The Anomalous Sodium Hydride Reduction of Norcamphor and 5-Norbornen-2-one

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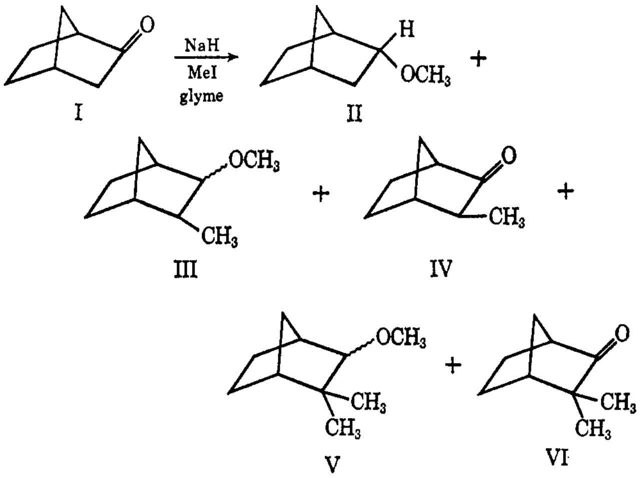
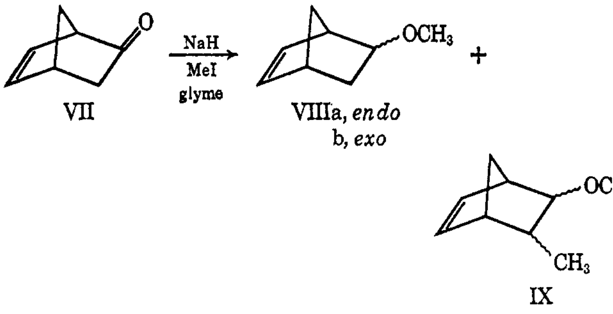
Norcamphor and 5-norbornen-2-one both gave significant yields of reduction products (methyl ethers) when treated with sodium hydride and methyl iodide in glyme. Thus, norcamphor (I) gave 2-methoxynorbornane (II, 10% yield), 3-methyl-2-methoxynorbornane (III, 22%), 3-methylnorcamphor (IV, 27%), 3,3-dimethyl-2-methoxynorbornane (V, 1.4%), and 3,3-dimethylnorcamphor (VI, 38%). 5-Norbornen-2-one (VII) gave *endo*- and *exo*-2-methoxy-5-norbornene (VIII, 63%) and 3-methyl-2-methoxy-5-norbornene (IX, 32%). With excess ketone in the latter case, 3-methyl-5-norbornen-2-one (X) was also formed. It was shown that the carbonyl is the species being reduced and not the O-alkylation products, 2-methoxynorbornene and 2-methoxynorbornadiene. Possible reasons why these ketones are so easily reduced are suggested.

An extensive literature exists on the reactions of sodium hydride with carbonyl compounds. Nearly all is concerned with the formation of an enolate ion and its subsequent reactions, although there is no reason to suppose *a priori* that hydride attack on the carbonyl itself cannot occur, but such attack has been observed only with non-enolizable ketones—thus Swamer and Hauser[1] showed that benzophenone is reduced by sodium hydride in boiling xylene to benzhydrol. Benzaldehyde was converted into benzyl benzoate which itself was inert to sodium hydride under these conditions. Apparently a small amount of benzaldehyde was reduced to the alcoholate which then catalyzed the well-known[2] reaction to form the ester. Lewis[3] reported that *p*-nitrobenzaldehyde, on treatment with sodium hydride in tetrahydrofuran at room temperature, gave *p*-nitrobenzoic acid plus smaller amounts of *p*-nitrobenzyl alcohol. Under the reaction conditions *p*-nitrobenzoic acid was formed by autoxidation of the alcohol, which itself was not formed to any significant extent by direct hydride reduction, but by a process similar to that observed by Swamer and Hauser in the case of benzaldehyde.

We wish to report the first case of sodium hydride reduction of enolizable ketones. On treatment with sodium hydride and methyl iodide in refluxing glyme, both norcamphor and 5-norbornen-2-one gave significant yields of reduction products, especially in the latter case. Such products were methyl ethers, formed by reduction to the sodium alcoholate followed by methylation. Thus, reaction of norcamphor (I, 0.0139 mol) with sodium hydride (0.051 mol) and methyl iodide (0.063 mol) in 50 ml of glyme at reflux gave the products (yields based on starting ketone) 2-methoxynorbornane (II, 10%), 3-methyl-2-methoxynorbornane (III, 22%), 3-methylnorcamphor (IV, 27%), 3,3-dimethyl-2-methoxynorbornane (V, 1.4%), and 3,3-dimethylnorcamphor (camphenilone) (VI, 38%). The combined yield is 98%, indicating that no other products were formed to any significant extent. The stereochemistry of these products was not proved, except for II, which is identical with the authentic *endo* isomer. IV is a single isomer, probably the *exo*, by analogy with the work of Corey and his coworkers[4] on the alkylation of norcamphor using sodium amide and triphenylmethylsodium as bases. III is a mixture of two isomers in the ratio 2:1, and, since III must be formed from IV which has the methyl group *exo*, then the two components of III are the *endo*- and *exo*-methoxy isomers.



Reaction of 5-norbornen-2-one (VII) under identical conditions led to a mixture of products with the reduction product, 2-methoxy-5-norbornene (VIII) formed in 63% yield. The *endo* (VIIIa) and *exo* (VIIIb) isomers were formed in the ratio of 4:1. The higher boiling products were identified as a mixture of isomers of 3-methyl-2-methoxy-5-norbornene (IX) with trace amounts of higher boiling products present. These were formed in a combined yield of 32%.



Reaction under similar conditions but with a twofold excess of ketone over sodium hydride gave, in the case of norcamphor, reduction product II and alkylated product IV in the ratio of about 1:9, plus trace amounts of the other products. 5-Norbornen-2-one gave reduction product VIII and alkylated product 3-methyl-5-norbornen-2-one (X) in the ratio of about 2:1, plus trace amounts of other materials. Thus for the satu-

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(1) F. W. Swamer and C. R. Hauser, *J. Amer. Chem. Soc.*, **68**, 2647 (1946).

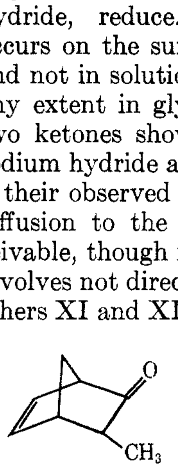
(2) O. Kamm and W. F. Kamm in "Organic Syntheses," Coll. Vol. I, H. Gilman and A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1932, p 104.

(3) G. E. Lewis, *J. Org. Chem.*, **30**, 2433 (1965).

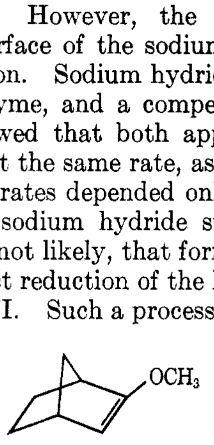
(4) E. J. Corey, R. Hartmann, and P. A. Vatakencherry, *J. Amer. Chem. Soc.*, **84**, 2611 (1962).

rated ketone I the rate of alkylation was nine times the rate of reduction; for the unsaturated ketone VII the rate of alkylation was one-half the rate of reduction.

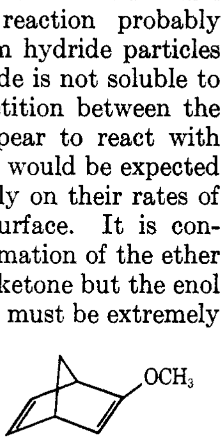
The mechanism for this reduction is apparently hydride addition to the carbonyl possibly preceded by complexation of the carbonyl, which is essentially the way that other hydrides, such as lithium aluminum hydride, reduce. However, the reaction probably occurs on the surface of the sodium hydride particles and not in solution. Sodium hydride is not soluble to any extent in glyme, and a competition between the two ketones showed that both appear to react with sodium hydride at the same rate, as would be expected if their observed rates depended only on their rates of diffusion to the sodium hydride surface. It is conceivable, though not likely, that formation of the ether involves not direct reduction of the ketone but the enol ethers XI and XII. Such a process must be extremely fast, much more rapid than other modes of reaction, since no enol ethers were found, but, if such reduction could occur, the product ratios obtained would reflect not the relative rates of reduction and enolization, but the rates of O and C alkylation. However, this possibility can be eliminated by consideration of the fact that a small amount of the reduction product V from the dimethyl ketone VI was formed (further treatment of the reaction mixture containing VI with sodium hydride and methyl iodide in glyme gave much greater quantities of the ether V). Enolization is not possible for VI; so V must arise by direct reduction of the ketone. In addition, the enol ether XI was synthesized and shown to be inert to sodium hydride under the reaction conditions. Thus the vinyl ethers cannot be formed at any time during the course of the reaction.



X



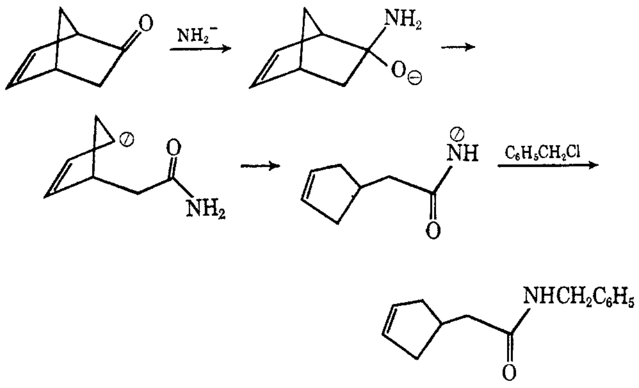
XI



XII

The question arises as to why the two ketones studied by us give such a large proportion of reduction products, in contrast to all the other enolizable ketones which have been studied. (Reaction of cyclopentanone under identical conditions gave only a 0.5% yield of the reduction product methoxycyclopentane.) It is probably due to the fact that these ketones are slow to enolize and possibly that they are also very reactive toward nucleophiles. Woods and Roberts[5] have measured the rate of the base-catalyzed bromination of norcamphor, shown to proceed through the enol, in 75% aqueous acetic acid, at 35°, using sodium acetate as the base. The second-order rate constant is 4.12×10^{-7} mol $l.^{-1}$ sec^{-1}, which is about one-fiftieth the rate of acetone[6] under the same conditions. Of course these conditions do not even approximate those on the surface of a sodium hydride particle, but the data do reflect the reluctance of norcamphor to form the enolate. The rate of enolization of 5-norbornen-2-one should be even slower but not greatly so—hydrogenation experiments[7] have shown that the strain of a second double bond in a norbornadiene system is not much greater than that of the first.

It is not so evident that norcamphor and 5-norbornen-2-one are particularly reactive toward nucleophiles. Wheeler, Cetina, and Zabicky[8] have measured the dissociation constants of the cyanohydrins of a number of ketones, among them norcamphor and 5-norbornen-2-one. Both ketones were about the same: norcamphor had $K_D = 3.07 \times 10^{-2}$, 5-norbornen-2-one had $K_D = 1.11 \times 10^{-2}$, and both were quite similar to cyclopentanone ($K_D = 2.05 \times 10^{-2}$). Cyclohexanone was very different, with a $K_D = 0.059 \times 10^{-2}$. These differences were attributed mainly to steric effects, so that cyclohexanone cyanohydrin was quite stable, but the cyanohydrin of cyclopentanone, along with those of the other ketones, was destabilized by eclipsing of the adjacent hydrogens. Although the sodium hydride reduction is a kinetically controlled reaction, and not equilibrium controlled, these results imply that the ketones are not particularly susceptible toward nucleophilic attack. However, 5-norbornen-2-one does seem to be unusually reactive toward nucleophiles—Cristol and Freeman[9] found that treatment of the ketone with sodium amide, followed by benzyl chloride, gave none of the expected alkylation product, but rather the ring-opened compound XIII, formed by amide attack on the carbonyl, cleavage to open the ring, and alkylation of the amide. Haller–Bauer cleavage of ketones is usually observed only with nonenolizable ketones, and the fact that it occurs here must be ascribed to unusual sensitivity of the ketone toward such cleavage. On the other hand, norcamphor does not cleave with sodium amide,[4] probably because there is no possibility for stabilization in the ring-opened anion.



XIII

Therefore it appears that these ketones are somewhat slow to enolize and may also be unusually sensitive toward nucleophilic attack, although the evidence for this sensitivity is meager. Such sensitivity may be due to a combination of strain and steric effects, and there may also be some participation of the double bond of 5-norbornen-2-one in the form of a homoconjugative effect, although the evidence certainly offers no clear proof that such an effect is operative. However, it is clear that sodium hydride can reduce enolizable ketones and, when used with highly strained systems, cannot be considered a base with no tendency to reduce

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[5] W. G. Woods and J. D. Roberts, *J. Org. Chem.*, **22**, 1124 (1957).

[6] T. G. Bonner, D. P. Evans, and H. B. Watson, *J. Chem. Soc.*, 1353 (1939).

[7] R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Amer. Chem. Soc.*, **79**, 4116 (1957).

[8] O. H. Wheeler, R. Cetina, and J. Z. Zabicky, *J. Org. Chem.*, **22**, 1153 (1957).

[9] S. J. Cristol and P. K. Freeman, *J. Amer. Chem. Soc.*, **83**, 4427 (1961).

the ketone, since it has been shown here that nucleophilic attack can occur.

Experimental Section

Product mixtures were separated by vapor phase chromatography using an Aerograph Series 1200 instrument equipped with flame detector and effluent splitter. Columns used for analytical work were 10 ft × 0.0625 in. stainless steel columns packed with either SE-30 or Carbowax 20M on 100–120 mesh Aeropak 30. Columns used for preparative work were 0.25 in. columns of these same substrates. Compounds were identified by their ir, nmr, and mass spectra. Infrared spectra were taken in carbon tetrachloride solution on a Beckman IR-8 instrument. Nmr spectra were taken in carbon tetrachloride solution on a Varian A-60 instrument and peak position are reported in δ values (parts per million downfield from tetramethylsilane). Mass spectra were taken on a CEC-104 mass spectrometer–vpc combination using a rapid scan technique.

Preparation of 5-Norbornen-2-one.—The synthesis of 5-norbornen-2-one was similar to the procedure of Cristol and Freeman[9] by chromium trioxide–pyridine oxidation of 5-norbonen-2-one. The material had bp 98–101° (90 mm) and was prepared in 63% yield.

Preparation of *endo*-2-Methoxynorbornane[10] (II).—In a 50-ml three-necked flask equipped with stirrer, reflux condenser, and addition funnel, under nitrogen, was placed 1.0 g of a sodium hydride dispersion (0.027 mol). After the sodium hydride was washed two times with benzene, 10 ml of anhydrous ether was added, followed by 2.0 g of *endo*-2-norbornanol[11] (0.018 mol), prepared by the lithium aluminum hydride reduction of norcamphor, dissolved in 10 ml of ether. The solution was refluxed 15 min until the solution was thick with precipitated salt. Then 4.0 g (0.028 mol) of methyl iodide in 10 ml of dimethyl sulfoxide was added dropwise over 15 min, and the solution was refluxed for 30 min. To the cooled solution was added 15 ml of water and 10 ml of hexane. The layers were separated; the organic one was washed five times with water and then with saturated sodium chloride solution and dried (Na_2SO_4). After filtration, the solvent was removed by distillation through a short, packed column and the product distilled under vacuum, bp 75–85° (60 mm). The yield was 1.6 g (71%).

Preparation of a Mixture of *endo*- and *exo*-2-Methoxy-5-norbornene[12] (VIII).—This was prepared in the same manner as the saturated ether II, from a mixture of *endo*- and *exo*-5-norbornen-2-ol (about 3:1, obtained by hydrolysis of the mixture of esters formed by condensing cyclopentadiene with vinyl acetate): bp 50–53° (18 mm).

Reactions of the Ketones with Sodium Hydride and Methyl Iodide in Glyme.—The following general procedure was used for all reactions. In a three-necked flask of appropriate size equipped with a stirrer and reflux condenser, under nitrogen, was placed a sodium hydride dispersion. This was washed twice with benzene; then freshly distilled dry glyme was added, followed by methyl iodide and the ketone. The solution was rapidly stirred and quickly brought to reflux. Usually the reaction seemed to be over after 1 hr, but it was allowed to stir and reflux for about 18 hr. Work-up involved addition of water and ether (each about half the volume of glyme used). After the layers were separated, the aqueous layer was washed with ether; then the combined organic layers were washed with ammonium chloride solution, water, and saturated sodium chloride solution. After drying over sodium sulfate the solution was filtered, and either made up to volume in a volumetric flask (for analytical work) or the solvent was removed by distillation (for preparative work).

Reaction of Norcamphor with Sodium Hydride and Methyl Iodide.—Norcamphor (1.53 g, 0.0139 mol), procured from Aldrich, 98–99% pure by vpc, was treated with a sodium hydride dispersion (2.1 g, 0.051 mol) and methyl iodide (9.0 g, 0.063 mol) in 50 ml of glyme in the usual manner. The products are given in the order of their elution from a SE-30 column.

endo-**2-Methoxynorbornane (II)** was obtained in 10% yield: ir spectrum showed no carbonyl; nmr, tertiary H–C–O hydrogen at δ 3.4–3.7 (m, 0.8 hydrogen), methoxy hydrogens at δ 3.17 (s, 3.0 hydrogens), all other hydrogens at δ 0.7–2.5 (m, 11.6 hydrogens) (confirmed by identity with authentic compound).

3-Methyl-2-methoxynorbornane (III), two peaks in ratio of 2:1, was obtained in a combined yield of 22%: ir showed no carbonyl; nmr of mixture, methoxy hydrogens, two peaks, ratio 2:1, at δ 3.20 and 3.24 (s) and tertiary H–C–O hydrogens at δ 3.0–3.5 (m, combined integral 4.0 hydrogens), all other hydrogens at δ 0.7–2.5 (m, 12 hydrogens). The methyl protons appeared as three broad singlets between δ 0.8 and 1.0 (integral about three hydrogens). The mass spectrum showed no significant parent peak at *m/e* 140, a small peak at *m/e* 125 (loss of methyl), and a peak at *m/e* 108 (loss of methanol).

3-Methylnorcamphor[4] (IV) was obtained in 27% yield: ir, carbonyl at 1740 cm^{-1}; nmr, methyl group at δ 1.0 (d, 3.0 hydrogens), all other hydrogens at δ 1.2–0.24 (m, 8.7 hydrogens); mass spectrum, parent peak at *m/e* 124.

3,3-Dimethyl-2-methoxynorbornane (V) was obtained in 1.4% yield: ir showed no carbonyl; nmr, methoxy group at δ 3.2 (s), tertiary H–C–O hydrogen at δ 3.1 (b d, combined integral 4.0 hydrogen), methyl groups at δ 0.85 and 1.0 (2 s, 6.6 hydrogens), all other hydrogens at δ 1.0–2.5 (m, 7.4 hydrogens).

3,3-Dimethylnorcamphor (camphenilone) (VI) was obtained in 38% yield; ir, carbonyl at 1740 cm^{-1}; nmr, methyl groups at δ 0.95 and 1.0 (2 s, 6.0 hydrogens), all other hydrogens at δ 1.1–2.6 (m, 8.1 hydrogens); mass spectrum, parent peak at *m/e* 138.

Reaction of a Mixture Containing 3,3-Dimethylnorcamphor with Sodium Hydride and Methyl Iodide.—The distilled products from the previous reaction (0.64 g) were treated with 1.0 g of a sodium hydride dispersion and 4.2 g of methyl iodide in 25 ml of glyme. The results were that 3-methylnorcamphor (IV) had completely disappeared, 3,3-dimethylnorcamphor (VI) had decreased somewhat, and 3,3-dimethyl-2-methoxynorbornane (V) had greatly increased. Since the yield of VI had decreased and the yield of V had increased, the conclusion is that VI is reacting to form V. The absence of any IV in the product mixture indicates that IV is being converted into a mixture of III and VI, which is then reduced to V.

Reaction of 5-Norbornene-2-one with Sodium Hydride and Methyl Iodide.—5-Norbornen-2-one was treated with sodium hydride and methyl iodide in glyme in a manner identical with that used for norcamphor. The products are given in the order of their elution from a SE-30 column.

exo-**2-Methoxy-5-norbornene**, followed by *endo*-**2-methoxy-5-norbornene (VIIIb and a)** were obtained in a ratio of 1:4: 63% yield; ir showed no carbonyl; nmr of the mixture, vinyl hydrogens at δ 5.9 and 6.2 (AB quartet), each line further split into a doublet (2.0 hydrogens), tertiary H–C–O hydrogen at δ 3.95 (m, 0.8 hydrogen), methoxy hydrogens at δ 3.18 and 3.24 (2 s, ratio 4:1, 3.0 hydrogens), bridgehead hydrogens at δ 2.75 and 3.05 (two broad peaks, 1.9 hydrogens), all other hydrogens from δ 0.7 to 2.2 (m, 4.3 hydrogens). In the mass spectrum, both isomers had nearly identical mass spectra, with a parent peak at *m/e* 124. The vpc retention times of the two isomers were identical with those of the independently prepared compounds, and the spectra of the mixtures of isomers were identical.

3-Methyl-2-methoxy-5-norbornene (IX) was obtained as a mixture of isomers: yield 32%; ir showed no carbonyl; nmr, vinyl protons at δ 6.0 and 6.3 (AB quartet), each line further split into a doublet, but lines are broad (2.3 hydrogens), methoxy hydrogens at δ 3.37 and a small peak at 3.25 (s, 3.0 hydrogens), tertiary H–C–O hydrogen at δ 3.20 (b, 1.1 hydrogen), methyl groups at δ 0.9, 1.0, and 1.2 (3 s, 2.9 hydrogens), bridgehead hydrogens at δ 2.3 and 2.9 (two broad peaks, 2.3 hydrogens), all other hydrogens from δ 1.3 to 2.p (m, 3.6 hydrogens); mass spectrum, parent peak at *m/e* 138.

Reaction of Norcamphor with 0.5 Equiv of Sodium Hydride and Methyl Iodide.—Norcamphor (1.65 g, 0.015 mol) was treated with 0.31 g (0.0076 mol) of a sodium hydride dispersion and 2.1 g (0.015 mol) of methyl iodide in 25 ml of glyme. The results were that the major products were 2-methoxynorbornane (II) and 3-methylnorcamphor (IV) in a ratio of about 1:9. Small amounts of other compounds were also present.

Reaction of 5-Norbornene-2-one with 0.5 Equiv of Sodium Hydride and Methyl Iodide.—5-Norbornene-2-one was treated with sodium hyride and methyl iodide in glyme in a manner identical with that used for norcamphor. The products formed were *exo*- and *endo*-2-methoxy-5-norbornene (VIII) and 3-methyl-5-norbornen-2-one (X) in a ratio of about 2:1.

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(10) The *exo* isomer has been prepared. See H. Toivonen, *Ann. Acad. Sci. Fennicae, Ser. A II*, **72**, 49 (1956); *Chem. Abstr.*, **52**, 2808 (1958).

(11) H. C. Brown and H. R. Deck, *J. Amer. Chem. Soc.*, **87**, 5620 (1965).

(12) H. B. Hendgest and B. Nicholls, *J. Chem. Soc.*, 221 (1959).

3-Methyl-5-norbornen-2-one (X) had the following spectral data: ir, carbonyl at 1745 cm^{-1}; nmr, vinyl hydrogens at δ 6.1 and 6.5 (m, 2.0 hydrogen), methyl group at δ 1.1 (d, 2.8 hydrogens), all other hydrogens from δ 1.4 to 3.0 (m, 5.3 hydrogens).

Reaction of Mixtures of Norcamphor and 5-Norbornene-2-one with Sodium Hydride and Methyl Iodide.—The following reactions were run with 0.31 g (0.0076 mol) of a sodium hydride dispersion: a mixture of 1.65 g (0.015 mol) each of norcamphor and 5-norbornene-2-one with 2.1 g (0.015 mol) of methyl iodide; a mixture of 1.65 g (0.015 mol) of 5-norbornene-2-one and 6.6 g (0.060 mol) of norcamphor with 10.5 g (0.07 mol) of methyl iodide; and a mixture of 1.65 g (0.015 mol) of 5-norbornene-2-one and 0.83 g (0.0075 mol) of norcamphor with 2.1 g (0.015 mol) of methyl iodide. The main products were 2-methoxy-5-norbornene (VIII), 2-methoxynorbornane (II), and 3-methylnorcamphor (IV). The ratio of products indicated that both ketones reacted with sodium hydride at the same rate. The reason that no 3-methyl-5-norbornen-2-one (X) was formed is probably due to rapid proton transfer from norcamphor to the enolate of 5-norbornen-2-one. This transfer, much faster than methylation with methyl iodide, would give a product derived from the more stable enolate of norcamphor.

Preparation of 2-Methoxy-2-norbornene (XI).—2-Methoxy-2-norbornene (XI) was prepared in two steps by a procedure similar to that of Johannissian and Akunian.[13]

In a 50-ml flask under nitrogen was placed 4.4 g (0.09 mol) of norcamphor, 16 ml of methanol, a little *p*-toluenesulfonic acid, and 13 ml of trimethyl orthoformate. After refluxing 1 hr, the solution was cooled, a little potassium *t*-butoxide was added to neutralize the acid, and the solvent was boiled off. The product was distilled at 76–77° (20 mm); the yield of 2,2-dimethoxynorbornane was 5.5 g (88%).

A mixture of 5.3 g of this material and a little *p*-toluenesulfonic acid in a distillation apparatus was heated in an oil bath around 220°. The solution boiled vigorously and material slowly distilled over under nitrogen. The distillate was redistilled through a Nester/Faust Teflon spinning-band annular still, and the enol ether collected at 77–79° (75 mm). The yield of 2-methoxy-2-norbornene was 0.90 g: ir showed a strong C=C band at 1610 cm^{-1}; nmr, vinyl hydrogens at δ 4.62 (d, 0.8 hydrogen), methoxy hydrogens at δ 3.52 (s, 3.1 hydrogens), bridgehead hydrogens at δ 2.75 and 2.90 (b, 1.7 hydrogens), all other hydrogens at δ 1.0–2.0 (m, 6.0 hydrogens). The material was very sensitive to moisture and could be stored only under a dry atmosphere.

Reaction of 2-Methoxy-2-norbornene (XI) with Sodium Hydride and Methyl Iodide.—2-Methoxy-2-norbornene (100 μl) was treated with 0.30 g (0.0074 mol) of a sodium hydride dispersion and 2.0 g (0.014 mol) of methyl iodide in 25 ml of glyme. Analyses of the reaction mixture after work-up showed the chief product to be norcamphor (formed by hydrolysis of the enol ether during work-up). Also present in small amounts were the products from the sodium hydride reduction of norcamphor in their normal proportion, probably owing to some hydrolysis of the enol ether before work-up because of traces of water in the reaction mixture. The yield of 2-methoxynorbornene was not unusually high; therefore the enol ether was not being reduced directly to the saturated ether.

Reaction of 2-Methoxy-2-norbornene (XI) and Norcamphor with Sodium Hydride and Methyl Iodide.—Norcamphor (1.53 g, 0.0139 mol) was treated with sodium hydride and methyl iodide in glyme as before, but in the presence of 0.51 g (0.0041 mol) of 2-methoxy-2-norbornene (XI). Analysis of the reaction mixture after work-up showed that the ratio of products formed was identical with that obtained in the absence of 2-methoxy-2-norbornene. Also present was some norcamphor, formed by hydrolysis of the enol ether during work-up. Since the yield of 2-methoxynorbornene was the same as in the absence of 2-methoxy-2-norbornene, the latter was not reduced by sodium hydride.

Reaction of Cyclopentanone with Sodium Hydride and Methyl Iodide.—Cyclopentanone (1.68 g, 0.02 mol) was treated with 4.1 g (0.10 mol) of a sodium hydride dispersion and 18 g (0.13 mol) of methyl iodide in 50 ml of glyme under the usual conditions. After work-up the products were analyzed by vpc. The only major product was 2,2,5,5-tetramethylcyclopentanone,[14] formed in 93% yield. Several small peaks indicated trace amounts of other products—one of these had a retention time identical with that of methoxycyclopentane,[15] and its size corresponded to a yield of 0.5% of this compound.

Registry No.—Sodium hydride, 7646-69-7; I, 17190-61-3; II, 10395-55-8; III (*exo*-OMe), 17206-77-8; III (*endo*-OMe), 17190-62-4; IV, 3915-75-1; V, 17190-85-1; VI, 13211-15-9; VII, 694-98-4; VIIIa, 17190-92-0; VIIIb, 17190-87-3; IX, 17190-88-4; X, 17190-89-5; XI, 17190-90-8; methyl iodide, 74-88-4.

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[13] A. Johannissian and E. Akunian, *Bull. Univ. État RSS Armenie*, **5**, 235, 245 (1930); *Chem. Abstr.*, **25**, 921 (1931).

[14] J. M. Conia, *Ann. Chim.* (Paris), **8**, 709 (1953).

[15] A. I. Vogel, *J. Chem. Soc.*, 1809 (1948).

Addition Reactions of Benzonorbornadiene[1]

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Only products derived from initial *exo* attack by the reagent have been detected in the following reactions of benzonorbornadiene: the polar addition of *p*-toluenesulfenyl chloride, the radical additions of bromotrichloromethane and carbon tetrachloride, the catalytic additions of trichlorosilane, deuteriotrichlorosilane, and deuterium gas, and the reactions with dideuteriodiimide, *p*-tosyl azide, and picryl azide. From the radical addition of trichlorosilane and the chloroplatinic acid catalyzed additions of methyldichlorosilane and trimethylsilane, small amounts of the products of *endo* attack were obtained along with the predominant product of *exo* attack. The extent of *endo* addition is significantly greater than that observed in comparable addition reactions of norbornene, and considerably less than that observed with norbornadiene. From these results it is concluded that coordination control plays a much less important role in the chemistry of benzonorbornadiene than it does in the chemistry of norbornadiene. The value of pmr spectroscopy in elucidating the structures of substituted benzonorbornenes is discussed and illustrated.

A vast literature has accumulated which conclusively establishes that addition reactions of norbornene (I) proceed predominantly by way of initial attack from the *exo* side, regardless of the mechanistic category into which the reaction falls.[4] Only two accounts have appeared which report high yields of products derived from *endo* attack.[5] The overwhelming preference for *exo* attack is a consequence of the greater accessibility

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[1] This work is taken from the Ph.D. Thesis of R. A. Koster, University of Michigan, 1968.

[2] Alfred P. Sloan Foundation Fellow, 1966–1968.

[3] Minnesota Mining and Manufacturing Fellow, 1965–1966; Petroleum Research Fund Fellow, 1966; NASA, Trainee, 1967.

[4] See footnotes 4, 5, and 6 of M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 4293 (1965), for an extensive bibliography of representative addition reactions of I.

[5] (a) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *ibid.*, **87**, 2596 (1965); (b) A. C. Oehlschlager and L. H. Zalkow, *Chem. Commun.*, 5 (1966).