uent. The cyclohexane was removed from each fraction at water-pump pressure, and the residues were weighed. The fractions were as follows. Fraction 1 (70 ml) contained no olefins and was discarded. Fraction 2 (450 ml) contained 150 mg of the two olefins and no starting material. Fraction 3 (100 ml) contained neither olefins nor starting alcohol and was discarded. Fraction 4 (200 ml) contained 58 mg of material, primarily the starting alcohol and no olefins. Samples of fractions 2 and 4, dissolved in a little cyclohexane, were analyzed by GLC (silicon gum rubber column at 180°). The *Z* olefin had a retention time of 7.8 min while the *E* olefin had a retention time of 13.6 min. The results are tabulated in Table I.

General Procedure Using PTSA. Compound **2** (250 mg), 12 mg of PTSA monohydrate, and 5 ml of *p*-xylene were heated with refluxing for 3 hr. The mixture was allowed to cool to room temperature and washed with 20% sodium carbonate solution and water. After removal of the solvent the NMR spectrum showed no indication of starting alcohol. Accordingly, the chromatography on silica gel was omitted. The olefin mixture was analyzed by GLC as before and the results are in Table I.

General Procedure Using Methyltriphenoxyphosphonium Iodide. This followed ref 5. Compound **2** (296 mg), 1.86 g of methyltriphenoxyphosphonium iodide, and 9 ml of dry hexamethylphosphoramide (dried over calcium hydride and stored over molecular sieves 4A) were heated in an oil bath at 80° for 1 hr. The reaction mixture was poured over 20 ml of 10% potassium hydroxide solution and extracted with four 10-ml portions of cyclohexane. These were washed with water and dried ($MgSO_4$), the solvent was removed, and the oil was analyzed by NMR and GLC. The results are in Table I.

Equilibration of 3 and 4. Olefin **3** (315 mg) was refluxed with 13 mg of PTSA monohydrate in 10 ml of *p*-xylene. Samples were removed for analysis of the *E* and *Z* olefins from time to time, and injected directly into the GLC. The results were as follows (hr, % **3**): 0, 100; 0.5, 88; 1.0, 79; 3.0, 78; 20, 73.

The experiment was repeated with 109 mg of **4** (containing 15% of **3**) and 6 mg of PTSA in 4 ml of refluxing *p*-xylene. The results were as follows (hr, % **3**): 0, 15; 0.5, 17; 1.0, 21; 1.5, 39; 2.0, 44; 4.0, 50; 24.0, 61; 44, 70.

Registry No.—**1**, 7693-84-7; **2**, 7693-85-8; **3**, 833-81-8; **4**, 1017-22-7; iodine, 7553-56-2; *p*-toluenesulfonic acid, 104-15-4; methyltriphenoxyphosphonium iodide, 17579-99-6; triphenoxymethyliodophosphorane, 4167-91-3.

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Selective Oxidation of Allylic Alcohols with Chromic Acid

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Received January 17, 1975

Although examples of synthesis of aldehydes by oxidation of primary alcohols with chromic acid reagents are in the literature, many reviews and advanced texts[1] suggest that other reagents (chromic anhydride–pyridine, activated manganese dioxide) or special conditions (removal of aldehyde as it is formed) are necessary for effecting this conversion in high yields. This note demonstrates that primary allylic alcohols can be converted to the corresponding α,β-unsaturated aldehydes in high yield using chromic acid in acetone (Jones reagent).[2]

In other synthetic work[3] we had observed that some α,β-unsaturated aldehydes were inert to normal conditions for Jones oxidation. Although an extensive investigation of the reaction did not seem warranted, we have examined the behavior of some simple primary allylic alcohols upon treatment with Jones reagent.

The oxidation of cinnamyl alcohol to cinnamaldehyde has frequently been cited as an illustration of the utility of the chromic anhydride–pyridine complex.[1a,c] Holum[4] obtained cinnamaldehyde in 87% yield using the complex. We found that simple oxidation with Jones reagent gave the aldehyde in an 84% yield.[5]

Geraniol and nerol were used as examples of simple terpenoid primary allylic alcohols. Treatment of these alcohols with Jones reagent gave aldehydes in high yield. Geraniol was converted into aldehyde in a 91% yield. However, GLC investigation showed that a small amount of isomerization of the double bond had occurred. The GLC data indicated that the product consisted of about 96% geranial and 4% neral. Oxidation of 95% nerol gave aldehyde in 84% yield, and GLC indicated that isomerization had occurred to the extent of about 8%. Thus the oxidation with Jones reagent does have the disadvantage of causing some loss of double-bond stereochemistry in these two cases.

Oxidation of benzyl alcohol to benzaldehyde with Jones reagent also proceeded in good yield, although this reaction appeared more sensitive to experimental variations than the other oxidations. Thus benzaldehyde was obtained in 76% yield using Jones reagent.

These results demonstrate that oxidation of allylic or benzylic alcohols to the corresponding aldehydes occurs using the simple Jones oxidation procedure without the need to use large amounts of expensive activated manganese dioxide or to use a chromic acid–pyridine reagent.

Experimental Section

Proton NMR spectra were recorded on a Varian T-60 spectrometer employing tetramethylsilane as an internal standard and CCl_4 as a solvent. The ir spectra were recorded on a Beckman IR-8 spectrophotometer. GLC analyses were performed on a Hewlett-Packard 700 gas chromatograph using an SE-30 column (6 ft × 0.1875 in., 10% on Chromosorb W) and a Carbowax 20M column (6 ft × 0.1875 in., 10% on Chromosorb W).

The products from the oxidations were identified by comparison of the ir and NMR spectra with spectra of authentic samples or with spectra recorded in the literature.

Jones Oxidation of Cinnamyl Alcohol. A solution of 500 mg (3.72 mmol) of cinnamyl alcohol and 10 ml of reagent-grade acetone was placed in a 50-ml round-bottom flask under nitrogen and cooled to 0° (ice–water bath). To the magnetically stirred solution was added dropwise a solution consisting of 2 ml of 8 *N* Jones reagent and 18 ml of reagent acetone. The Jones solution was added over a period of ca. 20 min until an orange tint persisted in the reaction mixture. Isopropyl alcohol was then added dropwise to destroy excess Jones reagent, as indicated by the reappearance of a deep green color. The reaction mixture was then extracted twice with ether, and the combined ether extracts were washed (water, sodium bicarbonate, and brine), dried over anhydrous magnesium sulfate, and concentrated. Evaporative distillation (0.1 mm, 100°) yielded 420 mg (2.96 mmol, 84%) of a cinnamon-smelling, pale yellow oil (>92% pure by GLC) identified as cinnamaldehyde by comparison of the ir and NMR spectra with literature spectra.

Jones Oxidation of Geraniol. A solution of 500 mg (3.24 mmol) of 99+% geraniol and 10 ml of reagent-grade acetone was placed in a 50-ml round-bottom flask and cooled to 0° (ice–water bath). This solution was treated with Jones reagent in the manner described above. Evaporative distillation of the crude product (0.1 mm, 100°) yielded 450 mg (2.92 mmol, 91%) of a light yellow oil having a citrus odor. GLC (Carbowax) showed 96% geranial and 4% neral as the only significant (>94%) components. The ir and NMR

spectra were consistent with those of an authentic sample of geranial, obtained from GLC separation of citral.

Jones Oxidation of Nerol. A solution of 500 mg (3.24 mmol) of 95% nerol and 10 ml of reagent-grade acetone was placed in a 50-ml round-bottom flask and cooled to 0° (ice–water bath). Oxidation as described for cinnamyl alcohol gave material which upon evaporative distillation (0.1 mm, 100°) yielded 420 mg (2.72 mmol, 84%) of a pale yellow oil having a citrus odor. GLC (Carbowax) showed a 7:1 ratio (87.5%) of neral to geranial as the only significant (97%) components. The NMR and ir spectra were consistent with those of an authentic sample of neral, obtained from GLC separation of citral.

Jones Oxidation of Benzyl Alcohol. A solution of 500 mg (4.63 mmol) of benzyl alcohol and 10 ml of reagent-grade acetone was placed in a 50-ml round-bottom flask and cooled to 0° (ice–water bath). Oxidation in the same manner gave material which upon evaporative distillation (water aspirator pressure, 100°) yielded 380 mg (3.52 mmol, 76%) of a clear oil (>99% pure by GLC) identified by ir and NMR as benzaldehyde.

Acknowledgments. We thank the Robert A. Welch Foundation and the National Cancer Institute (PHS Research Grant CA 15736) for support of this research.

Registry No.—Cinnamyl alcohol, 104-54-1; cinnamaldehyde, 104-55-2; geraniol, 106-24-1; geranial, 141-27-5; neral, 106-26-3; nerol, 106-25-2; benzyl alcohol, 100-51-6; benzaldehyde, 100-52-7; chromic acid, 7738-94-5.

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220-MHz Nuclear Magnetic Resonance Spectra of Bicyclo[3.2.1]octan-6-ones

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Received December 2, 1974

Over the past few years we have accumulated a number of substituted bicyclo[3.2.1]octan-6-ones, both as substrates and as products in diverse photochemical investigations. Examination of the 220-MHz NMR spectra of these compounds has permitted consistent assignments for the various low-field proton resonances in each case, and these results are presented here. Other investigators have previously underscored the advantages and value of NMR studies of this bicyclic ring system,[1] and indeed our results allow worthwhile comparisons with the large store of information now on hand for norbornanes.[2] Furthermore, they permit generalizations which should facilitate future determinations of structure and stereochemistry for related bicyclooctanes.

Synthesis of most of these ketones has been described in earlier work,[3] and details of the preparation of the epimeric methoxy ketones **15** and **16** are given at the end of the present article. The remaining new compounds, **5–7**, are formed on photolysis of appropriate cyclopentenones,[4] and their preparation and other data defining their structures will be reported in a forthcoming publication.

The methyl and low-field resonances of the 220-MHz NMR spectra of these 16 bicyclooctanones are collected in Table I. For comparison the completely interpreted spectrum[3] of the closely related oxabicyclic ketone **17** is also presented.

Typically the lowest field signals in the simple alkylated ketones of this series are those of the bridgehead positions at C(1) and C(5), H_A and H_B, respectively, with H_A the farther downfield (compare, for example, **1**, **2**, and **4**). The positions of these protons closely parallel those of the bridgehead hydrogens of norbornanone (**18**): C(4) H, δ 2.57, 2.61, and C(1) H, 2.39, 2.41 ppm.[2b,5] Interestingly, these effects do not appear in bicyclo[2.2.2]octanone (**19**); here the two bridgehead protons at C(1) and C(4), along with the C(3) methylene protons, all appear at 2.15 ppm ($W_{1/2}$ = 5 Hz).[5] The bridgehead proton more distant from the carbonyl both in norbornanones and in bicyclo[3.2.1]octan-6-ones then appears downfield from the bridgehead proton adjacent to the carbonyl. The reason for this is not known with certainty; for norbornanones it has been suggested[5] that excess s character and abnormal polarizability in the bridgehead bonding orbital may be responsible. In this regard it is noteworthy that in the bicyclo[3.2.1]octanones a qualitatively similar low-field shift is also seen for methyl groups at the distant bridgehead position. For example, the C(1) methyl of **2** appears well downfield from the C(5) methyl of **4** (1.13 vs. 0.936 ppm).

The next two signals upfield are those of the endo and exo protons at C(7), H_N and H_X. These are characterized by two, and occasionally three, coupling constants. First, the geminal coupling is typically 18 Hz (J_{NX}). Second, H_X shows a vicinal coupling constant (J_{XA}) of 6–7 Hz, while the corresponding interaction for H_N is not seen or else is small (J_{NA} = 0–1 Hz). Finally, there are long-range splittings over four bonds; H_N couples with H_K in all cases (J_{NK} = 3–4 Hz),[6] and H_X occasionally does so with H_D (J_{XD} = 0–0.5 Hz). All these interactions are analogous to those well documented in norbornanes, although the range of values observed is slightly different in some cases. Thus, in norbornanes the vicinal coupling constant corresponding to J_{XA} is a little smaller (3–4 Hz[2]), and the long-range coupling constant corresponding to J_{XD} is a little larger (1–1.5 Hz[2]). The noted difference in vicinal coupling constants between the two systems would appear primarily attributable to the increase in the dihedral angle involving H_A and H_X on passing from the bicyclo[3.2.1]octane to the bicyclo[2.2.1]heptane skeleton. The high value of the geminal coupling in the bicyclooctanes (J_{NX} = 18 Hz) is due largely to the effect of the carbonyl group. There is good evidence[7] that adjacent π bonds can enhance geminal coupling if the geometry is appropriate, and models indicate that the rigid geometry of the five-membered ring here should lead to a maximum contribution from the carbon–oxygen double bond to the value of J_{NX}.

H_N and H_X appear at about 2.0 ppm, with the exact position of each influenced by substitution not only at the adjacent bridgehead position but also at C(2) and C(3). The difference in chemical shift between these protons is usually 0.2 ppm or less. For these reasons assignment of the two signals to one or the other of the C(7) protons is based on the magnitude of the observed vicinal and long-range coupling constants, as discussed above, and not on the chemical shifts of these protons. In the ketones bearing hydrogen at C(1), H_X appears at lower field in six of the nine exam-