In a three-necked flask fitted with stirrer and condenser, 10 g. of the appropriate 2,6-diaroyloxyacetophenone, 12 g. of anhydrous potassium carbonate, and 100 ml. of 2,6-lutidine (or pyridine) were placed, and the resulting mixture heated under reflux for 2 hr. The resulting yellow precipitate and 2,6-lutidine (or pyridine) were dissolved in water and poured cautiously into an excess of ice-cold 6 *N* hydrochloric acid. The resulting pale yellow to bright orange precipitate was collected by filtration and dried. Presumably this product consisted of a mixture of di- and triaroylmethanes, as well as some of the corresponding flavones. It was used in the cyclization step without further purification.

Cyclization of Rearrangement Products to Flavones.—A 2-g. quantity of the mixture of aroylmethanes (prepared as in section immediately preceding), 50 ml. of glacial acetic acid, and 2 ml. of concentrated sulfuric acid were heated at 95° for 1 hr. The resulting solution was poured into ice water, and the precipitate collected by filtration. The crude product, consisting chiefly of 3-benzoyl-5-hydroxyflavone with a small amount of 5-hydroxyflavone, or of the 3-aroyl-5-hydroxy-*n*-methoxyflavone (n = 2', 3', or 4') with a small amount of 5-hydroxy-*n*-methoxyflavone, was separated into the components by fractional crystallization. The more insoluble 3-aroylflavone was separated fairly readily by crystallization from ethyl acetate. Concentration of the ethyl acetate mother liquors produced a small amount of 5-hydroxyflavone unsubstituted at the 3-position. The latter was collected by filtration, and purified by repeated recrystallization from ethanol.

5-Acetoxy-3-(*m*-methoxybenzoyl)-3'-methoxyflavone.—In a small flask were placed 200 mg. of 5-hydroxy-3-(*m*-methoxybenzoyl)-3'-methoxyflavone and 5 ml. of acetic anhydride. The mixture was warmed to about 120°, 3–4 drops of pyridine were added, and the resulting solution was heated an additional 3 hr. Then 15 ml. of water was added to the cooled solution. The precipitate resulting was collected by filtration, dissolved in hot dilute alcohol, the solution treated with charcoal, and the mixture filtered. The filtrate was cooled to precipitate the product, which was collected and recrystallized from dilute ethanol to give the colorless, analytically pure acetate; m.p. 145–146°.

Anal. Calcd. for $C_{26}H_{20}O_7$: C, 70.26; H, 4.54. Found: C, 70.03; H, 4.61.

Markedly similar acetylation procedures with the appropriate 3-aroyl-5-hydroxyflavone gave the following: 3-benzoyl-5-acetoxyflavone, m.p. 193–194°, lit.,[10] m.p. 189–190°; 3-anisoyl-5-acetoxy-4'-methoxyflavone, m.p. 222–223°, lit.,[4] m.p. 220°; 3-(*o*-methoxybenzoyl)-5-acetoxy-2'-methoxyflavone, m.p. 184.5–186°, lit.,[9] m.p. 180–181°.

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[10] S. Sugasawa, *J. Chem. Soc.*, 1483 (1934).

Synthesis and Interconversion of 1-Acetyl-$\Delta^{1,8}$-hydrindene and 1-Acetyl-$\Delta^{8,9}$-hydrindene

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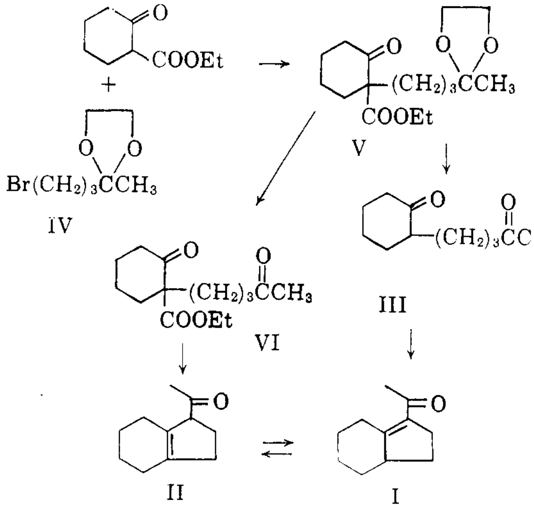
A new synthesis of 1-acetyl-$\Delta^{1,8}$-hydrindene (I) utilizing base-catalyzed cyclization of 2-(3'-acetylpropyl)cyclohexanone is reported. Treatment of I with acids or bases produces a 1:4 equilibrium mixture of I and its $\Delta^{8,9}$ isomer.

In connection with our study of the stereochemistry of conjugate addition at bridgehead positions of polycyclic unsaturated carbonyl compounds,[2] we desired to examine 1-acetyl-$\Delta^{1,8}$-hydrindene (I).[3] This ketone provides a model of potentially useful intermediates for syntheses of 18-functional steroids, and we thus desired a synthesis of I which could be readily adapted to the construction of tetracyclic homologs.[4] Such a synthesis of I and a study of its isomerization to the β,γ-unsaturated isomer II are the subjects of the present paper.

The synthetic approach involved 2-(3'-acetylpropyl)cyclohexanone (III) as the key intermediate which on aldol cyclization was expected to afford I. Early attempts to prepare diketone III by ozonolysis of 1-methyl-$\Delta^{1,9}$-octalin were discarded when we failed to find conditions for selective dehydration of 1-methyl-*trans*-1-decalol to



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[1] United States Public Health Service Predoctoral Fellow 1960–1962.

[2] W. L. Meyer and N. G. Schnautz, *J. Org. Chem.*, **27**, 2011 (1962).

[3] L. E. Coles, W. H. Linnell, D. W. Mathieson, and A. S. Shoukri, *J. Chem. Soc.*, 2617 (1954).

[4] Such an approach to 18-norsteroids has been reported by (a) R. Anliker, M. Müller, M. Perelman, J. Wohlfahrt, and H. Heusser, *Helv. Chim. Acta*, **42**, 1071 (1959). Very recently intermediates of this type together with the conjugate addition reaction for introduction of C-18 functionality have been utilized in total syntheses by (b) W. Nagata, I. Kikkawa, and K. Takeda, *Chem. Pharm. Bull.* (Tokyo), **9**, 79 (1961), and (c) J. A. Marshall and W. S. Johnson *J. Am. Chem. Soc.*, **84**, 1485 (1962).

the $\Delta^{1,9}$-olefin,[5] and we turned to sequences for attachment of a suitable side chain to a cyclohexanone precursor. Alkylation of 2-carbethoxycyclohexanone with ethyl γ-bromobutyrate produced ethyl 4-(1′-carbethoxy-2′-oxocyclohexyl)-butyrate,[6] which on acidic hydrolysis and decarboxylation smoothly afforded 4-(2′-oxocyclohexyl)butyric acid. However, numerous attempts to convert the keto acid to the desired diketone either *via* the acid chloride and dimethylcadmium or diethyl malonate or through the enol lactone with methyl Grignard reagent failed, apparently due to nonformation of the acyl chloride or enol lactone.

Alkylation of 2-carbethoxycyclohexanone with 2-(3′-bromopropyl)-2-methyl-1,3-dioxolane (IV)[7] in the presence of potassium *t*-butoxide in refluxing *t*-butyl alcohol[8] was accomplished satisfactorily to afford 2 - carbethoxy - 2 - (4′,4′ - ethylenedioxypentyl)cyclohexanone (V) in 71% yield. When V was treated with methanolic hydrochloric acid, the ketal was cleaved and 72% of 2-carbethoxy-2-(3′-acetylpropyl)cyclohexanone (VI) was isolated. This diketo ester seemed to be an ideal intermediate for synthesis of I without isolation of the diketone III, since saponification of the ester should be accompanied by decarboxylation and intramolecular aldol cyclization.[9,10] Treatment of VI with aqueous potassium hydroxide at reflux for twenty-four hours produced an 82:18 mixture of two neutral compounds, neither of which was starting material VI or diketone III as shown by gas chromatography. This mixture had the characteristic ultraviolet absorption at 256 mμ expected for I,[3] but the extinction coefficient (2500) was quite low. The infrared spectrum of the mixture had a strong band at 5.85 μ characteristic of a saturated ketone and three other less intense bands at 5.98, 6.05, and 6.20 μ indicating the presence of α,β-unsaturated carbonyl functionality. The spectral data and the gas chromatogram indicated that I was present in the product but that the major product was a nonconjugated carbonyl compound.

In order to define better the course of this cyclization we returned to synthesis of the intermediate diketone (III). Alkaline saponification of the keto ester ketal V followed by mild acidification to decarboxylate the keto acid and cleave the ketal produced the diketone III in 62% yield. The infrared spectrum of the diketone had a single carbonyl band at 5.85 μ and its gas chromatogram showed no evidence of contaminants. When a small sample of III was refluxed with sodium methoxide in methanol, there was produced a mixture of two components which had a gas chromatogram and infrared spectrum very similar to those of the mixture obtained from alkaline treatment of the diketo ester VI. The ultraviolet absorption of this product likewise showed absorption at 256 mμ, but the extinction coefficient had been increased to 4200 and the second component from the gas chromatogram represented 29% rather than 18% of the total product. Treatment of III under a variety of basic conditions gave mixtures of the same two components in varying proportions. These data were all consistent with formation of the desired ketone I (the second gas chromatographic component) accompanied by substantial amounts of a nonconjugated ketone. The two substances could not be separated by distillation. The proportion of I in the mixtures was greater when weaker bases, shorter reaction times, or lower temperatures were used.

When III was refluxed with 5% potassium carbonate, the gas chromatogram of the crude reaction product showed the same two components, but the first peak represented only 17% of the total and the infrared band at 5.85 μ was quite weak. Careful fractional distillation of this material afforded in 67% yield a sample which was 88% pure according to the gas chromatogram, and which had infrared absorption at 5.85 (very weak), 5.98, 6.05, and 6.20 μ and ultraviolet absorption at 256 mμ (ϵ 11,000).[11] The n.m.r. spectrum displayed no resonance due to vinyl proton and had a band at 7.9 τ[12] characteristic of the acetyl group. Although aldol cyclization of III might possibly lead to derivatives of three bicyclic ketones, VII, VIII, or IX, the only possible α,β-unsaturated ketone in these series which has an acetyl group and no vinyl hydrogens is $\Delta^{1,8}$-VII (I), and thus the conjugated cyclization product indeed has this structure. Except for the ultraviolet extinction coefficient of I,[11] the properties of our sample and its semicarbazone correspond well with those reported by Coles for I prepared by a different sequence.[3] The doublet infrared carbonyl absorption at 5.98 and 6.05 μ may be due to the presence of both the *s-cis* and *s-trans*[13] forms of I (in carbon disulfide),[14]

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(5) J. English and G. Cavaglieri, *J. Am. Chem. Soc.*, **65**, 1085 (1943), prepared III by lead tetraacetate cleavage of 1-methyl-1,9-*trans*-dihydroxydecalin which they were able to isolate in low yield from a mixture of $\Delta^{1,9}$- and $\Delta^{1,2}$-1-methyloctalins.

(6) J. Tinker, *J. Org. Chem.*, **16**, 1417 (1951).

(7) C. A. Grob and R. Moesch, *Helv. Chim. Acta*, **42**, 728 (1959).

(8) Potassium *t*-butoxide was preferred to sodium ethoxide because use of the latter base gave rise to varying amounts of a higher-boiling by-product. This material, which had a single infrared carbonyl absorption at 5.75 μ, is probably the product of reverse Dieckmann cyclization. W. G. Dauben, J. W. McFarland, and J. B. Rogan, *J. Org. Chem.*, **26**, 297 (1961) have also observed that reverse Dieckmann reaction is minimized when potassium *t*-butoxide is used as the base in alkylations of 2-carbethoxycyclohexanone.

(9) J. A. Hartman, *J. Org. Chem.*, **22**, 466 (1957).

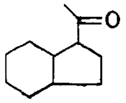
(10) A. M. Islam and R. A. Raphael, *J. Chem. Soc.*, 4086 (1952).

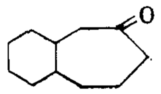
(11) Coles and co-workers, ref. 3, report a λ_{max} of 253 mμ (ϵ 8000) for 1-acetyl-$\Delta^{1,8}$-hydrindene purified *via* its semicarbazone. In our hands regeneration of the ketone from purified semicarbazone always resulted in formation of some of the nonconjugated isomer. Such contamination may account for their low ϵ value.

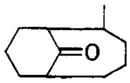
(12) N.m.r. resonances are expressed throughout in terms of the τ scale of G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(13) R. S. Mulliken, *Revs. Mod. Phys.*, **14**, 265 (1942).

(14) R. Mecke and K. Noack, *Chem. Ber.*, **93**, 210 (1960).


VII


VIII

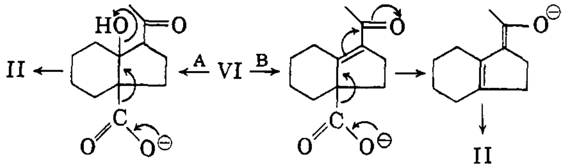

IX

although the high extinction coefficient (in ethanol) is more characteristic of the *s-trans* conformer.[15]

After the identity of the conjugated material obtained by cyclization of III or VI had been established, the structure of the nonconjugated by-product remained a problem. In view of the spectral data obtained from mixtures and the increased proportion of by-product produced under more alkaline cyclization conditions a β,γ-unsaturated isomer of I was suspected. Indeed, Coles, *et al.*,[3] obtained predominantly such an isomer, although the position of the olefinic linkage was not known, in an attempt to prepare I under strongly acidic conditions. A pure sample of this component was obtained by chromatography of the cyclization mixture on Florisil, and elemental analysis of its semicarbazone showed the ketone to be isomeric with I. Its infrared spectrum had only one band at 5.85 μ in the carbonyl region and its ultraviolet spectrum was devoid of absorption in the 200 to 280-mμ range, the only maximum appearing at 290 mμ (ϵ 131) because of a saturated ketone. An iodoform test was positive, and the n.m.r. spectrum had a strong band at 8.03 τ characteristic of the acetyl group, but no absorption in the vinyl proton region. Of the possible nonconjugated unsaturated derivatives of VII, VIII, and IX, only $\Delta^{8,9}$-VII (II) contains an acetyl group and no vinyl proton, and thus II must be the by-product ketone. Most of the physical properties of our sample and its semicarbazone compare favorably with those reported by Coles[3] for his β,γ-isomer.[16]

On treatment of either I or II with sodium methoxide, the same equilibrium mixture is obtained. This consists of 80% of II and 20% of I as determined by gas chromatography and ultraviolet spectroscopy. The rate of isomerization of I to II is slower than is that of the cyclization-dehydration of III, since under typical conditions disappearance of III is accompanied by appearance of I and only later do substantial quantities of II appear (at the expense of I) in the gas chromatogram of the reaction mixture. The occurrence of I as the primary dehydration product of the intermediate ketol is, of course, expected, since there is no activation of the C-9 (γ) hydrogen for a base-catalyzed dehydration. The obvious corollary of these observations is that for preparation of I, the use of a weak base and a short reaction time is preferred. Acidic reagents are also effective in promoting the equilibration, and indeed attempted cyclization of III to I with alumina, a reagent which gave no reported β,γ-isomer in a related tetracyclic system,[4a] produced only the equilibrium mixture of I and II.

Although I is the primary unsaturated product from cyclization of the diketone III, and more slowly isomerizes to II, such does not appear to be the case for the reaction leading to I and II from the diketo ester VI. Extensive relative rate data for the saponification, cyclization, dehydration, and decarboxylation steps of the latter preparation have not been obtained, but in one pair of experiments under comparable conditions of time, temperature, and basicity, III afforded an approximately 50:50 mixture of I and II, while VI produced a 15:85 mixture. In neither case was equilibrium (20:80) established, and thus it is clear that VI produces the unconjugated isomer II without the intermediacy of I. Such sequences as A, B, or variants are quite reasonable if cyclization precedes decarboxylation.[17]



The equilibration data, 20% I and 80% II, lead to a value of 0.8 kcal./mole for the free energy difference between the isomeric ketones. Clearly the small (approximately 2 kcal./mole[18]) resonance stabilization of the conjugated system in I has been offset by decreased unfavorable steric interactions in II. The most prominent of these differences is the relief of the eclipsing of the equatorial C-7 hydrogen with the acetyl group on going from I to II, a change associated with the endocyclic location of the double bond with respect to both rings of II.[19] Indeed, relief of this interaction is particularly important since in order to obtain the resonance stabilization, the acetyl group and double bond must approach coplanarity in I, while in the absence of conjugation (II) the acetyl group is free to assume a conformation (roughly perpendicular to the plane of the five-membered ring) which considerably separates the methyl

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[15] R. B. Turner and D. M. Voitle, *J. Am. Chem. Soc.*, **73**, 1403 (1951).

[16] The ultraviolet extinction coefficient of our semicarbazone (11,300) is much lower than that reported in ref. 3 (17,380), a situation for which we have no explanation other than to note that our value seems nearer that expected for the structure (A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," 2nd ed., Edward Arnold Ltd., London, 1957, p. 58; see also ref. 15).

[17] An analogous path for a related decarboxylation has been suggested by G. Stork and F. H. Clark, *J. Am. Chem. Soc.*, **83**, 3114 (1961). See also ref. 8. Participation of a β-lactone is, of course, possible but not required in our case.

[18] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith, and W. E. Vaughan, *ibid.*, **60**, 440 (1938), report a value of 2.4 kcal./mole for crotonaldehyde.

[19] See R. B. Turner and R. H. Garner, *ibid.*, **80**, 1424 (1958), and references cited therein for data and discussion of this problem.

and oxygen from C-7 and C-2 hydrogens.[20] Numerous examples are known of unsaturated ketones structurally related to I and II in which β,γ-isomers occur with or predominate over the conjugated forms at equilibrium,[15,21] and the structural factors involved have been discussed.[19,22] It is interesting to note that in syntheses of tetracyclic analogs of I, no evidence for the corresponding β,γ-isomers has been reported.[4] It is not clear, however, whether this is due to a reversed stability relationship of α,β and β,γ forms (due to subtle steric effects resulting from fusion of additional rings), or use of nonequilibrating conditions in preparation of those α,β-isomers.

Experimental[23]

2-Carbethoxy-2-(4′,4′-ethylenedioxypentyl)cyclohexanone (V).—To a solution of potassium *t*-butoxide [prepared from 6.35 g. (0.162 g.-atom) of potassium metal and 150 ml. of anhydrous *t*-butyl alcohol] at room temperature was added with stirring 27.6 g. (0.162 mole) of 2-carbethoxycyclohexanone[24] [b.p. 103–107° (10 mm.)]. After 15 min., 34 g. (0.162 mole) of 2-(3′-bromopropyl)-2-methyl-1,3-dioxolane[7] was added rapidly and the reaction mixture was heated to reflux and stirred at that temperature for 7 hr. After being cooled to room temperature the mixture was diluted with 500 ml. of ice water and extracted with methylene chloride. The extracts were washed with water, dried over calcium chloride, and concentrated. On distillation the crude product yielded two fractions; the first, b.p. 73–148° (0.5 mm.), consisted primarily of starting material as evidenced by its infrared spectrum and gas chromatogram; the second fraction, b.p. 148–153° (0.5 mm.) consisted of 34.4 g. (71%) of V, $\lambda_{\max}^{CS_2}$ 5.8 μ (shoulder) and 5.85 μ. An iodoform test was negative but after treatment of a sample with dilute methanolic hydrochloric acid for few minutes a positive test was obtained. An analytical sample prepared from the second fraction had b.p. 152° (0.3 mm.), n^{25}D 1.4692.

Anal. Calcd. for $C_{16}H_{26}O_5$: C, 64.40; H, 8.78. Found[25]: C, 64.2; H, 8.5.

2-Carbethoxy-2-(3′-acetylpropyl)cyclohexanone (VI).—A 10-g. (0.033 mole) sample of the ketal V [b.p. 150–162° (1.0–1.5 mm.)] was allowed to stand at room temperature for 7 hr. with 25 ml. of methanol and 5 ml. of 5% hydrochloric acid. The mixture was diluted with 100 ml. of water and extracted with ether. The extracts were washed with 5% sodium bicarbonate solution and water, then dried over sodium sulfate and concentrated. Distillation of the crude product furnished 6.27 g. (72%) of VI, b.p. 138–140° (0.8 mm.), $\lambda_{\max}^{CS_2}$ 5.75 μ (shoulder) and 5.85 μ. The distilled product gave an immediate iodoform precipitate, and its gas chromatogram showed only one component. The analytical sample had b.p. 126° (0.4 mm.), n^{25}D 1.4697.

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found[25]: C, 65.8; H, 8.7.

2-(3′-Acetylpropyl)cyclohexanone (III).—A 15.0 g. sample (0.0503 mole) of the ketal V [b.p. 154° (0.8 mm.)] was refluxed for 26 hr. under nitrogen with 100 ml. of 95% ethanol and 150 ml. of 5% sodium hydroxide. The reaction mixture was allowed to cool to room temperature and the ethanol was removed at reduced pressure. The resulting solution was acidified with 5% hydrochloric acid (gas evolution) to pH 2 and stirred at room temperature for 1 hr. The product was extracted with ether and the extracts dried over sodium sulfate and concentrated to yield a light yellow liquid. Distillation of this material afforded 5.74 g. (62%) of the diketone III as a colorless liquid, b.p. 105–107° (0.8 mm.), (reported[6] b.p., pot temperature 170–175° (1.0 mm.)); $\lambda_{\max}^{CS_2}$ 5.85, 7.1, 7.4 μ. An analytical sample had b.p. 94–95° (0.6 mm.), n^{25}D 1.4703.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found[26]: C, 72.7; H, 9.9.

Cycyclization of the Diketo Ester VI.—A 5.74-g. (0.0225 mole) sample of VI, b.p. 142–143° (1.0 mm.), was refluxed for 24 hr. under a nitrogen atmosphere with 150 ml. of 5% potassium hydroxide. The solution was cooled and neutralized with 3 *N* sulfuric acid and the resulting solution was extracted with ether. The extracts were washed with 5% sodium bicarbonate and water, dried over sodium sulfate, and concentrated to yield 2.79 g. of light yellow oil, $\lambda_{\max}^{\text{neat}}$ 5.85 (s), 6.0 (m), 6.1 (m), and 6.2 μ (m); $\lambda_{\max}^{95\%\,\text{EtOH}}$ 256 mμ (ϵ 2,500). The gas chromatogram showed two peaks, the first material eluted comprising 82% of the mixture and the second 18%, neither of which corresponded to starting material. Distillation at 96° (5.0 mm.) afforded very little separation of the two components. Treatment of samples of distilled material with potassium *t*-butoxide or methanolic potassium hydroxide left the infrared spectrum, ultraviolet spectrum, and gas chromatogram unchanged.

Methoxide- and Hydroxide-Catalyzed Cyclizations of III. 1-Acetyl-Δ-^{8,9}hydrindene (II).—A 200-mg. sample of diketone III in 8 ml. of methanol was added to a solution of sodium methoxide prepared from 20 ml. of absolute methanol and 0.23 g. of freshly cut sodium metal. The reaction mixture was allowed to stand for 1 hr. at room temperature and then refluxed for 2 hr. under a nitrogen atmosphere. Dilution with water was followed by extraction with ether. The ether extracts were dried over sodium sulfate and concentrated to yield 175 mg. of a light yellow liquid, $\lambda_{\max}^{\text{neat}}$ 5.85, 5.98, 6.05, and 6.20 μ; $\lambda_{\max}^{95\%\ \text{EtOH}}$ 256 mμ (ϵ 4200). The gas chromatogram of this unrefined material showed two components and no starting diketone. The component appearing first on the chromatogram (II) amounted to 71% of the total material and the second (I) represented 29%.

When III was refluxed for 5 hr. with 5% potassium hydroxide solution, the crude product had $\lambda_{\max}^{\text{neat}}$ 5.85, 5.98, 6.05 and 6.20 μ; $\lambda_{\max}^{95\%\ \text{EtOH}}$ 256 mμ (ϵ 5900). The gas chromatogram again showed the absence of starting material and the presence of the same two components, 47% of the more volatile one (II) and 53% of the second, higher boiling one (I). Distillation of the reaction mixture through a micro

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(20) Certainly other steric and hyperconjugative effects play a part in determining the exact position of the equilibrium, and we do not intend to imply that such effects are insignificant. However, the energy factors involved are all small and in a complex molecule difficult to assess quantitatively, and further discussion of an individual case thus does not seem profitable at this point.

(21) For example (a) A. H. Dickens, W. E. Hugh, and G. A. R. Kon, *J. Chem. Soc.*, 572 (1929); (b) G. A. R. Kon and R. P. Linstead, *ibid.*, 1269 (1929); (c) G. A. R. Kon and R. S. Thakur, *ibid.*, 2217 (1930); (d) T. Takeshima, *J. Am. Chem. Soc.*, **75**, 3309 (1953). See ref. 19 and 22 for reference to further examples.

(22) H. C. Brown, J. H. Brewster, and H. Shechter, *ibid.*, **76**, 467 (1954).

(23) Infrared spectra were obtained on Perkin-Elmer Models 21 and 137 spectrophotometers. Ultraviolet spectra were taken using a Cary 14 ultraviolet spectrophotometer. N.m.r. spectra were obtained from dilute solutions in carbon tetrachloride using a Varian DP-60 Spectrometer operating at 60 Mc. and equipped with a Model 3506 Flux Stabilizer. Resonance positions were determined by the audio side-band technique relative to tetramethylsilane as an internal standard. Gas chromatograms were run at 170–225° on a 2-m. column containing 9% silicone gum SE-30 on Chromosorb W with helium as the carrier gas. The compositions of the mixtures were determined by measuring the ratios of the individual peak areas, *cf.* M. Dimbat, P. E. Porter, and F. H. Stross, *Anal. Chem.*, **28**, 290 (1956). All melting points were taken on a microscope hot stage and are corrected for stem exposure.

(24) H. R. Snyder, L. A. Brooks, and S. H. Shapiro, "Organic Syntheses," Vol. II, John Wiley & Sons, Inc., New York, 531 (1943).

(25) Microanalysis by Midwest Microlab, Inc., Indianapolis 20, Indiana.

(26) Microanalysis by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany.

spinning-band column afforded material of b.p. 90–98° (6 mm.), but resulted in poor separation as evidenced by the gas chromatograms and infrared spectra of the various fractions. A 400-mg. sample of crude cyclized material was dissolved in 25 ml. of methanol containing a few drops of concd. hydrochloric acid and allowed to stand overnight. Dilution with water followed by ether extraction afforded 300 mg. of product which had $\lambda_{\max}^{\text{neat}}$ 5.85 (s), 5.98 (w), 6.05 (w) and 6.20 μ (w); $\lambda_{\max}^{95\%\ \text{EtOH}}$ 256 mμ (ε 1950). The gas chromatogram had the same appearance as before except that the first component represented 80% of the total sample and the second 20%.

A 1.4-g. sample of such a mixture was chromatographed on 50 g. of Florisil. Elution with 600 ml. of benzene–cyclohexane (1:9) afforded 300 mg. of II, $\lambda_{\max}^{CS_2}$ 5.85 μ; $\lambda_{\max}^{95\%\ \text{EtOH}}$ 290 mμ (ε 130); τ 8.03; positive iodoform test. The gas chromatogram of this material had only one peak corresponding to the component appearing first in the chromatogram of the cyclization reaction mixtures. The semicarbazone prepared from 100 mg. of II was recrystallized five times from aqueous methanol to afford colorless needles, m.p. 141–143° (reported[3] 139–141°); $\lambda_{\max}^{95\%\ \text{EtOH}}$ 228 mμ, (ε 11,300) [(reported[3] 228 mμ (17,380)[16]].

Anal. Calcd. for $C_{12}H_{19}ON_3$: C, 65.12; H, 8.65; N, 18.99. Found[26]: C, 65.1; H, 8.7; N, 19.3.

Potassium Carbonate-Catalyzed Cyclization of III. 1-Acetyl-$\Delta^{1,8}$-hydrindene (I).—A 4.0-g. (0.022 mole) sample of 2-(3′-acetylpropyl)cyclohexanone, b.p. 105–107° (0.8 mm.), was refluxed for 3 hr. with 100 ml. of 5% potassium carbonate solution under a nitrogen atmosphere. The reaction mixture was extracted with ether, washed with water, and dried over sodium sulfate. Concentration of the extracts produced 3.6 g. of yellow oil, the gas chromatogram of which showed two components, the first representing 17% of the total. Careful distillation of the crude material through a micro spinning-band column afforded 2.42 g. (67%) of I, b.p. 98° (5.0 mm.) (reported[3] 117–119 (12 mm.); 102° (8.0 mm.)); $\lambda_{\max}^{CS_2}$ 5.85 (very weak shoulder), 5.98, 6.05, and 6.20 μ; τ, 7.90; $\lambda_{\max}^{95\%\ \text{EtOH}}$ 256 mμ (ε 11,000) (reported[3] 253 mμ (ε 8,000)). The gas chromatogram of this material showed the first component still present as less than 12% of the total. An analytical sample was prepared by microdistillation of the fraction containing the least amount of β,γ-isomer.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found[26]: C, 80.0; H, 9.5.

A semicarbazone was prepared in 78% yield from material having b.p. 98° (5.0 mm.). Six recrystallizations from aqueous methanol afforded 1.39 g. of colorless plates, m.p. 198–200° (dec.) (reported[3] needles, m.p. 211–212°); $\lambda_{\max}^{95\%\ \text{EtOH}}$ 270 mμ (ε 19,500) [reported[3] 268 mμ (20,000)].

Anal. Calcd. for $C_{12}H_{19}N_3O$: C, 65.12; H, 8.65; N, 18.99. Found:[26] C, 65.3; H, 8.5; N, 19.3.

Regeneration of the ketone from its semicarbazone by means of phthalic anhydride and water[27] yielded a mixture of 73% I and 27% II rather than the pure $\Delta^{1,8}$-isomer, as evidenced by the gas chromatogram and the increased intensity of infrared absorption at 5.85 μ of the recovered ketone mixture.

Equilibration of 1-Acetyl-$\Delta^{1,8}$- and-$\Delta^{8,9}$-hydrindenes.—(a) A 329-mg. sample of 1-acetyl-$\Delta^{1,8}$-hydrindene (I) containing 12% of the $\Delta^{8,9}$-isomer (II), (ε 11,000) was dissolved in a sodium methoxide solution prepared from 0.46 g. of sodium and 20 ml. of methanol. The mixture was stirred at room temperature under a nitrogen atmosphere and 2 ml. aliquots were taken at appropriate intervals for 48 hr. The aliquots were diluted with water, extracted with ether, and, after concentration of the extracts, the residual material was analyzed by gas chromatography and ultraviolet spectroscopy. After 3 hr. II amounted to 24% of the total [$\lambda_{\max}^{95\%\ \text{EtOH}}$ 256 mμ (ε 8,300)]. After 11 hr. II represented 57% of the mixture [$\lambda_{\max}^{95\%\ \text{EtOH}}$ 256 mμ (ε 5,130)] and after 48 hr. the mixture had come to equilibrium with 80% of $\Delta^{8,9}$-hydrindene and 20% of the $\Delta^{1,8}$-isomer [$\lambda_{\max}^{95\%\ \text{EtOH}}$ 256 mμ (ε 3000)].

(b) A 500-mg. sample of 1-acetyl-$\Delta^{8,9}$-hydrindene (II) containing less than 5% of the conjugated isomer I was added to a sodium methoxide solution prepared from 0.46 g. of sodium in 20 ml. of methanol. Aliquots were taken as in *a* and analyzed over a period of 24 hr. After 8 hr. I represented 14% of the mixture [$\lambda_{\max}^{95\%\ \text{EtOH}}$ 253 mμ (ε 1850)], and after 24 hr. the mixture had reached equilibrium with 20% of the $\Delta^{1,8}$-isomer and 80% of the nonconjugated $\Delta^{8,9}$-isomer [$\lambda_{\max}^{95\%\ \text{EtOH}}$ 253 mμ (ε 2700)]. Although there is a difference of 300 in the final extinction coefficients of the two equilibrium mixtures, their gas chromatograms are identical within ±1%. The spectra were taken on the crude aliquots and residual traces of solvent may have affected the extinction coefficient to some extent. Thus the gas chromatographic estimates of composition are no doubt the more reliable.

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[27] E. A. Braude *et al.*, *J. Chem. Soc.*, 1890 (1949).