The Effect of Molecular Structure upon the Course of Lead Tetraacetate Allylic Oxidation. The Reaction of Norcamphene and 2-Methylnorbornene with Lead Tetraacetate

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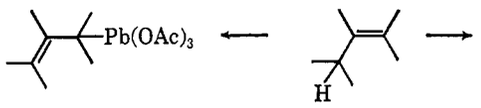
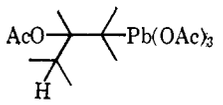
Oxidation of norcamphene (**1**) with lead tetraacetate in benzene afforded 3-*exo*-acetoxynorcamphene (**3**, 93%) and 2-acetoxymethylnorbornene (**4**, 7%) in 26% yield. Oxidation of 1-methylnorbornene (**2**) yielded 7-*syn*-acetoxy-7-methylnorborn-2-ene (**5**, 35%), 3-methyl-3-nortricyclyl acetate (**6**, 56%), acetate **3** (9%), and acetate **4** (trace) in 35% yield. The contrasting courses of reaction of these two olefins are discussed in terms of the effect of molecular structure upon the relative rates of elimination from initially produced carbonium ions. For purposes of comparison mercuric acetate oxidation of **1** afforded an unidentified acetate (5%), 2-*endo*-methyl-2-*exo*-norbornyl acetate (**29**, 30%), 3-ketonorcamphene (**8**, 28%), and acetate **3** (37%) in 9% yield.

In general, reactions of lead tetraacetate with cyclic olefins[1] under conditions which produce allyl acetates follow one of two reaction sequences. Thus, the products of oxidation of cyclohexene,[2] 1-methylcyclohexene,[2] 1-*p*-menthene,[2] and β-pinene[3] can be depicted as arising *via* an allyl organolead derivative of type I, while products of oxidation of α-pinene,[4] 3-*p*-menthene,[5] camphene,[6] and norbornene[7] are best assumed to arise *via* an acetoxy organolead adduct of type II.[8]



I



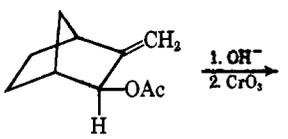
II

A priori it is difficult to explain why the closely related structures 1-*p*-menthene and 3-*p*-menthene should follow such radically different courses of reaction. Almost as perplexing is the fact that oxidations of β-pinene and α-pinene follow two distinctly different paths. In order to understand better the influence of steric, electronic, and conformational factors on the course of these oxidations we chose to compare the lead tetraacetate oxidation of norcamphene (**1**) and 1-methylnorbornene (**2**). The bicyclo[2.2.1]heptane system offers several advantages over other cyclic systems: (1) the molecule is held rigidly in one conformation, thereby eliminating guesswork about preferred conformations; (2) initial attack of lead tetraacetate should be directed from the *exo* side of the molecule so that assumptions about the stereochemistry of intermediate species can be made with reasonable confidence; and (3) the products of the reaction can be readily elucidated by spectroscopic means or by unambiguous syntheses. If the oxidation experiments are performed in benzene solvent, protonation and rearrangement of the initially formed olefinic products and intermediate acetoxy compounds should be held to a minimum, *i.e.*, products of kinetic control rather than thermodynamic control should be generated.[4]

Results

Treatment of norcamphene (**1**) with an equimolar quantity of lead tetraacetate in benzene[9] afforded the two acetates, **3** (3-*exo*-acetoxynorcamphene) and **4** (2-acetoxymethylnorbornene) in 26% yield in the ratio 93:7 (see Chart I). Oxidation of 2-methylnorbornene (**2**) under the same conditions yielded a mixture of four monoacetates in 35% yield: 7-*syn*-acetoxy-7-methylnorborn-2-ene (**5**, 35%), 3-methyl-3-nortricyclyl acetate (**6**, 56%), acetate **3** (9%), and acetate **4** (trace) (see Chart II).

Acetate **3**[10] was defined as a 3-acetoxynorcamphene by alkaline hydrolysis to 3-hydroxynorcamphene (**7**) and subsequent oxidation to 3-ketonorcamphene (**8**). The spectral properties[10] and gas chromatography retention time of the latter ketone (**8**) were identical with those of an authentic specimen of **8** prepared from 3-N,N-dimethylammoniummethyl-2-norcamphor hydrochloride (**9**).[11] The *exo* stereochemistry of the acetoxy



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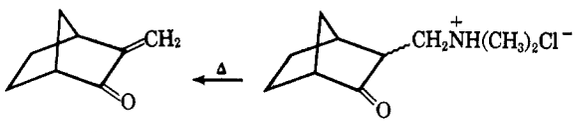

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(1) For pertinent references to the original work on lead tetraacetate oxidation of olefins, see R. Criegee, "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, pp 335–351.

(2) K. B. Wiberg and S. D. Nielsen, *J. Org. Chem.*, **29**, 3353 (1964), and references cited therein.

(3) M. P. Hartshorn and A. F. A. Wallis, *J. Chem. Soc.*, 5254 (1964).

(4) G. H. Whitham, *ibid.*, 2232 (1961).

(5) T. Sato, *Kogyo Kagaku Zasshi*, **65**, 889 (1964); *Chem. Abstr.*, **62**, 13181 (1965).

(6) (a) S. Wakabayashi, *Nippon Kagaku Zasshi*, **63**, 627 (1960); *Chem. Abstr.*, **56**, 7165 (1962); (b) W. Hückel, *Ber.*, **80**, 41 (1947), and references cited therein.

(7) K. Alder, F. H. Flock, and H. Wirtz, *ibid.*, **91**, 609 (1958).

(8) For a discussion of these and related mechanistic pathways, see ref 2 and Z. Rappoport, P. D. Sleezer, S. Winstein, and W. G. Young, *Tetrahedron Letters*, 3719 (1965).

(9) The general procedure of Whitham[4] was employed for the oxidations. When calcium carbonate was added to consume liberated acetic acid according to the procedure of Hartshorn and Wallis[3] similar results were obtained (see the Experimental Section).

(10) The nuclear magnetic resonance, infrared, and mass spectral properties were completely consistent with the structure and are listed in the Experimental Section.

(11) H. Krieger, *Suomen Kemistilehti*, **34B**, 160 (1961); *Chem. Abstr.*, **57**, 14959 (1962).

CHART I

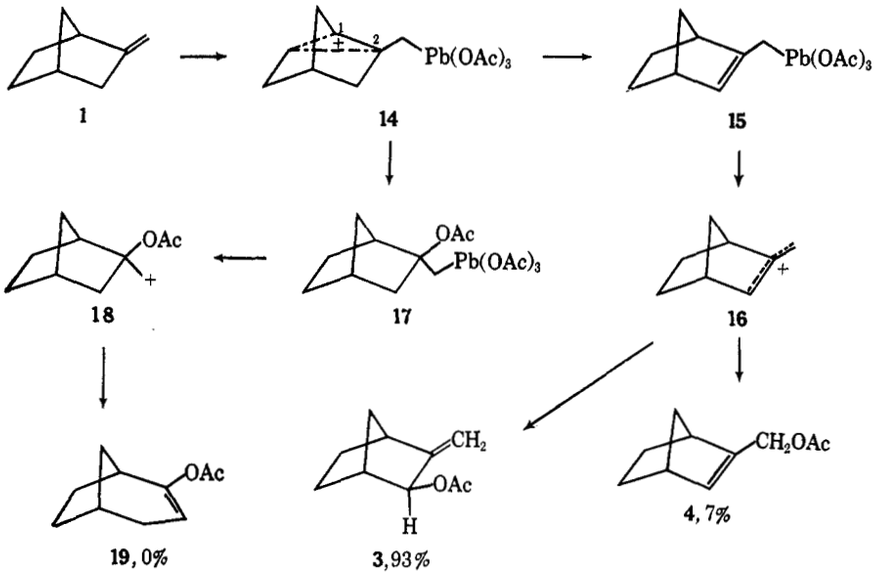
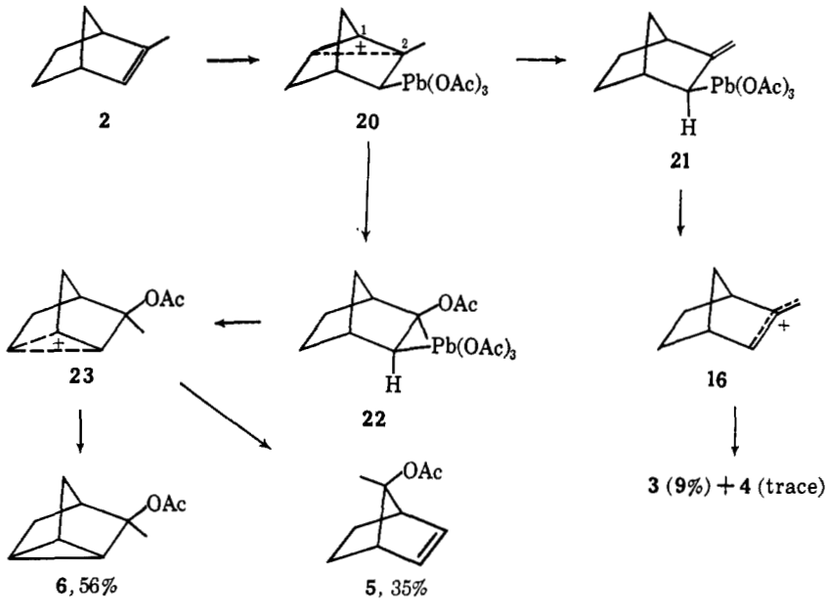


CHART II



group was defined by the nmr spin-coupling pattern of the C-3 hydrogen which appeared as a slightly broadened singlet at τ 5.18. The C-3-*endo* proton should show no substantial coupling with the C-4 proton[12] but can exhibit long-range coupling with the C-7-*anti* proton (1–3 cps)[12] and with the vinyl protons (0–1 cps).[12] Whereas the C-3-*exo* proton would show small, long-range interaction with the C-5-*exo* proton (0.5–1.0 cps) and the vinyl proton (0.5–1.0 cps), a definite and larger coupling with the C-4 proton (3–4 cps) should be observed. Double-resonance experiments in which the C-4 proton was irradiated effected no significant change in the pattern of the C-3 peak at τ 5.18. Consequently, the C-3 proton must be defined as *endo* and structure **3** confirmed.

The infrared, mass, and nmr spectra clearly defined the structure of acetate **4**. The infrared spectrum was that of an acetate (5.75 and 8.10 μ)[13] with typical absorption at 6.13 and 12.30 μ[13] for a trisubstituted olefin. The mass spectrum was devoid of a parent mass peak but revealed strong signals at 106 and 105 for loss of acetic acid, a typical characteristic of unstable acetates.[14,15] Except for the C-4, C-5-*exo*, and C-7 protons which occur as superimposed multiplets in the τ 8.3–8.6 region, the proton signals in the nmr spectrum of **4** are well separated and easily interpreted (see the Experimental Section). The distinguishing features of the nmr spectrum of **4** are the C-3 vinyl proton signal at τ 4.21 which occurs as a doublet (J = 2.0 cps) and the pattern of the methylene protons of the C-2 ace-

(12) For pertinent references, see (a) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965); (b) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964); (c) J. I. Musher, *Mol. Phys.*, **6**, 93 (1963).

(13) General examples are recorded in L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958.

(14) K. Biemann, "Mass Spectrometry. Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 109; A. G. Sharkey, J. L. Shultz, and R. A. Friedel, *Anal. Chem.*, **31**, 87 (1959).

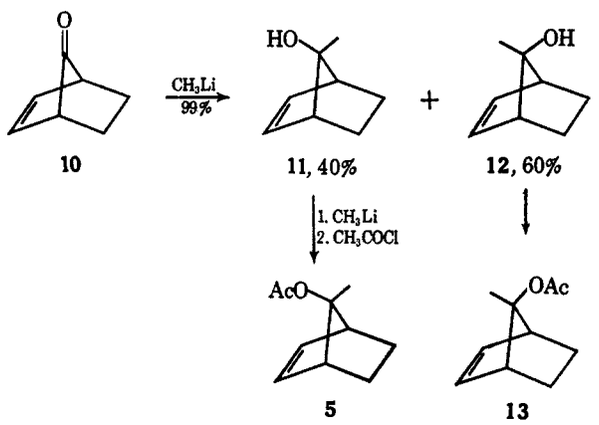
(15) It should be mentioned that the mass spectrum of acetate **3** was significantly different from **4** with major peaks at 166 (parent) and 124 (CH_3CO^+) and only minor peaks at 107, 106, and 105. In contrast, the mass spectrum of **4** showed no parent peak at 166 and only a minor peak at 124.

toxymethylene group, which is revealed as a singlet at τ 5.49.

The structure of acetate **5**[10] was determined by an unambiguous synthesis from 7-ketonorbornene (**10**). Treatment of **10** with methyllithium afforded two alcohols (**11** and **12**) in 99% yield in the ratio 40:60.[16] Stereochemical delineation was made on the basis that only the hydroxyl group of the *syn* isomer can undergo intramolecular hydrogen bonding with the double bond. That the one isomer (**11**) does display such hydrogen bonding is shown by the following observations. (1) The gas chromatography retention time of **11** on a polar column is significantly shorter (14 min) than that of **12** (23 min). [The reverse order of emission from the same column is noted for the corresponding acetates **5** (16.4 min) and **13** (18.6 min).] (2) At high dilution *syn* isomer **11** exhibits strong intramolecular hydrogen bonding in the hydroxyl region at 3575 cm^{-1} while *anti* isomer (**13**) shows absorption at 3623 cm^{-1}.[17] The values are in excellent agreement with the hydroxyl stretching frequencies for 7-*syn*-hydroxynorbornene (3572 cm^{-1}) and 7-*anti*-hydroxynorbornene (3628 cm^{-1}), respectively.[16]

Acetylation of alcohol **11** by successive treatment with methyllithium and acetyl chloride afforded the desired 7-*anti*-methyl-7-*syn*-acetoxynorbornene. Spectral and gas chromatography retention comparisons revealed its identity with acetate **5** isolated from the oxidation of 1-methylnorbornene. Formation of *anti* acetate **13** in the same manner eliminated this latter structure from consideration (see Chart III).

CHART III



Preparation of acetate **6**[11] from nortricyclanone by successive treatment with methyllithium and acetyl chloride conclusively revealed its identity.

Discussion

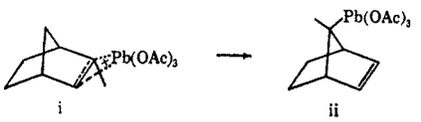
The products from the oxidation of norcamphene (**1**) may be treated as generating from allyl organolead adduct **15** (Chart I). In contrast, the principal products from oxidation of 2-methylnorbornene (**2**) must germinate from the acetoxy compound **22** (Chart II) and, in fact, parallel the products from oxidation of norbornene.[18] A rationale can be presented to explain the contrasting courses of oxidation of these two isomers by examining, first of all, the two initially formed lead triacetate adducts [*i.e.*, carbonium ions **14** (Chart I) and **20** (Chart II)]. Acetate should add to ion **14** to yield the intermediate acetate **17**[19] or to **20** to produce **22**[21] by a kinetically controlled process[22] competitive with the elimination process to olefins **15** and **21**, respectively. Once formed, allyllead triacetate derivatives **15** and **21** should undergo rapid elimination to mesomeric ion **16**.[2] Addition of nucleophile under conditions of kinetic control should occur at the more electron-deficient or secondary position of mesomeric ion **16**, thus accounting for product distribution.[23]

Similarly acetate adduct **22** once formed should undergo rapid elimination to **23** at a rate faster than acetate elimination to ion **20**. Whether elimination of lead triacetate to primary carbonium ion **18** is faster

(16) R. K. Bly and R. S. Bly [*J. Org. Chem.*, **28**, 3165 (1963)] reported that interaction of 7-ketonorbornene (**10**) and methylmagnesium bromide afforded only *anti* alcohol **12**. Apparently methyllithium is less subject to steric factors than the Grignard reagent.

(17) We thank Dr. E. C. Taylor for suggesting the infrared experiments and Dr. W. L. Courchene for performing and interpreting the infrared measurements.

(18) Although nortricyclylacetate and 7-acetoxynorbornene were reported to be the principal products from lead tetraacetate oxidation of norbornene in benzene, the stereochemistry of the latter acetate was not determined.[7] That at least acetate **5** from oxidation of 1-methylnorbornene is formed *via* the intermediate **22** rather than directly from an initially formed π complex (i) by an anti-Markovnikov process is indicated by the stereochemistry of acetate **5**. If elimination to the organolead adduct ii



i ii

occurred before nucleophilic addition of acetate, then the *anti*-acetate **13**[18a,b] or ring-contraction products[18c] would be the expected products of the reaction: (a) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); (b) W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956); (c) S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

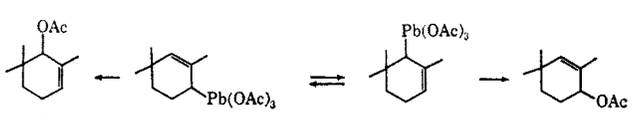
(19) Under conditions of kinetic control nucleophilic addition to the norbornyl cation should occur from the "*exo* side" at the more highly substituted position of the resonance hybrids or rapidly equilibrating carbonium ions.[20]

(20) J. A. Berson, *Tetrahedron Letters*, **No. 16**, 17 (1960).

(21) The lead tetraacetate addition to 1-methylnorbornene should parallel that of mercuric acetate,[21a] nitrosylhalide,[21b,c] and hydrogen bromide[21d] addition to norbornene and methanol addition to trimethylenenorbornene:[21c] (a) T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963); (b) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *ibid.*, **86**, 4074 (1964); (c) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *ibid.*, **85**, 2513 (1963); (d) H. Kwart and J. L. Nyce, *ibid.*, **86**, 2601 (1964); (e) S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Letters*, 185 (1963).

(22) Although acetates **17** and **22** may also be formed by direct 1,2 addition to olefins **1** and **2**, respectively, it has been implied that this process is rapidly reversible[8] and would not play a role in olefin formation.

(23) The hypothesis that a mesomeric ion is involved in these oxidations was first made by Wiberg[2] to account for the isolation of racemic products from the lead tetraacetate oxidation of (+)-1-*p*-menthene. However, the question arises[8] whether lead tetraacetate adducts **15** and **21** are interconvertible and are transformed to allyl acetate products **3** and **4** by a cyclic, rather than mesomeric carbonium ion, process. Although our work does not distinguish between these two possibilities, at least one recorded example of lead tetraacetate allylic oxidation is more consistent with the idea of a mesomeric ion. Oxidation of 1,5,5-trimethylcyclohex-1-ene with lead tetraacetate in acetic acid affords only 6-acetoxy-1,3,3-trimethylcyclohex-1-ene (i) rather than the more crowded acetate, 6-acetoxy-1,5,5-trimethylcyclohex-1-ene (ii).[24] A cyclic mechanism requires prior rearrangement of adduct iii



ii iii iv i

to highly hindered adduct iv. If a cyclic process were responsible for formation of products one might expect a predominance of acetate ii since lead adduct iii should predominate in an equilibrium mixture of iii and iv. On the other hand, acetate addition to the least hindered position of a mesomeric ion is more consistent with the observation of exclusive production of the less crowded acetate.

(24) I. Alkonyi, *Ber.*, **96**, 1873 (1963).

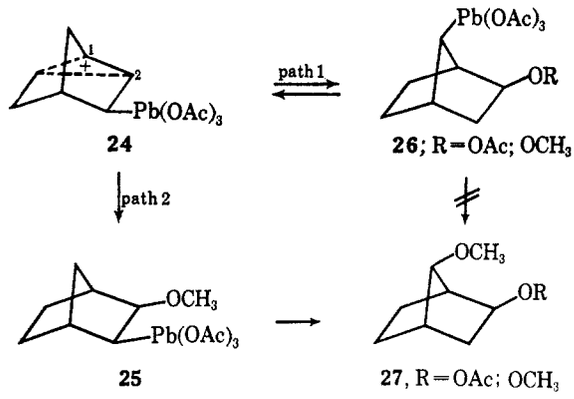
than acetate elimination to **14** may be questionable. However, the production of the ring-enlarged product, 2-acetoxy-3,3-dimethylbicyclo[3.2.1]oct-2-ene, in excellent yield from the lead tetraacetate oxidation of camphene,[6] rather than products of Wagner–Meerwein rearrangement (*i.e.*, addition or elimination from the secondary carbonium ion of type **14**) suggests that the rate of elimination to **18** is the faster process.

If these arguments are accepted, then the rate-controlling steps would be elimination from and acetate addition to ions **14** and **20**. In order to explain the favored formation of **15** from **14** relative to formation of **21** from **20**, we must assume, then, that elimination to trisubstituted olefin **15** occurs under conditions of kinetic control at a faster rate than elimination to disubstituted olefin **21**.[25] Such a hypothesis is in accord with the theory of "dominating electrometric control" set forth by Hughes, Ingold, and Shiner.[26] Although it has been implied that formation of the allyl organolead adducts such as **15** and **21** may proceed directly from **1** and **2**, respectively, an SEi′ or SE2′ mechanism[8] (in analogy to the mechanism for formation of allyl organomercurial derivatives), the formation of only *endo* olefin rather than *exo* olefin products from the lead tetraacetate oxidation of 1-methylcyclohexene seems more consistent with olefin formation from a preformed carbonium ion.[2]

The mechanistic arguments used here also accommodate the stereochemical course of diaddition product formation from the lead tetraacetate oxidation of norbornene.[7] For example, the production of *syn*-7-methoxy-3-*exo*-substituted norbornanes (**27**) from norbornene oxidation in methanol solvent surely proceeds from intermediate **25**, rather than from intermediate **26** as suggested by Alder.[7] Solvolysis of latter adduct **26** should, most assuredly, lead to ring-contraction products[18b] or, at best, to a mixture containing both 7-*syn*- and 7-*anti*-methoxyl isomers. Since the rate of addition of acetate or methanol to ion **24** should indeed occur with greater facility at C-1 than C-2 (since C-1 is the least hindered of the two secondary ions), the organolead adduct **26** undoubtedly is produced initially. However, since the rate of solvolysis of 7-substituted norbornanes is at least 10^{-4} times as fast as solvolysis of C-5 *exo*-substituted norbornanes,[27] an equilibrium probably is achieved between cation **24** and acetate **26** and products are generated only from **25** (Chart IV).

Finally, from a synthetic standpoint, it is interesting to compare the reactions of mercuric acetate and lead tetraacetate with norcamphene. In contrast to the cyclohexene series[2] the mercuric acetate oxidation of norcamphene was more complex than the lead tetraacetate oxidation. Thus, treatment of norcamphene with 1 mole of mercuric acetate afforded a mixture of an unidentified acetate (**28**, 5%), 2-*endo*-methyl-2-*exo*-norbornyl acetate (**29**, 30%), 3-ketonorcamphene (**8**, 28%), and acetate **3** (37%) in 9% yield. Mercuric

CHART IV



acetate probably adds to norcamphene in the same manner envisioned for lead tetraacetate. At the higher temperature of reaction, liberated acetic acid adds to unreacted norcamphene to produce **29**. Ketone **8** is undoubtedly generated from initially formed acetate **3** by further reaction with mercuric acetate.

Experimental Section

Melting points were determined on a Thomas–Hoover capillary apparatus or on a micro hot stage and are corrected; boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Infracord spectrophotometer as 5% solutions in carbon tetrachloride unless otherwise stated. Nuclear magnetic resonance spectra were run by Dr. T. J. Flautt and associates of these laboratories on 10% solutions of the compound in carbon tetrachloride on a Varian HA-100 spectrometer using tetramethylsilane as an internal reference. Chemical shifts are recorded as ppm on the τ scale, with coupling constants as cps. Nuclear magnetic resonance data are recorded in the order chemical shift (multiplicity where s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet, coupling constant, interpretation). Gas chromatography separations were made on one of four columns: column 1, a 10 ft × 0.25 in. stainless steel column packed with 20% DC-200 silicone oil on 70–80 mesh Anakrom ABS; column 2, a 10 ft × 0.25 in. stainless steel column packed with 20% Reoplex 400 on 60–80 mesh Anakrom ABS 300; column 3, a 10 ft × 0.25 in. stainless steel column packed with 20% diethylene glycol succinate polymer on 60–80 mesh Chromosorb W; column 4, a 10 ft × 0.25 in. stainless steel column packed with 20% GE-SF-96 silicon on 60–80 mesh Chromosorb W. Microanalyses were performed by T. Atanovich and associates of these laboratories and by Spang Microanalytical Laboratories, Ann Arbor, Mich. Mass spectra were determined on a Bendix Model 12-100 time-of-flight or Atlas CH4 mass spectrometer by Dr. J. H. Collins and associates of these laboratories.

Preparation of 1-Methylnorbornene (2).—The general procedure of Broaddus[28] for metalation of olefins was employed for metalation of norbornene.[29] To a suspension of *n*-butylsodium, from 23.0 g (1.00 g-atom) of sodium and 46.53 g (0.5 mole) of butyl chloride, in 200 ml of tridecane, maintained at 0–5° was added 47.08 g (0.50 mole) norbornene with high-speed stirring. Stirring was continued for 30 min at which time the reaction mixture was stored at ~27° for 3 days. To the rapidly stirred suspension was added dropwise 65 ml (148.14 g, 1.04 moles) of methyl iodide while maintaining the reaction temperature at 15–20°. The mixture was stirred for 7.0 hr (temperature rose to 40–55°) and stored at ~27° for 16 hr, an additional 32.5 ml (74.07 g, 0.5 mole) of methyl iodide was added, and stirring was continued for an additional 5.5 hr at 50–55°. The reaction mixture was cooled to 0–5° and 10 ml of methanol was added dropwise with stirring followed by 50 ml of water. The mixture

(25) The assumption is made that acetate addition to **14** is at least as fast as addition to **20**. An alternate proposal, that acetate simply adds more rapidly to ion **20** than to **14**, seems implausible since steric hindrance to addition, either intramolecularly or intermolecularly, would be at least as great in ion **20** as in ion **14**.

(26) E. D. Hughes, C. K. Ingold, and V. J. Shiner, Jr., *J. Chem. Soc.*, 3827 (1953).

(27) For pertinent references see J. A. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 192–201.

(28) C. D. Broaddus, T. J. Logan, and T. J. Flautt, *J. Org. Chem.*, **28**, 1174 (1963); *cf.* A. A. Morton, *et al.*, *J. Am. Chem. Soc.*, **72**, 3785 (1950).

(29) Finnegan has metalated norbornene and obtained 2-norbornene-2-carboxylic acid in 60% yield after carboxylation. Our comparatively lower yield of 1-methylnorbornene (5.5%) is probably explained by our shorter metalation period (3 days *vs.* 17 days): R. A. Finnegan and R. S. McNees, *J. Org. Chem.*, **29**, 3234 (1964).

was diluted with 100 ml of water, and the organic layer was partitioned and washed four times with 100 ml of water and dried over magnesium sulfate. Unreacted methyl iodide and norbornene were removed by distillation while the product—2-methyl norbornene—codistilled with octane formed by dimerization of butyl chloride. There was isolated 6.21 g of a 1:1 mixture (gas chromatographic analysis on column 3 at 60° and a 100-ml/min helium flow rate) of octane and 1-methylnorbornene (**2**, 3.10 g, 5.5%). Careful refractionation afforded 1.2472 g of **2** of >97% purity, bp 117–118° (744.8 mm). The olefin was purified for analysis by preparative gas chromatography on column 3, as described above, followed by chromatography on column 1 at 75°; infrared spectrum λ 6.15, 12.5 μ (trisubstituted olefin); nmr spectrum 4.56 (broad s, C-3 proton), 7.28, 7.42 (broad s, C-1, C-4 protons), 8.3 (d, J = 1.0 cps, C-2-methyl proton), 8.2–8.8 (m, C-4-*exo*, C-5-*exo*, C-7 protons), 8.8–9.1 (m, C-4-*endo*, C-5-*endo* protons).

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.52; H, 11.29.

The gas chromatography retention times on columns 2 and 3, the infrared and nmr spectra, and physical constants were identical with those of a sample of 2-methylnorbornene prepared by the method of Sauers.[30]

Reaction of Norcamphene (1) with Lead Tetraacetate.[31]—To a solution of 6.726 g (0.062 mole) of norcamphene[32] (**1**) in 100 ml of reagent grade benzene heated to 62° was added in portions with stirring 28.191 g (0.0637 mole) of lead tetraacetate over a period of 12 min, the temperature rising to 82° during the addition. The mixture was cooled to and maintained at 76° for 1.5 hr with rapid stirring. The mixture was cooled to 27° and the precipitated lead acetate was removed by filtration. To the filtrate was added 50 ml of water and the mixture was shaken vigorously. After separation of water the benzene layer was washed successively with 10 ml of saturated sodium bicarbonate, and three 20-ml portions of water and dried over magnesium sulfate and the solvent was evaporated under reduced pressure to afford 7.801 g of light yellow oil. A 6.798-g portion of the oil was distilled from an 18-in. spinning-band column to afford 2.185 g (25.5%) of liquid, bp 51–54° (1.0–1.2 mm), comprised of 3-*exo*-acetoxynorcamphene (**3**, 93%) and 2-acetoxymethylnorbornene (**4**, 7%) (as determined by gas chromatographic analysis on column 2 at 150° and a 60-ml/min helium flow).

Acetate **3** (retention time 10.37 min) was isolated in pure form by fractionation on the same column as a colorless liquid: bp 53–54° (1.2 mm); infrared spectrum λ 5.76, 8.13 (acetate), 6.01, 11.10 μ ($R_2C{=}CH_2$); nmr spectrum 5.05, 5.13 (s, $C{=}CH_2$), 5.18 (broad s, C-3 proton), 7.34 (s, C-1 proton), 7.71 (broad s, C-4 proton), 8.08 (s, acetoxy methyl proton), 8.1–8.9 (m, C-5, C-6, C-7 protons); mass spectrum parent mass peak m/e 166; principal peaks 124, 78, and 42.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.31; H, 8.44.

The acetate **4** (retention time 12.90 min) was isolated in pure form by preparative gas chromatography under the same conditions as described above as a colorless liquid: bp 53–54° (1.2 mm); infrared spectrum λ (10% in CS_2) 5.75, 8.10 (acetate), 6.13, 12.30 μ (trisubstituted olefin); nmr spectrum 4.21 (d, 2.0, C-3 proton), 5.49 (s, C-2-acetoxymethylene protons), 7.2 (broad m, C-1, C-4 protons), 8.03 (s, acetoxymethyl proton), 8.2–8.7 (m, C-7, C-4-*exo*, C-5-*exo* protons), 8.8–9.1 (m, C-4-*endo*, C-5-*endo* protons); mass spectrum no parent mass peak, major peaks at m/e 106, 105, 91, 78.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.07; H, 8.68.

The same products were obtained in almost identical ratio but slightly poorer yields when the procedure of Hartshorn and Wallis[3] (employing calcium carbonate to consume the acetic acid liberated from the reaction) was employed. From 6.944 g of norcamphene, 28.523 g of lead tetraacetate, and 2.157 g of calcium carbonate there was isolated after work-up and distillation 1.567 g (18%) of the mixture of monoacetates consisting of **3** (92%) and **4** (8%).

Reaction of 2-Methylnorbornene (2) with Lead Tetraacetate.—The same procedure was employed as described above for oxidation of norcamphene. Treatment of 0.873 g (0.008 mole) of **2** in 20 ml of benzene with 3.506 g (0.008 mole) of lead tetraacetate afforded 854 mg of crude product. Short-path distillation afforded 472 mg (35%) of monoacetate product, bp 100–130° (5.0 mm), consisting of 7-*syn*-acetoxy-7-methylnorborn-2-ene (**5**, 35%), 3-methyl-3-nortricyclylacetate (**6**, 56%), acetate **3** (9%), and acetate **4** (trace) (analysis on column 3 at 110° and a 100-ml/min helium flow rate). Acetates **5**, **6**, **3**, and **4** were isolated for analysis by preparative gas chromatography on column 3 as above.

Acetate **5** was isolated as a colorless liquid: bp 108° (7 mm); infrared spectrum λ 5.78, 8.0 (acetate), 6.15, 13.98, 14.24 μ (*cis* olefin); nmr spectrum 4.0 (m, C-2, C-3 vinyl protons), 6.97 (m, C-1, C-4 protons), 8.15 (s, acetoxy methyl proton), 8.0–8.4 (m, C-4-*exo*, C-5-*exo* protons), 8.66 (s, C-7 methyl proton), 8.85–9.20 (m, C-4, C-5-*endo* protons).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.07; H, 8.58.

The gas chromatography retention time and infrared and nmr spectra of the acetate **5** isolated above were identical with those of 7-*syn*-acetoxy-7-methylnorborn-2-ene prepared from 7-ketonorbornene below.

Acetate **6** was isolated as a colorless liquid: bp 100° (2.0 mm); infrared spectrum, λ (10% in CS_2) 5.77, 7.95 (acetate), 9.20, 9.90, 12.45 μ (characteristic strong absorption); nmr spectrum 8.08 (s, acetoxy methyl proton), 8.60 (s, 3-methyl proton), 7.9–8.9 (m, remaining protons).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.93; H, 8.44.

The gas chromatography retention times on columns 2 and 3, and the infrared and nmr spectra of acetate **6** isolated above were identical with those of 3-methyl 3-nortricyclylacetate (**6**) prepared from nortricyclanone below.

The gas chromatography retention times and infrared and nmr spectra of acetates **3** and **4** were identical with the two acetates **3** and **4** isolated from the oxidation of norcamphene.

Preparation of 3-Hydroxynorcamphene (7).—To a solution of 494 mg (0.012 mole) of sodium hydroxide in 5.0 ml of methanol was added a solution of 913 mg (0.006 mole) of the acetate **3** in 5.0 ml of methanol and the mixture was stored at 27° for 16 hr. The bulk of the solvent was removed under reduced pressure and the residual liquid was diluted with 20 ml of water and extracted with 75 ml of ether. The ethereal layer was washed with four 15-ml portions of water, dried over magnesium sulfate, and evaporated to afford 519 mg (76%) of crude alcohol. Short-path distillation afforded 280 mg (41%) of 3-hydroxynorcamphene (**7**) as a colorless liquid, bp 105° (11.5 mm) of 95% purity. Final purification was achieved on column 2 at 125° and a 60-ml/min helium flow; infrared spectrum λ 2.9 (broad, OH), 6.0, 11.05 ($R_2C{=}CH_2$), 9.40, 9.80 μ (characteristic bands); nmr spectrum 5.06, 5.07 (s, vinyl protons), 6.21 (s, C-3-*endo* proton), 7.30 (broad s, C-1 proton), 7.71 (broad s, C-4 proton), 8.0–9.0 (m, C-4, C-5, C-7 protons).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 76.84; H, 9.64.

Preparation of 3-Ketonorcamphene (8). A. From 3-*exo*-Hydroxynorcamphene (7).—A solution of 467 mg of 3-*exo*-hydroxynorcamphene in 35 ml of acetone was oxidized at 27–34° by dropwise addition of 0.8 ml of standard chromate solution.[33] Excess chromic acid was destroyed by addition of 5 ml of isopropyl alcohol, the mixture was filtered, and solvent was removed under reduced pressure. The residue was extracted with 100 ml of ether, and the ethereal layer was washed with two 20-ml portions of water, 10 ml of saturated sodium bicarbonate, two 20-ml portions of water, and dried over magnesium sulfate. Evaporation of solvent afforded 100 mg (21%) of crude **8** which was purified by preparative gas chromatography on column 2 at 125° and a 60-ml/min helium flow rate as a colorless liquid, the gas chromatography retention time and infrared and nmr spectra of which were identical with the authentic sample of 3-ketonorcamphene (**8**) prepared below.

B. From N,N-Dimethylammoniummethyl-2-norcamphor Hydrochloride (9).—The method of Krieger[11] was employed. From 2.867 g of hydrochloride **9**,[34] mp 198.5–199.5°, there was isolated (after pyrolysis at 340°, work-up, and distillation), 0.2950 g (14.5%) of **8** as a colorless liquid: infrared spectrum λ 5.75

(30) R. R. Sauers, *J. Am. Chem. Soc.*, **81**, 4873 (1959).

(31) Essentially the procedure of G. H. Whitham[4] was employed for these oxidations.

(32) We are indebted to Professor Richard A. Finnegan, State University of New York at Buffalo, for a generous supply of norcamphene.

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

(34) H. Krieger, *Suomen Kemistilehti*, **35B**, 10 (1962); *Chem. Abstr.*, **57**, 11041 (1962).

(carbonyl), 6.05, 10.69 μ ($R_2C{=}CH_2$); nmr spectrum 4.41, 4.97 (s, vinyl protons), 6.91 (broad m, C-1 proton), 7.38 (broad m, C-4 proton), 8.0–8.6 (m, C-4, C-5, C-7 protons).

The ketone was analyzed as the semicarbazone which crystallized in plates from ethanol, mp 198–199.2° (lit.[35] mp 195–196°).

Anal. Calcd for $C_9H_{13}N_3O$: C, 60.31; H, 7.31; N, 23.45. Found: C, 59.81; H, 7.34; N, 23.39.

Preparation of Nortricyclanone (30).—Nortricyclanone was prepared from nortricyclanol[36] by Jones oxidation.[33] Treatment of 7.012 g (0.064 mole) of nortricyclanol (mp 104–105°) in 125 ml of acetone with 20 ml of standard chromate reagent at 20–30° afforded, after work-up and distillation from an 18-in. spinning-band column 3.286 g (47%) of nortricyclanone as a colorless liquid: bp 49–50° (4.5 mm); $n^{25}D$ 1.4850 [lit.[10] bp 78–79° (24 mm), $n^{25}D$ 1.4878]; infrared spectrum λ 5.68 μ (carbonyl); nmr spectrum 7.97 (broad d, 5.0, C-2, C-6 protons superimposed with lower half of C-5, C-8 AB doublet), 8.02 (broad d, 10.0, C-5, C-8 protons), 8.20 (broad s, C-4 proton), 8.31 (d, 10.0, C-6 C-7 protons), 8.85 (t, 5.0, C-2 proton).

Anal. Calcd for C_7H_8O: C, 77.75; H, 7.46. Found: C, 77.92; H, 7.34.

Preparation of 3-Methyl 3-Nortricyclylacetate (6).—To a solution of 1.586 g (0.015 mole) of nortricyclanone in 50 ml of anhydrous ether was added slowly with stirring 10.0 ml of a 2.30 *M* solution of methyllithium in ether over a period of 7 min. The mixture was stirred for an additional 30 min when 3.0 ml (3.3 g) of acetyl chloride was added dropwise with stirring to the cooled mixture (0–5°) over a period of 15 min and the mixture was stored overnight at 27°. The reaction mixture was poured cautiously over ice–water (100 g:25 ml), and the ethereal layer was partitioned and washed successively with 20 ml water, two 15-ml portions of saturated sodium bicarbonate, and four 20-ml portions of water and dried over magnesium sulfate. Evaporation of solvent afforded 1.933 g of colorless oil which, on short-path distillation, afforded 1.487 g of crude acetate **6**: bp 100–105° (5.0 mm), $n^{25}D$ 1.4755. The acetate was isolated in pure form by preparative gas chromatography on column 2 at 135° and a 70-ml/min helium flow rate. The physical constants and spectra of this acetate and the acetate **6** isolated from the lead tetraacetate oxidation of 2-methylnorbornene were identical as described above.

Preparation of 7-*anti*-Hydroxy-7-methylnorborn-2-ene (12) and 7-*syn*-Hydroxy-7-methylnorborn-2-ene (11).—To 1.351 g (0.013 mole) of 7-ketonorbornene[38] in 50.0 ml of anhydrous ether cooled to 0–5° was added dropwise with stirring 9.0 ml of a 2.30 *M* solution of methyllithium in ether over a period of 10 min. The mixture was stirred vigorously for 1 hr at 0–5°, then was hydrolyzed by dropwise addition of 20 ml of water and extracted with 75 ml of ether, and the ethereal layer was washed with four 15-ml portions of water and dried over magnesium sulfate. Evaporation of solvent under reduced pressure afforded 1.545 g (99%) of colorless, crystalline needles (mp 47–67°) comprised of alcohols **11** (40%) and **12** (60%) (analysis on column 3 at 108° and a 60-ml/min helium flow rate). Although the two alcohols were partially resolved by column chromatography over silica gel, complete resolution could be achieved only by gas chromatography on column 2 above.

Alcohol **12** (relative retention time 23.0 min) was isolated as colorless needles: mp 79.5–80.5°; infrared spectrum λ (5% CCl_4, Infracord) 6.12, 13.95 (*cis* olefin), 8.6–8.9, 10.75 μ (characteristic strong bands); λ (0.023 *M* in CCl_4, Perkin-Elmer 421, 1-mm sodium chloride cell) 3623 cm^{-1} (nonintramolecularly hydrogen-bonded OH);[16] nmr spectrum 4.0 (m, C-2, C-3 vinyl protons), 7.62 (m, C-1, C-4 protons), 8.9 (s, hydroxyl proton), 7.95 (m, C-5, C-6-*exo* protons), 8.76 (s, C-7-methyl proton), 8.9–9.1 (m, C-5, C-6-*endo* protons).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.68; H, 9.84.

Alcohol **11** (relative retention time 14.0 min) was isolated as colorless needles: mp 30–31°; infrared spectrum λ 6.12, 14.0 (*cis* olefin), 10.60 μ (strong characteristic band); λ (0.023 *M* in CCl_4), 3575 cm^{-1} (intramolecularly bonded OH); nmr spectrum 3.95 (t, 1.5, C-2, C-3 vinyl protons), 7.58 (m, C-1, C-4 protons), 7.71 (s, OH), 8.21 (m, C-5, C-6-*exo* protons), 8.83 (s, C-7-methyl proton), 9.05 (m, C-5, C-6-*endo* protons).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.14; H, 9.72.

Preparation of 7-*anti*-Acetoxy-7-methylnorborn-2-ene (13).—To a solution of 28 mg (2.3×10^{-4} mole) of 7-*anti*-hydroxy-7-methylnorborn-2-ene (mp 79.5–80.5°) in 15 ml of ether was added dropwise with cooling (0–5°) 1.0 ml of a 2.30 *M* solution of methyllithium in ether. The mixture was stirred at room temperature for 45 min, cooled to 0–5°, 2.0 ml of acetyl chloride was added, and the mixture was stirred for 1 hr at 0–5° and stored for 16 hr at 27°. The ethereal layer was washed with 10 ml of water, 5 ml of saturated sodium bicarbonate, and three 10-ml portions of water, and dried over magnesium sulfate; the solvent was removed under reduced pressure, and the residue was distilled from a modified Hickman still to afford 31 mg (86%) of acetate **13** as a colorless liquid, bp 100° (7 mm). This acetate was identical with acetate **13** of relative retention time 16.4 min isolated below from the reaction of methyllithium with 7-ketonorbornene and subsequent treatment with acetyl chloride (*i.e.*, gas chromatography relative retention time, and infrared and nmr spectral comparisons).

Preparation of 7-*syn*-Acetoxy-7-methylnorborn-2-ene (5).—The same procedure was employed as for preparation of acetate **13**, above. From 23 mg (2.2×10^{-4} mole) of 7-*syn*-hydroxy-7-methylnorborn-2-ene (mp 30–31°) treated successively with 1.0 ml of 2.30 *M* ethereal methyllithium and 1.0 ml of acetyl chloride there was isolated (after work-up and preparative gas chromatography on column 1 at 110° and a 60-ml/min helium flow rate) 10 mg (61%) of acetate **5** as a colorless liquid. The gas chromatography retention time and infrared and nmr spectra of this material were identical with the acetate **5** of relative retention time 18.6 min isolated below from 7-ketonorbornene.

Preparation of 7-*anti*-Acetoxy-7-methylnorbornene (13) and 7-*syn*-Acetoxy-7-methylnorbornene (5) from 7-Ketonorbornene.—The same procedure was employed as above. From 1.341 g (0.012 mole) of 7-ketonorbornene[37] in 50 ml of ether, treated successively with 10.0 ml of 2.30 *M* ethereal methyllithium and 3.0 ml of acetyl chloride, was obtained, after work-up and distillation, 561 mg (27%) of a mixture of 59% **13** and 41% **5** as a colorless liquid, bp 90–110° (9.0 mm). The two acetates were isolated in pure form by preparative gas chromatography on column 1 at 100° and a 60-ml/min helium flow.

Acetate **13** (relative retention time 16.4 min) was isolated as a colorless liquid: infrared spectrum: λ 5.75, 8.01 (acetate), 7.30 (methyl), 6.12, 13.95 (*cis* olefin), 9.01 μ (characteristic strong absorption); nmr spectrum 4.05 (m, C-2, C-3 vinyl protons), 7.12 (m, C-1, C-4 protons), 8.10 (s, acetate methyl), 8.1–8.3 (m, C-5, C-6-*exo* protons), 8.61 (s, C-7 methyl proton), 8.9–9.15 (m, C-4, C-5-*endo* methyl protons).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.21; H, 8.48.

Acetate **5** (relative retention time 18.6 min) was isolated as a colorless liquid: infrared spectrum λ 5.76, 8.0 (acetate), 13.95, 14.20 μ (*cis* olefin); nmr spectrum 4.12 (m, C-2, C-3 vinyl protons), 7.08 (m, C-1, C-4 protons), 8.20 (s, acetate methyl proton), 8.1–8.4 (m, C-5, C-6-*exo* protons), 8.69 (s, C-7 methyl proton), 8.9–9.2 (m, C-5, C-6-*endo* protons).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.93; H, 8.50.

Reaction of Norcamphene (1) with Mercuric Acetate.—Essentially the procedure of Wiberg[2] for oxidation of carvomenthene was employed. A mixture of 5.382 g (0.050 mole) of norcamphene and 15.808 g (0.050 mole) of mercuric acetate was heated in a 300-ml, sealed glass tube in a rocking autoclave for 3 hr at 150°. The cooled, brown oil was dissolved in ether and washed with three 15-ml portions of saturated sodium bicarbonate solution and five 20-ml portions of water and dried over magnesium sulfate. Evaporation of solvent afforded 5.089 g of residual oil which on short-path distillation afforded 755 mg (9%) of colorless liquid, bp 90–100° (11.0 mm), consisting of four compounds: an unidentified acetate **28** (5%), 2-*endo*-methyl-2-*exo*-norbornyl acetate (**29**, 30%), 3-ketonorcamphene (**8**, 28%), and 3-*exo*-acetoxynorcamphene (**3**, 37%). Each of acetates **28**, **29**, **8**, and **3** was isolated by preparative gas chromatography on column 2 at 125° and a 65-ml/min helium flow rate.

The unidentified acetate (**28**, relative retention time 15.3 min) was isolated as a colorless liquid: infrared spectrum λ (5% CS_2) 5.78, 8.10 μ (acetate), absence of olefin bands.

Acetate **29** (relative retention time 17.9 min) was isolated as a colorless liquid: infrared spectrum λ 5.75, 8.0–8.3 μ (acetate); nmr spectrum 7.4 (m, C-1 proton), 7.8 (m, C-4 proton), 8.09

(35) K. Alder and A. Grell, *Ber.*, **89**, 2198 (1956).

(36) Prepared from nortricyclyl formate[37] by the procedure of L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956).

(37) H. K. Hall, Jr., *ibid.*, **82**, 1209 (1960).

(38) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

(s, acetate methyl proton), 8.49 (s, C-2-*endo* methyl proton), 8.0–9.0 (m, C-3, C-4, C-5, C-7 protons); mass spectrum parent mass peak 168, principal peaks 111, 110, 108, 80, and 43.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6. Found: C, 70.2; H, 9.3.

Ketone **8** (relative retention time 19.8 min) was isolated as a colorless liquid, the infrared and nmr spectra of which were identical with those of the authentic specimen of 3-ketonorcamphene (**8**) prepared from N,N-dimethylammoniummethyl-2-norcamphor hydrochloride above.

The gas chromatography retention times and infrared and nmr spectra of acetate **3** (relative retention time 21.6 min) were identical with those of acetate **3** isolated from the lead tetraacetate oxidation of norcamphene.

Registry No.—**1**, 497-35-8; **2**, 694-92-8; lead tetraacetate, 546-67-8; **3**, 7593-21-7; **4**, 7593-22-8; **5**, 7593-23-9; **6**, 7593-24-0; **7**, 7593-25-1; **8**, 5597-27-3; semicarbazone of **8**, 7593-27-3; **30**, 695-05-6; **29**, 770-92-3; **12**, 7593-29-5; **11**, 7593-30-8; **13**, 7435-66-7.

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The Structure of α-Keto Hydroperoxides

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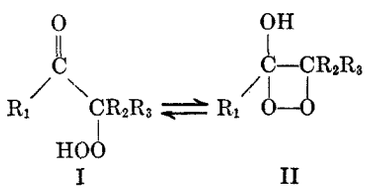
The structure of α-keto hydroperoxides was investigated in carbon tetrachloride and chloroform solution. Intra- as well as intermolecular hydrogen bonding was observed for 2,4-dimethyl-2-hydroperoxy-3-pentanone in carbon tetrachloride solution. The equilibrium constant for intermolecular hydrogen bonding at 33.1, 50.3, and 70.2° is given along with the corresponding enthalpy, free-energy, and entropy values. In addition, the enthalpy of intramolecular hydrogen bonding is reported. These values are discussed with relationship to intermolecular hydrogen bonding of *t*-butyl hydroperoxide. Both aryl- and alkyl-α-keto hydroperoxides exist solely in the hydroperoxide form. No cyclic peroxide tautomer could be detected by infrared or ultraviolet spectral analysis.

Only a limited amount of quantitative data is available for hydrogen bonding of hydroperoxides.[1] Quantitative data are invaluable for the interpretation of the kinetics of hydroperoxide decomposition. Our interest in the mechanism of α-keto hydroperoxide decomposition and the role of perepoxides in certain reactions[2] led us to study the structure of α-keto hydroperoxides. Particular attention is given to the importance of intra- *vs.* intermolecular hydrogen bonding. Although previous work[3] suggests that equilibrium (eq 1) is far or completely to the left when R_1 is aryl,



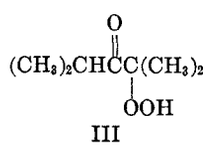
(1)

I II

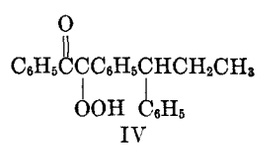
we desired to test this proposal. In addition, we wanted to determine if equilibrium (eq 1) was established with R_1 = alkyl. Here addition to the carbonyl group to give II would be more favorable than with R_1 = aryl.[4]

Results and Discussion

Both infrared and nmr spectra of 2,4-dimethyl-2-hydroperoxy-3-pentanone (III) show that it is mainly in the hydroperoxide form (I) rather than the cyclic peroxide form (II). A strong carbonyl absorption is observed in the infrared spectrum at 1717 cm^{-1} and the oxygen-bound proton is found far downfield (9.39 ppm) in the nmr spectrum. Hydroperoxy protons characteristically show low-field nmr absorption.[5] Further examination of the infrared spectrum of III



III



IV

at low concentrations (down to 6.35×10^{-3} *M*) reveals no evidence for the cyclic form II. At low concentrations where monomeric peroxide is favored, the opportunity to detect cyclic form II is maximized. Yet only two oxygen–hydrogen stretching bands are seen in the infrared spectrum. A broad band at 3450 cm^{-1} is assigned to hydrogen-bonded species, while a reasonably sharp band at 3546 cm^{-1} is assigned to the free oxygen–hydrogen stretching mode of the hydroperoxy group. The frequency of the latter band is low for free hydroxyl groups as required by the cyclic peroxide form (II), but is consistent with the free hydroperoxy group of *t*-butyl hydroperoxide (3554 cm^{-1}).[1] A free hydroxyl oxygen–hydrogen stretching band that would give support to the cyclic form (II) is not observed in the infrared spectrum of III. The ultraviolet spectrum of 2,3-diphenyl-2-hydroperoxyvalerophenone (IV) should show a change in the molar extinction coefficient (ϵ) with changing peroxide concentration if equilibrium (eq 1) is valid. This also assumes that some dimeric hydroperoxide species are present over this concentration range. When the concentration of IV was varied from 0.150×10^{-2} to 1.50×10^{-2} *M* in chloroform solution, the ϵ value was constant at the wavelength

(1) C. Walling and L. Heaton, *J. Am. Chem. Soc.*, **87**, 48 (1965).

(2) W. H. Richardson, J. W. Peters, and W. P. Konopka, *Tetrahedron Letters*, 5531 (1966).

(3) (a) J. Rigandy, *Compt. Rend.*, **226**, 1993 (1948); (b) R. C. Fuson and H. L. Jackson, *J. Am. Chem. Soc.*, **72**, 1637 (1950).

(4) For example, the equilibrium constant for cyanohydrin formation is 4.4×10^{-3} at 20° in ethanol solvent for benzaldehyde [J. W. Baker, G. F. C. Barrett, and W. T. Tweed, *J. Chem. Soc.*, 2831 (1952)] and about 1.4×10^{5} for acetaldehyde in water at 25° [W. F. Yates and R. L. Heider, *J. Am. Chem. Soc.*, **74**, 4153 (1952)].

(5) S. Fujiwara, M. Katayama, and S. Kamio, *Bull. Chem. Soc. Japan*, **32**, 657 (1959).