had mp 52–53° (lit.,[22] 54–55°); a mixture melting point with the tosylate of authentic 7-hydroxynorbornane was 52–53°.

Reaction of Norcamphor with Potassium *t*-Butoxide and Dimethyl Sulfoxide.—To a solution of 1.6 g (0.014 mole) of potassium *t*-butoxide in 15 ml of dimethyl sulfoxide was added 1.28 g (0.012 mole) of norcamphor. The reaction was stirred under nitrogen at room temperature for 18 hr. The reaction mixture was neutralized with concentrated hydrochloric acid and extracted three times with 20-ml portions of ether. The ethereal solution was washed twice with 10 ml of 10% sodium bicarbonate solution from which 0.052 g of oil (3.4% yield) was isolated by neutralization with 6 *N* hydrochloric acid followed by ether extraction. Infrared analysis indicated the material to be a mixture of ketones and carboxylic acid. From the original ether extract 0.92 g (74.5% yield) of neutral material was isolated; infrared analysis indicated a mixture of norcamphor and its self-condensation product.

Acknowledgment.—The author gratefully acknowledges useful discussions with Professors H. C. Brown and S. J. Cristol and Dr. Boris Franzus regarding this work.

(22) S. Winstein and M. Shatavsky, *J. Am. Chem. Soc.*, **78**, 592 (1956).

Thermal Isomerization of Bicyclo[3.2.0]hept-6-en-2-ols[1]

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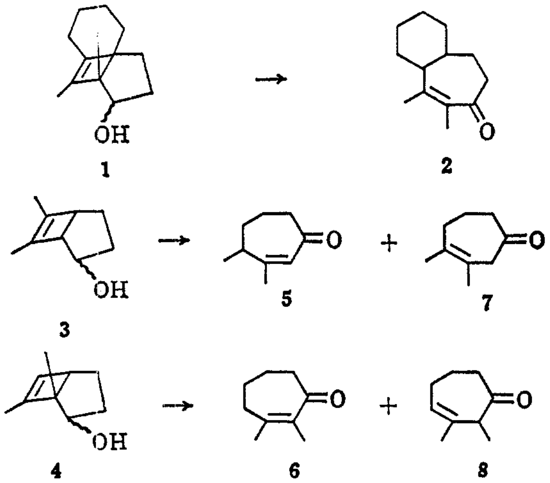
We have previously reported that pyrolysis of alcohol **1** (Scheme I) provides, along with dehydration products, the α,β-unsaturated ketone **2**.[2] We have also investigated the pyrolysis of alcohols **3** and **4**, obtained by reduction of the corresponding ketones,[3] and we now report our findings.

SCHEME I



Pyrolysis of alcohol **3** at 405° gave a mixture of which ketones **5** and **7** (ratio 3:7) amounted to 38%. Each ketone was isolated by gas chromatography and identified by analysis of the infrared, ultraviolet, nmr, and mass spectra[4] (see Experimental Section for pertinent spectral data). In a similar manner, pyrolysis of **4** gave a mixture containing ketones **6** and **8** (ratio 4:1) as 38% of the pyrolysate. The ratios of ketones **5** and **7**, and **6** and **8**, in the respective pyrolysates are the same as these ratios at thermodynamic equilibrium (25°) in accord with the suggested mode of formation of these ketones.[2] As in the case of **2** the isomer having a tetrasubstituted double bond is the more stable regardless of the α,β or β,γ nature of the double bond.[5]

The ultraviolet spectra of ketones **7**, λ_{max} 295 mμ (ε 450), and **8**, λ_{max} 290 mμ (ε 236), when compared with those of cycloheptanone, λ_{max} 274 mμ (ε 20), and 3-cycloheptenone, λ_{max} 284 (ε 80),[6] show marked shifts to longer wavelength and increased extinction. These data indicate efficient overlap of double bond and carbonyl in the excited state which is possible only in the chair conformation.[5,7]

Experimental Section[8]

1,7-Dimethylbicyclo[3.2.0]hept-6-en-2-ol (4).—A solution of 540 mg (3.97 mmoles) of 1,7-dimethylbicyclo[3.2.0]hept-6-en-2-one[3] in 5 ml of anhydrous ether was mixed with a suspension of lithium aluminum hydride. After the reaction was complete the excess reagent was destroyed by addition of water. The ether layer was separated and dried ($MgSO_4$), and the product was obtained by short-path distillation: 470 mg, 86.5%, bath temperature 100° (6 mm), mp 36–37°. Gas chromatography (DEGS, 10 ft, 170°) indicated the presence of a single compound.[2]

Anal. Calcd for $C_9H_{14}O$ (138.11): C, 78.21; H, 10.21. Found: C, 78.11; H, 10.27.

The nmr spectrum of **4** has absorptions at τ 4.43 (1 H, vinyl, coupling with vinyl methyl unresolved), 6.43 (1 H, triplet, $J_{ax} + J_{bx} = 8$ cps, carbinol), 7.58 (1 H, br, bridgehead), 8.33 (3 H, triplet, vinyl methyl coupled to vinyl H and bridgehead H with equal $J = 1.7$ cps), and 8.79 (3 H, singlet, bridgehead methyl).

6,7-Dimethylbicyclo[3.2.0]hept-6-en-2-ol (3).—Reduction of 6,7-dimethylbicyclo[3.2.0]hept-6-en-2-one[3] in the above manner gave **3**, bp 110–115° (22 mm) (bath temperature), in 79.5% yield. The clear oil appeared to be a single isomer by glpc.

Anal. Calcd for $C_9H_{14}O$ (138.11): C, 78.21; H, 10.21. Found: C, 78.57; H, 10.33.

The nmr spectrum of **3** has τ 6.15 (1 H, multiplet, carbinol), 7.26 (2 H, br, bridgeheads), 8.35 and 8.47 (broadened singlets over broad multiplet, vinyl methyls).

Pyrolysis of Alcohols 3 and 4.—In general, sealed, evacuated (0.75 mm) Pyrex tubes with an average volume of 1.5 ml containing 30–40 mg of sample were heated in an electric furnace maintained at 405 ± 5°.

Pyrolysis of 3 for 23 min gave a mixture containing at least 13 compounds. Ketones **5** and **7** (ratio 3:7, respectively) amounted to 38% of the volatile pyrolyzate (from glpc areas, uncorrected). Collection gave 55 mg of **7** and 81 mg of **5** from the contents of 35 tubes.

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(1) We thank the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this research.

(2) R. L. Cargill, M. E. Beckham, A. E. Siebert, and J. Dorn, *J. Org. Chem.*, **30**, 3647 (1965).

(3) P. E. Eaton, *Tetrahedron Letters*, 3695 (1964); R. Criegee and H. Furrer, *Ber.*, **97**, 2949 (1964).

(4) We thank Professor A. L. Burlingame for mass spectra of ketones **5**, **6**, **7**, and **8**, all of which appeared to be consistent with the assigned structures and Professor G. Büchi who also provided a mass spectrum of **6**.

(5) I. Maclean and R. P. A. Sneeden, *Tetrahedron*, **21**, 31 (1965).

(6) A. C. Cope, S. Moon, and C. H. Park, *J. Am. Chem. Soc.*, **84**, 4843 (1962).

(7) For chemical evidence of this interaction in β,γ-unsaturated ketones, see R. L. Cargill, J. R. Damewood, and M. M. Cooper, *ibid.*, **88**, 1330 (1966), and references cited there.

(8) Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were taken on a Perkin-Elmer Model 337 grating spectrophotometer in carbon tetrachloride solution. Ultraviolet spectra in 95% ethanol were recorded on a Perkin-Elmer Model 202 spectrophotometer. The nmr spectra were recorded on a Varian A-60 nmr spectrometer[9] in carbon tetrachloride using tetramethylsilane and chloroform as internal standards. Gas–liquid partition chromatographic analyses and separations were performed with an Aerograph, Model A-90-P-3, gas chromatograph. Melting points and boiling points are uncorrected.

(9) We thank the National Science Foundation for funds toward the purchase of the nmr spectrometer.

3,4-Dimethyl-2-cycloheptenone (**5**), $C_9H_{14}O$, had mol wt 138; λ_{max} 238 mμ (ϵ 11,300); ν_{max} 1660 and 1650 cm^{-1}; and τ 4.28 (1 H, vinyl, coupling with vinyl methyl unresolved), 7.5 (3 H, br, allylic and methylene adjacent to carbonyl), 8.09 (3 H, doublet, J = 1.5 cps, vinyl methyl coupled with vinyl), 8.15 (4 H, multiplet, methylene), and 8.82 (3 H, doublet, J = 6.8 cps, *sec*-methyl).

3,4-Dimethyl-3-cycloheptenone (**7**), $C_9H_{14}O$, had mol wt 138; λ_{max} 295 mμ (ϵ 450); ν_{max} 1705 and 1661 cm^{-1}; and τ 6.98 (2 H, singlet, methylenes at C_2), 7.6 (4 H, multiplet, methylenes at C_5 and C_7), and 8.00 (2 H, multiplet, C_6), 8.20 (6 H, singlet, vinyl methyls).

Pyrolysis of 4 for 18 min gave a mixture of 13 compounds. Ketones **6** and **8** (ratio 4:1, respectively) amounted to 38% of the volatile pyrolysate. Collection gave 75 mg of **6** and 24 mg of **8** from the contents of 29 tubes.

2,3-Dimethyl-2-cycloheptenone (**6**), $C_9H_{14}O$, had mol wt 138; λ_{max} 248 mμ (ϵ 8700); ν_{max} 1665 and 1630 cm^{-1}; and τ 7.60 (4 H, multiplet, methylenes at C_4 and C_7), 8.16 (3 H, singlet, α-vinyl methyl), and 8.28 (3 H, broad singlet, β-vinyl methyl). Methylenes at C_5 and C_6 are obscured by methyl signal at 8.28. Ketone **6** formed a red dinitrophenylhydrazone, mp 146–147°. Attempts to form crystalline derivatives of the other cycloheptenones failed.

2,3-Dimethyl-3-cycloheptenone (**8**), $C_9H_{14}O$, had mol wt 138; λ_{max} 290 mμ (ϵ 236); ν_{max} 1710 and 1680 cm^{-1}; and τ 4.41 (multiplet, vinyl), 8.23 (singlet, vinyl methyl), and 8.82 (doublet, J = 7.0 cps, *sec*-methyl at C_2). The remainder of the spectrum was too ill defined to be of diagnostic value.

Isomerization of Ketones 5 and 7.—To a solution of 26.1 mg of **7** in 25 ml of ethanol was added 150 mg of solid sodium hydroxide and the ultraviolet spectrum was measured peridically over a period of several weeks. The extinction coefficient at 238 mμ increased from an initial value of 3040 to 6050. In like manner the extinction coefficient at 238 mμ of a solution of 3.4 mg of **5** in 25 ml of ethanol fell from 11,300 to 5300. The equilibrium concentration of **5** is, therefore, 28 ± 4%.

Isomerization of ketone 6 was carried out as above. The equilibrium extinction coefficient at 248 mμ was 7250, indicating 80% **6** at equilibrium (ketone **8** had ϵ_{248} 1700).

The Synthesis of 2-Phenyl-1,3-di(4-pyridyl)-2-propanol

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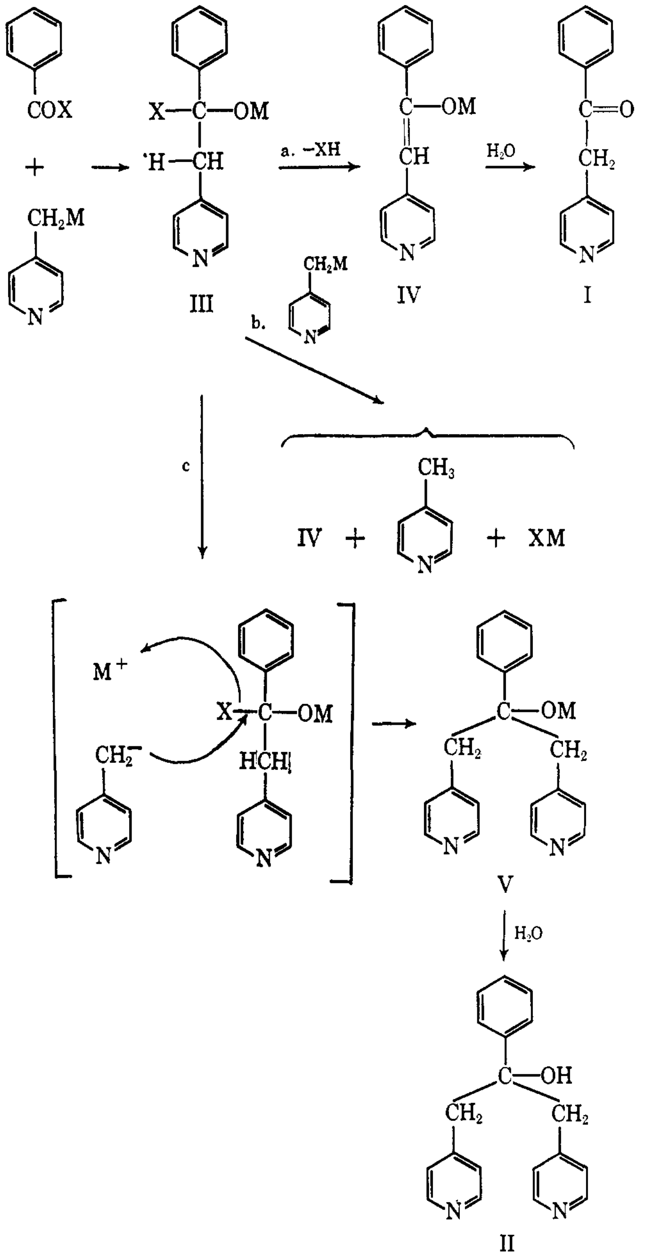
In connection with other work[1] large quantities of 4-(phenacyl)pyridine (I) were required. Using a variation of the method of Raynolds and Levine[1,2] we prepared compound I in several large batches, and isolated in some of these reactions small amounts (<2%) of the less soluble 2-phenyl-1,3-di(4-pyridyl)-2-propanol (II).

Since it had been reported that tertiary carbinols of this type were not formed under these conditions and could not be prepared from phenacylpyridines,[2] we studied this reaction and found that these substituted propanols can in fact be readily prepared by the reaction of picolyllithium with esters or acid chlorides. However, when we reexamined the reaction of picolylsodium and picolyllithium with phenacylpyridine under a wide variety of conditions (varying time, temperature, and solvents), we isolated only unchanged starting materials and therefore concur with Raynold's and Levine's,[2] explanation that picolylsodium (or picolyllithium) adds to phenacylpyridine by a process of anion formation to give the sodium (or lithium) enolate of I.[3]

It is apparent therefore, that in this instance, formation of the tertiary carbinol II cannot proceed *via* the ketone I. The yields of I and II, respectively, in such a reaction must depend on the relative ease with which an intermediate (III) can either be attacked further by picolyllithium to give the salt of II, or can undergo elimination to form the stable enolate IV.



By varying both M and X, we have shown that the formation of the carbinol from such an intermediate is strongly influenced by the metal in the order Mg < Na < Li. We have also shown that the over-all yield

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(1) R. I. Fryer, R. A. Schmidt, and L. H. Sternbach, *J. Pharm. Sci.*, **53**, 264 (1964).

(2) S. Raynolds, and R. Levine, *J. Am. Chem. Soc.*, **82**, 472 (1960).

(3) The yield of tertiary carbinol formed by the reaction of a ketone with a Grignard reagent has been reported to be substantially increased when carried out in the presence of an excess of metal halide: C. G. Swain and H. B. Boyles, *ibid.*, **73**, 870 (1951). We have also attempted to form compound II from I by the addition of a large excess of lithium chloride to the reaction mixture but were unable to detect any trace of the carbinol on work-up.