	0.08	30 (154–156)	Octalone I plus *trans*-ketol XI, no 9.6–9.7-μ band
	0.90	12 (151–154)	Mainly octalone I, no 9.6–9.7-μ band

Attempted Equilibrium of Ketol XIV.—The procedure described above was followed using 25 mg. of *cis*-ketol XIV, m.p. 129–131°, in 1.0 ml. of absolute ethanol at −7° for varying time intervals with varying added amounts of ethanolic sodium ethoxide with the following results. (1) Sodium ethoxide (3 *N*, 0.04 ml.) for 6 hr. gave 20 mg. (87%) of 1(9)-octalone-2 (XII). (2) Sodium ethoxide (3 *N*, 0.01 ml.) for 3 hr. gave 22 mg. of oil containing over 50% octalone XII estimated by relative intensities of the 5.87 (C=O) and 5.98 μ (conj. C=O) infrared bands. The infrared spectrum lacked a band at 10.42 μ (*trans*-ketol III C—O). Crystallization from hexane afforded 3 mg. of recovered *cis*-ketol XIV, m.p. 129.5–130.5°. (3) Sodium ethoxide (1 *N*, 0.01 ml.) for 3 hr. gave 24 mg. of solid containing recovered ketol XIV and octalone. The infrared spectrum lacked the 10.42-μ band. Crystallization from hexane afforded 16 mg. of recovered *cis*-ketol XIV, m.p. 130–131°.

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(28) The infrared spectrum was identical with a *cis*-9-decalol spectrum kindly provided by Professor W. G. Dauben.

(29) J. R. Durland and H. Adkins [*J. Am. Chem. Soc.*, **61**, 429 (1939)] reported m.p. 64.5–65°.

(30) (a) Prepared by steam distillation of ketol II from alkali; (b) prepared from the purified semicarbazone, m.p. 196–197°[3h]; (c) prepared by refluxing ketol II with aqueous oxalic acid.[28]

(31) The preparation of the *cis*-ketol II was initially investigated using potassium hydroxide. The results of these experiments were comparable with those in which ethanolic sodium ethoxide was used except for the yield of *cis*-ketol II which was greater with the ethoxide catalyst.