conclude that these oligomers were generated on the alumina in the column from cyclopentenylferrocenes unstable under these conditions. Failure to isolate I or any of its isomers, which were doubtlessly formed as cleavage products, is consistent with this inference.

It is of interest to note that, while the cleavage reactions discussed above proceeded readily in the presence of the zinc chloride–water system, no such reactions were observed with zinc chloride under anhydrous conditions. This suggests initiation by a protonation step, possibly one involving Fe–H bond formation, with subsequent cleavage *via* the protonated species VIIIa[11] and the tautomeric σ-complex VIIIb leading to the cyclopentenyl cation IV. The latter will immediately attack surrounding ferrocene to give cyclopentenylferrocenes[3b] or their respective cations VII, with further reaction then occurring as proposed.

The demonstrated ease with which the ferrocene system is cleaved by the zinc chloride–water catalyst[12] confirms the earlier suggestion that the presence of cyclopentylene groups should quite generally be expected in ferrocene polymers prepared under comparable experimental conditions. To what extent this competing side reaction will become significant is, then, merely a question of relative reactivities.

Experimental Section

The experiment described below, while not necessarily representing optimal cleavage conditions, may exemplify the general procedure.

The mixture of ferrocene (0.3 mole), zinc chloride (fused, anhydrous, 0.1 mole), and water (0.03 mole), contained in a round-bottom flask, was quickly heated to 180°, and the resulting melt was stirred for 1 hr at this temperature under N_2. The reaction product was washed with water, dried, and extracted with hexane. Extraction of the hexane-insoluble residue with benzene, followed by precipitation with isopropanol from the concentrated extract, gave a tan polymer in 5.9% yield (up to 15% under more rigorous conditions), which was soluble in dioxane, benzene, and chlorohydrocarbons: melting range, 125–135°; M_n, 2030 (determined by vapor pressure osmometry in benzene).

Anal. Calcd for $(C_{15}H_{16}Fe)_n$ (III): C, 71.45; H, 6.40; Fe, 22.15. Found: C, 71.88; H, 6.61; Fe, 21.30.

The hexane extract from the foregoing operations was chromatographed on Alcoa Grade F-20 activated alumina, using hexane as eluent. The first, fast-moving zone eluted gave ferrocene (87.6% recovery). The second band furnished 0.9% yield of crude II, which, after vacuum sublimation, had mp 139° (undepressed by admixture of authentic sample,[2,3b] identical X-ray diffractograms). The third band was rechromatographed on alumina slightly deactivated by a 4-hr exposure to air of 50% relative humidity. In addition to small amounts of unidentified orange oils and a few milligrams of two compounds melting at 74–76° (25.19% Fe, infrared spectrum indicates isomer of V, VI) and 167° (trinuclear; mol wt, 620), the two diferrocenylcyclopentanes V (mp 168–169°) and VI (mp 104–105°, both compounds recrystallized from ethanol) were eluted successively in yields of 0.4 and 0.2%, respectively.

Anal. Calcd for $C_{25}H_{26}Fe_2$ (V and VI: mol wt, 438): C, 68.53; H, 5.98; Fe, 25.49. Found for V: C, 68.54; H, 6.01; Fe, 25.55; mol wt, 445. Found for VI: C, 68.43; H, 5.99; Fe, 25.27; mol wt, 450.

The fourth, multilayer band was extracted with ether–benzene. Reprecipitation of the resinous evaporation residue from dioxane by aqueous isopropyl alcohol (1:1) provided yellow, powdery oligomer (3.9%) which dissolved readily in benzene, dioxane, and halohydrocarbons, but only with difficulty in hexane: melting range, 95–105°; M_n, 790.

Anal. Calcd for $(C_{15}H_{16}Fe)_n$ (III): C, 71.45; H, 6.40; Fe, 22.15. Found: C, 71.01; H, 6.71; Fe, 22.50.

Acknowledgment.—The authors are grateful to Mr. G. P. Kazokas and his staff for obtaining the infrared spectra and molecular weights. Dr. V. Weinmayr, E. I. du Pont de Nemours and Company, kindly provided a sample of ferrocenylcyclopentane for spectroscopic comparison.

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[11] M. Rosenblum and J. O. Santer, *J. Am. Chem. Soc.*, **81**, 5517 (1959). One is tempted to propose similar intermediary involvement of protonated species analogous to VIII in the facile aluminum chloride catalyzed ring exchange recently observed with ferrocene compounds [A. N. Nesmeyanov, N. A. Volkenau, and I. N. Bolesova, *Tetrahedron Letters*, **No. 25**, 1725 (1963); *Dokl. Akad. Nauk SSSR*, **149**, 615 (1963); D. E. Bublitz, *Can. J. Chem.*, **42**, 2381 (1964)]. Probably related herewith are the displacement reactions discussed by I. G. Morrison and P. L. Pauson [*Proc. Chem. Soc.*, 177 (1962)], in which the intermediacy of cations of the type VIIIa was postulated by the authors. It would not appear unreasonable to assume that in the last-named reactions, metal–ring bond cleavage, rather than simple substituent displacement, occurred much as in Nesmeyanov's and Bublitz's work, this cleavage being followed by π-cyclopentadienyl ring exchange.

[12] It should be of interest to study analogous reactions involving the more powerfully protonating ZnCl–HCl system, for which enhanced cleavage of the iron-ring bond and, hence, increased abundance of cyclopentylene groups in the products, can be predicted.

Metal–Olefin Complexes. A Convenient Synthesis of *syn*-7-Norbornenol[1a]

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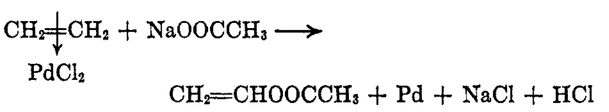
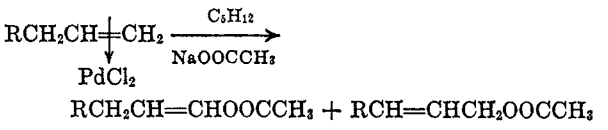
Received November 18, 1965

The preparation of vinyl esters, most notably vinyl acetate, by the reaction of the palladium chloride–ethylene π complex has been reported[2] (eq 1). Re-


$$\underset{\displaystyle\downarrow\ \mathrm{PdCl_2}}{\mathrm{CH_2{=}CH_2}} + \mathrm{NaOOCCH_3} \longrightarrow \mathrm{CH_2{=}CHOOCCH_3 + Pd + NaCl + HCl} \qquad (1)$$

cent experiments in these laboratories[3] have revealed that the reaction of palladium chloride complexes of olefins higher than ethylene are sensitive to both olefin structure and reaction medium. The influence of these factors is reflected in some instances by the formation of mixtures of isomeric unsaturated acetates[4] (eq 2)


$$\underset{\displaystyle\downarrow\ \mathrm{PdCl_2}}{\mathrm{RCH_2CH{=}CH_2}} \xrightarrow[\mathrm{NaOOCCH_3}]{\mathrm{C_5H_{12}}} \mathrm{RCH_2CH{=}CHOOCCH_3 + RCH{=}CHCH_2OOCCH_3} \qquad (2)$$

and in others by the formation of saturated bifunctional compounds such as di- and haloacetates (eq 3). Subjecting norbornene to the general reaction illustrated by eq 3 leads to the formation of *exo*-2-chloro-*syn*-7-acetoxynorbornane (I), a convenient precursor

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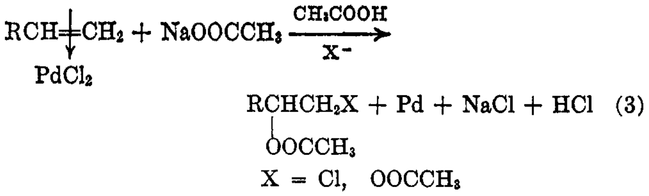
(1) (a) Presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966; (b) Enjay Chemical Laboratories, Linden, N. J.

(2) (a) I. I. Moiseev, M. N. Vargaftik, and Y. K. Sirkin, *Dokl. Akad. Nauk SSSR*, **133**, 377 (1960); (b) E. W. Stern and M. L. Spector, *Proc. Chem. Soc.*, 370 (1961).

(3) W. C. Baird, Jr., unpublished results. A manuscript entitled, "Metal–Olefin Complexes. The Synthesis of Acetate Esters," is in preparation.

(4) The formation of isomeric acetates had also been previously noted. See ref 2b.

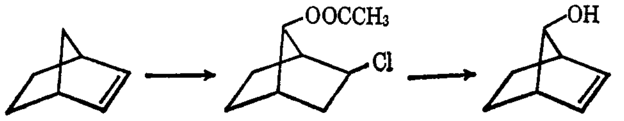


$$RCH{=}CH_2 + NaOOCCH_3 \xrightarrow[X^-]{CH_3COOH} RCHCH_2X + Pd + NaCl + HCl \quad (3)$$

$$\underset{PdCl_2}{\downarrow} \qquad \underset{OOCCH_3}{|}$$

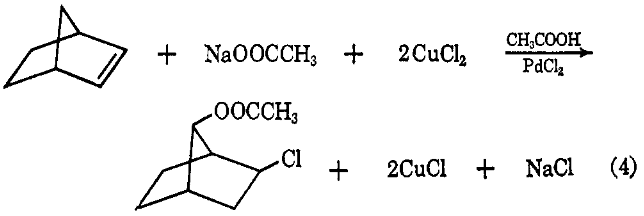
$$X = Cl,\ OOCCH_3$$

for *syn*-7-norbornenol (II). This two-step synthesis of the *syn*-alcohol offers a convenient and improved route to this difficultly accessible compound.[5]



I II

The chloroacetate (I) is prepared in 50–84% yields by heating norbornene with sodium acetate and cupric chloride in glacial acetic acid containing a catalytic quantity of palladium chloride. The utilization of a large excess of cupric chloride as an oxidation–reduction reagent for the palladium catalyst provides a convenient source of chloride ion, and the reaction stoichiometry is illustrated by eq 4. The high concentration of chloride ion relative to that of acetate ion accounts for the detection of only 5–10% of diacetate in the reaction product.

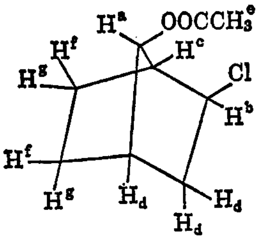


I

The proof of structure of *exo*-2-chloro-*syn*-7-acetoxynorbornane resides in its nmr spectrum (Table I) and in its chemical behavior.

TABLE I

NMR SPECTRUM OF *exo*-2-CHLORO-*syn*-7-ACETOXYNORBORNANE

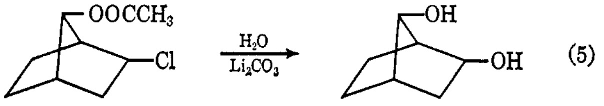


Hydrogen assignment	Cps (δ, ppm)	Area, % Calcd	Area, % Found	Ratio	S_H,[a] (cps)
a	278(4.63)	7.7	7.1	1	3
b	240(4.00)	7.7	7.5	1	13
c	153(2.55)	7.7	7.6	1	7
d	133(2.21)	23.0	22.8	3	..
e	119(1.98)	23.0	24.8	3	..
f	96(1.60) 72(1.20)	30.8	30.3	4	..

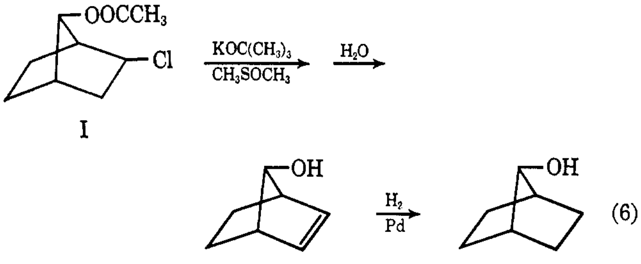
[a] S_H = sum total of coupling constants. See ref 7.

The skeletal positions and stereochemistry of the CHCl and CHOOCCH$_3$ protons were established by the similar nature of their chemical shifts and coupling constants compared to those of *exo*-2-acetoxy-*syn*-7-chloro-5-norbornene;[6] the isomeric 2,3-chloroacetate can be excluded on the same basis.[6] The chlorine atom has been assigned an *exo* configuration since the sum total of the coupling constants of the CHCl proton, S_b[7] = 13 cps, approximates the total coupling constants observed for similar *endo* protons (S = ~11–14 cps).[6–8] If the chlorine atom were to occupy an *endo* position (*exo* proton), then the value of S_b should lie in the range ~14–20 cps.[7,8] Furthermore, the CHCl proton in I does not appear as a doublet of triplets as has been reported for other *endo*-2-substituted norbornyl derivatives,[8] but rather as a broadened triplet.[9]

Hydrolysis of I with aqueous lithium carbonate[10] produced *exo,syn*-2,7-dihydroxynorbornane (eq 5), a result totally consistent with the structure of I and one that has been previously observed for other *exo,syn*-disubstituted norbornanes.[10,11]



Treatment of I with potassium *t*-butoxide in dimethyl sulfoxide gave *syn*-7-norbornenol (II) in 70% yield (eq 6). The structure of II was established by its nmr spectrum,[7a] and by comparison of its tosylate and that of its reduction product, 7-hydroxynorbornane (III), with those of authentic samples. No carbonyl-containing compound was detected in the isolated *syn*-alcohol (II), a result which demonstrates chemically the nonexistence of 2,3 substitution since norcamphor would be the anticipated product arising from such a structure.[12]



I II III

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[5] S. Winstein and E. T. Stafford, *J. Am. Chem. Soc.*, **79**, 505 (1957).

[6] R. S. Neale and E. B. Whipple, *ibid.*, **86**, 3130 (1964).

[7] Similar treatments of complex spectra have been reported by (a) E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964); (b) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).

[8] (a) P. Laszlo and P. V. R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964); (b) J. C. Davis, Jr., and T. V. van Auken, *ibid.*, **87**, 3900 (1965); (c) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

[9] Treatment of proton H$_b$ as the X portion of an ABX pattern leads to a value of 11 cps for ($J_{AX} + J_{BX}$). Since the total coupling constant, S_b, is 13 cps, the difference (2 cps) is too small to be attributed to an *exo* H$_b$ coupled with bridgehead proton H$_c$ (J = 2.9–4.3 cps[7b]). A long-range coupling between *endo*-2H-*anti*-7H, J = 2.8 cps, in norbornanes has been observed.[7b] It is suggested that the additional coupling found for H$_b$ in I arises from this source. Thus, the nmr evidence supporting *endo* H$_b$ (*exo* chlorine) appears sound.

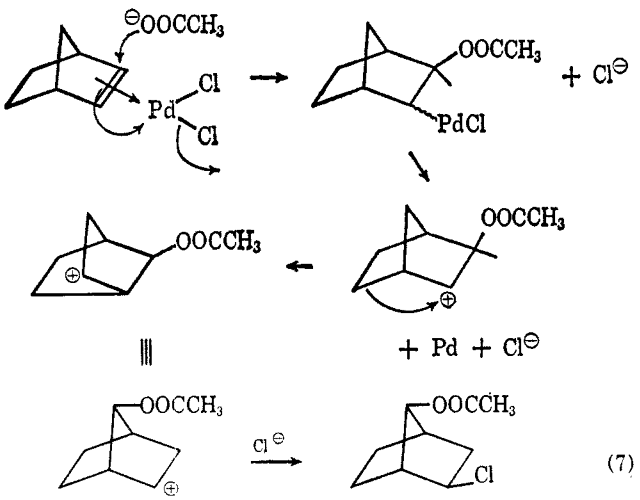
[10] H. M. Walborsky and D. F. Loncrini, *J. Org. Chem.*, **22**, 1117 (1957).

[11] J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Am. Chem. Soc.*, **76**, 5692 (1954).

[12] The cleavage of nonenolizable ketones by potassium *t*-butoxide in dimethyl sulfoxide to carboxylic acids has been observed by P. G. Gassman and F. V. Zalar, *Tetrahedron Letters*, **No. 40**, 3031 (1964). A control experiment with norcamphor has shown this ketone to experience only self-condensation under our reaction conditions. The presence of the condensation product was not noted in the *syn*-alcohol reaction mixture.

The preparation of *exo*-2-chloro-*syn*-7-acetoxynorbornane by the reaction of the palladium chloride–norbornene π complex may be of significance regarding the mechanism of the reactions of such complexes, a topic of some controversy. Previous interpretations of the chemistry of palladium chloride complexes have invoked both noncarbonium[13–15] and carbonium ion[16] mechanisms based on deuterium labeling and kinetic studies. Noncarbonium ion mechanisms are considered to involve hydride shifts occurring as the metal–olefin π complex experiences nucleophilic attack.[13,15] Other interpretations favor concurrent nucleophilic attack and rearrangement of the π complex to a σ complex as the rate-determining step. The reaction is subsequently completed by the σ complex undergoing a hydride shift, or by ionization of the σ complex to form a carbonium ion as the reactive intermediate.[16]

The reaction of the palladium chloride–norbornene complex described above provides good evidence in support of the carbonium ion mechanism, for it is difficult to rationalize the formation of *exo*-2-chloro-*syn*-7-acetoxynorbornane on any basis other than rearrangement of a norbornyl cation. The reaction path, as illustrated by eq 7, involves nucleophilic attack by acetate ion on the π complex to generate a β-acetoxyalkyl palladium chloride (σ complex) which subsequently experiences heterolytic cleavage to produce the acetoxynorbornylcarbonium ion.[17] Rearrangement and combination with chloride ion (or acetate ion) leads to the observed product. Reaction paths invoking hydride shift mechanisms[13–15] would yield in this case 2-acetoxy-2-norbornene or 1-acetoxy-2-chloronorbornane (bridgehead acetate), neither of which were detected in this reaction.



(7)

Experimental Section

Infrared spectra were recorded using a Beckman IR-5 spectrophotometer. Vapor phase chromatographic analysis was carried out on a Perkin-Elmer Model 154-D fractometer; preparative gas chromatography was performed using a Wilkens Aerograph Autoprep Model A-700. Nmr spectra were determined with a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard. All melting points with the exception of those taken in sealed capillaries are corrected; boiling points are not corrected.

***exo*-2-Chloro-*syn*-7-acetoxynorbornane (I).**—To 200 ml of glacial acetic acid were added 20.0 g (0.21 mole) of norbornene, 16.0 g (0.20 mole) of anhydrous sodium acetate, 50.0 g (0.37 mole) of anhydrous cupric chloride, and 1.0 g (0.056 mole) of anhydrous palladium chloride. The reagents were heated and stirred at 80° for 72 hr. The cooled reaction mixture was filtered, and the filter cake was washed twice with 50–100-ml portions of glacial acetic acid. The filtrate and the washings were combined and added to 1500 ml of water; the product was extracted five times with 100-ml portions of pentane. The combined pentane extracts were washed twice with 25 ml of 10% sodium carbonate solution and twice with 25 ml of water. The pentane solution was dried over magnesium sulfate, and the solvent was removed on a rotary evaporator to give 32.5 g of crude product. Vacuum distillation yielded 29.3 g (84%) of *exo*-2-chloro-*syn*-7-acetoxynorbornane: bp 63–65° (0.1 mm); $n^{20}\text{D}$ 1.4833; purity by vpc, 95% (2 m × 0.25 in. diethyleneglycol succinate column, 170°, 30 psig of helium); retention time from air, 10.0 min.

Anal. Calcd for $C_9H_{13}ClO_2$: C, 57.30; H, 6.94; Cl, 18.80. Found: C, 57.81; H, 7.02; Cl, 18.6.

Decreasing the reaction period to 16–24 hr gave product yields of 50–65%; the product purity in these cases was 85–92%.

Hydrolysis of *exo*-2-Chloro-*syn*-7-acetoxynorbornane.[10]—To a solution of 2.5 g (0.037 mole) of lithium carbonate in 50 ml of water was added 2 g (0.011 mole) of 2-chloro-7-acetoxynorbornane. The reaction was refluxed for 36 hr. The reaction mixture was filtered, and the filtrate was extracted continuously with ether for 24 hr. The ether was removed by distillation to yield 1.5 g of crude *exo,syn*-2,7-dihydroxynorbornane. After sublimation at 120° (1.0 mm) the diol melted at 175–176° (lit.[10] 181°). The bisphenylurethane recrystallized from benzene had mp 222–223° (lit.[10] 221°).

***syn*-7-Norbornenol (II).**—To a solution of 10 g (0.053 mole) of *exo*-2-chloro-*syn*-7-acetoxynorbornane in 25 ml of dimethyl sulfoxide was added all at one time a solution of 14 g (0.12 mole) of potassium *t*-butoxide in 75 ml of dimethyl sulfoxide. The reaction was stirred at room temperature overnight (22 hr). To the reaction mixture was added 100 ml of water, and the mixture was steam distilled until 300–500 ml of distillate had been collected. The distillate was extracted five times with 100-ml portions of ether. The combined ether extracts were washed twice with 50 ml of water and once with 50 ml of saturated sodium chloride solution. The ether solution was dried over magnesium sulfate, and the solvent was removed on a rotary evaporator to give 4.1 g (70%) of crude *syn*-7-norbornenol, which crystallized upon standing at room temperature. The alcohol was 83% pure by vpc analysis (2 m × 0.25 in. ethylene glycol succinate column, 125°, 60 ml/min), retention time from air, 6.4 min. The impurities were *t*-butyl alcohol (8.3%), an unknown alcohol[18] (4%), and an unknown hydrocarbon[19] (4.7%). No carbonyl-containing compounds could be detected by infrared analysis. Sublimation [75° (150–200 mm)] increased the purity of the alcohol to 88%. Preparative vpc[20] provided *syn*-alcohol of purity >98%, mp (sealed capillary) 88.5–89.5°. The nmr spectrum was identical with that previously reported.[9]

Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 75.64; H, 9.17.

The tosylate of the *syn*-7-norbornenol was prepared and recrystallized from pentane, mp 67.5–68.5° (lit.[5] 67–68°). A sample of *syn*-alcohol was hydrogenated in ethanol over 10% palladium on carbon; the product was identical with an authentic sample of 7-hydroxynorbornane[21] (infrared, vpc, melting point). The tosylate of the reduced alcohol recrystallized from pentane

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[13] J. Smidt, *Chem. Ind.* (*London*), 54 (1962).

[14] P. M. Henry, *J. Am. Chem. Soc.*, **86**, 3246 (1964).

[15] E. W. Stern, *Proc. Chem. Soc.*, 111 (1963).

[16] I. I. Moiseev and M. N. Vargaftik, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 759 (1965); *Chem. Abstr.*, **63**, 2862 (1965).

[17] The reaction path is similar to that encountered in the oxythallation of norbornene: K. C. Pande and S. Winstein, *Tetrahedron Letters*, **No. 46**, 3393 (1964).

[18] The alcohol was not the corresponding *anti* isomer as evidenced by vpc.

[19] Comparative vpc studies suggested that this material may be cycloheptadiene or cycloheptatriene.

[20] Preparative vpc conditions: 12 ft × 3/8 in. 30% FFAP column (Wilkens Instrument, Walnut Creek, Calif.); column temperature, 125°; injector temperature, 160°; detector temperature, 180°; flow rate, 100 ml/min.

[21] Kindly provided by Dr. B. Franzus of these laboratories.

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.

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[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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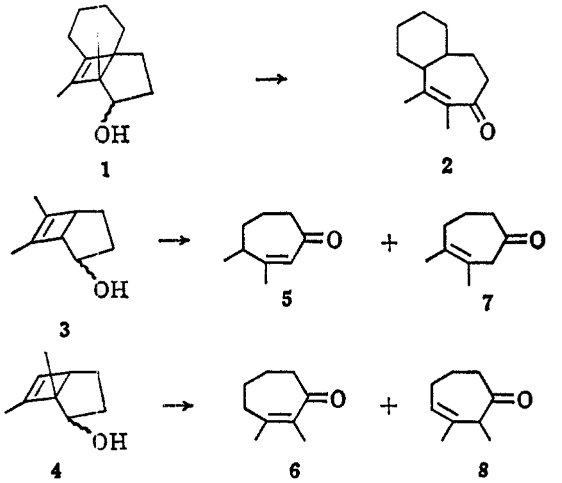
Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

Received March 2, 1966

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**, $\lambda_{\max}$ 295 mμ (ϵ 450), and **8**, $\lambda_{\max}$ 290 mμ (ϵ 236), when compared with those of cycloheptanone, $\lambda_{\max}$ 274 mμ (ϵ 20), and 3-cycloheptenone, $\lambda_{\max}$ 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.