

## ORGANOMETALLIC CHEMISTRY

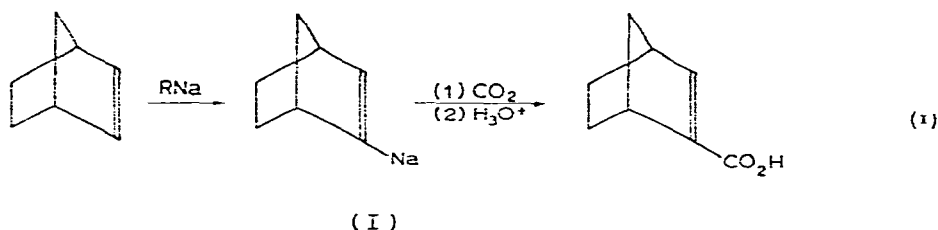
## X\*. THE REACTION OF 2-SODIONORBORNENE WITH BENZALDEHYDE AND BENZOPHENONE\*\*

R. A. FINNEGAN, W. H. MUELLER\*\*\* AND R. S. MCNEES†

*Department of Medicinal Chemistry, School of Pharmacy, State University of New York at Buffalo, Buffalo, N.Y. 14214 (U.S.A.)*

(Received March 19th, 1965)

A previous paper in this series<sup>2</sup> has described the preparation of norbornene-2-carboxylic acid in reasonably good yield by the sequence shown in eqn. (1). The metalation of norbornene with butyl- or amylsodium provides 2-sodionorbornene (I) which was characterized by the formation and proof of structure of its carboxylation



product. It seemed of interest to exploit this relatively facile formation of (I) for the preparation of other 2-substituted norbornene derivatives<sup>§§</sup>. In particular, we viewed the synthesis of norbornenyl carbinols (II) as suitable objectives since their subsequent behavior in acidic media might well reward our attention.

In an attempt, therefore, to prepare (II) (R = phenyl, R' = hydrogen), a suspension in pentane of (I) was added to an excess of benzaldehyde and the product, after hydrolysis, was divided into neutral and acidic fractions. The acidic product which constituted only a minor proportion of the total product (see EXPERIMENTAL PART), was readily identified as benzoic acid by comparison with an authentic sample. The more volatile part of the neutral fraction was separated by distillation and shown by infrared and gas-chromatographic comparisons to be mainly recovered benzalde-

\* For Part IX, see ref. 1.

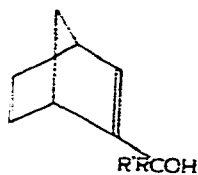
\*\* This research was supported by grants from the Research Corporation and from the Petroleum Research Fund of the American Chemical Society.

\*\*\* Present address: Esso Research and Engineering Co., Linden, N.J.

† Fredrick Gardner Cottrell Fellow, 1960-1961, 1962-1963; National Science Foundation Cooperative Fellow, 1961-1962; Petroleum Research Fund Fellow, 1963. These fellowships were held in the Department of Chemistry, Ohio State University. Present address: Chemical Abstracts Service, Columbus, Ohio.

§§ The metalation of norbornene with butylsodium has been advantageously employed for the production of 2,3-dideuteronorbornene<sup>4</sup>.

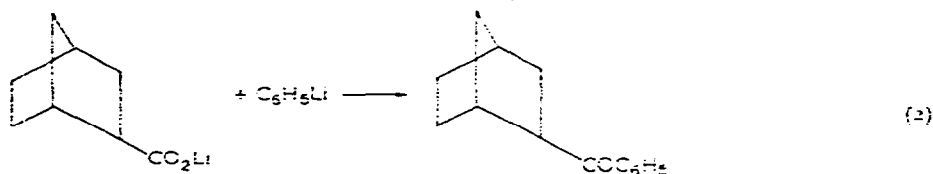
hyde accompanied by a smaller quantity of benzyl alcohol. The residue remaining after this distillation was found to consist of two major components by gas-chromatographic analysis. Although a clean separation of these components could not be achieved by fractional distillation, fractions enriched in either constituent were



(II)

obtained. The higher boiling and more abundant compound was correlated with a band in the infrared spectrum of the mixture at  $1724\text{ cm}^{-1}$ . This carbonyl absorption band suggested the presence of a benzoate ester, and taken with the presence, already mentioned, of benzoic acid and benzyl alcohol, pointed to the identity of this product as benzyl benzoate. This identification was verified by gas-chromatographic and infrared comparisons with an authentic specimen.

A sample of the lower-boiling component was isolated from a gas-chromatography column. The infrared, ultraviolet, and NMR spectra, as well as micro-analytical data obtained for this compound were consistent with its formulation as norbornyl phenyl ketone. Finally, the structure of this product, including its stereochemistry, was determined by comparison of its gas-chromatographic and infrared properties with those of a sample of *endo*-2-norbornyl phenyl ketone (III) prepared as shown in eqn. (2).

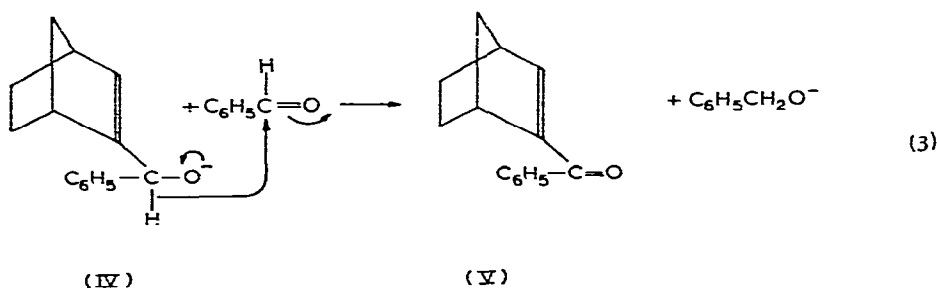


(III)

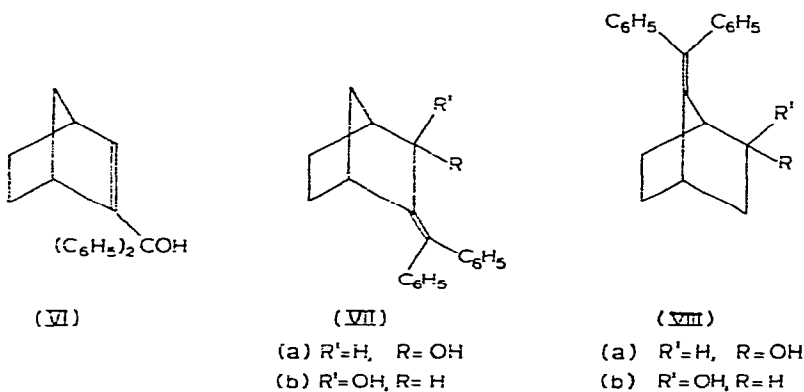
The results so far described indicate clearly that although (I) did add in reasonably good yield to benzaldehyde, subsequent side reactions prevented the obtention of the simple carbinol (II) ( $R = \text{phenyl}$ ,  $R' = \text{hydrogen}$ ). Generation of benzyl benzoate from benzaldehyde (Tishchenko reaction) is very likely initiated by hydride transfer from the first formed adduct (IV) to a second molecule of benzaldehyde [eqn. (3)]. The benzyloxy ion may then serve in normal fashion to catalyze the Tishchenko reaction. It is probable that the ketone (III) arose during the hydrolytic work-up\* by rearrangement of the carbinol (II) ( $R = \text{phenyl}$ ,  $R' = \text{hydrogen}$ ) although an alternate consists in the production of (III) by the 1,4-addition of hydride to the unsaturated ketone (V). In either event, the driving force for the reaction would

\* Similarly, hydrolysis during work-up of a small portion of the benzyl benzoate provides the simplest explanation for the presence of the benzoic acid in the product.

arise from the relief of strain accompanying the removal of the endocyclic double bond. Suitable hydride donors include, not only (IV) and benzyloxide, but also amyl-sodium and its derivative adducts.



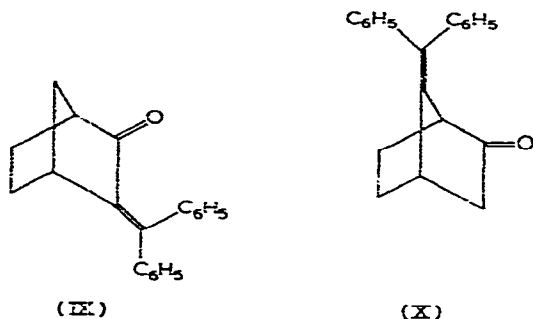
With a view to suppressing side reactions which stem from the presence of an aldehyde in this strongly alkaline medium, benzophenone was next selected for reaction with (I). In this case also, a complex reaction mixture was obtained from which the carbinol (II) ( $R = R' = \text{phenyl}$ ) [see (VI)] could not be isolated. The major product, present in about 40% yield\*, was eluted from an alumina column in an isohexane-ether (24:1) mixture and could be recrystallized from ether-hexane mixtures. The infrared spectrum of this material showed strong hydroxyl absorption and the microanalytical results were in accord with those expected for the adduct (VI). Structure (VI) was discarded, however, on the basis of NMR measurements which showed the absence of olefinic protons, and the ultraviolet maximum at  $251 \text{ m}\mu$  whose intensity ( $\epsilon = 10,500$ ) was much greater than expected for a simple alkyl-benzene chromophore. Isomeric structures (VII), resulting from allylic rearrangement,



and structures (VIII), resulting from a Wagner-Meerwein shift in addition to allylic rearrangement, were therefore considered likely; and a decision in favor of structure (VII) was based on the following evidence. Oxidation of the carbinol with manganese dioxide at room temperature provided in good yield a yellow, crystalline ketone which must be accommodated either by structure (IX) or by (X). Oxidation with manganese

\* This figure was calculated on the assumption that a 60% yield of (I) was obtained from norbornene. Based on the amount of benzophenone unaccounted for, the yield was 24%.

dioxide has previously been taken as an indication of the presence of an allylic or benzylic alcohol function<sup>4</sup>; however, the list of saturated alcohols oxidized by this reagent is growing<sup>5</sup>, thus diminishing its effectiveness as a diagnostic tool. The ketone was judged to be conjugated with the diphenylethylene unit on the basis of its intense ultraviolet maxima at 230 and 305  $m\mu$ . Although a number of  $\alpha,\beta$ -unsaturated



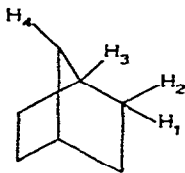
ketones display intensified ultraviolet bands<sup>6</sup>, compound (X) would not appear to fall into this class since 7-ketonorbornene, whose relevant orbitals are situated analogously, does not exhibit this enhancement of absorption<sup>7</sup>. The carbonyl absorption in the infrared at 1718  $cm^{-1}$  is also in much better agreement with that expected for the conjugated ketone (IX) than for the simple norcamphor (X)\*. Finally, the ketone could not be induced to exchange hydrogen for deuterium when refluxed in deuteromethanol containing sodium methoxide, a feature clearly in better accord with structure (IX).

With the assignment of structure (VII) to the product carbinol, it remained to determine the stereochemistry of the hydroxyl group. It should be pointed out that the carbinol (VII) obtained from the reaction mixture was shown by gas-chromatographic analysis to consist of two components in the ratio 4:1. Repeated recrystallization did not significantly change this composition ratio although samples with melting points varying over the range 60–71° were obtained. That we were dealing with a pair of epimeric alcohols was evident from the fact that oxidation gave but a single ketone (IX) in nearly 90% yield. The NMR spectrum of the alcohol provided evidence that the major epimer was the *exo* compound (VIIb). A signal in this spectrum at  $\tau$  5.89 can be assigned to the proton attached to the hydroxyl bearing carbon ( $C_2$ ) and the extent to which it is coupled to the neighboring bridgehead proton at  $C_1$ , as well as to the *anti*-bridge proton at  $C_7$ , is expected to be a function of its geometry. These expectations<sup>8</sup> are summarized in structure (XI). The pertinent signal (5.89  $\tau$ ) in the spectrum of (VII) appeared as a slightly broadened singlet showing (in some recordings) just the barest suggestion of splitting ( $\sim 1$  cps). This identifies the proton as  $H_1$  in (XI) and the geometry of the carbinol as in (VIIb). This assignment is in agreement with the *a priori* assumption that (VII) is formed from the allylic isomer (VI) by way of an intermediate carbonium ion<sup>10, \*\*</sup> which is solvolyzed from the *exo* face of the molecule<sup>11</sup>.

\* Norcamphor is reported<sup>8</sup> to have  $\nu_{max}$  1751  $cm^{-1}$  in  $CCl_4$ .

\*\* The apparent absence of skeletally rearranged products [*i.e.*, (VIII)] suggests that participation of the 1,6-bond adds little to the already highly resonance-stabilized diphenylvinylmethylcarbonium ion.

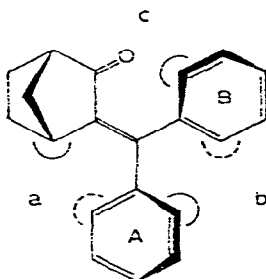
Reduction of the ketone (IX) with sodium borohydride regenerated the carbinols (VII), m.p. 113–134°, which was shown by gas chromatography to be a 9:1 mixture of components having the same retention times as the components in the original carbinol mixture. The major isomer from the reduction corresponded to the



(XI)

$$J_{1,2} = J_{2,4} = 0 \text{ cps. } J_{1,4} = 1-2 \text{ cps. } J_{2,3} = \sim 4 \text{ cps.}$$

major constituent of the original reaction mixture, and, if the arguments for the stereochemistry of the latter [*i.e.*, (VIIb)] are accepted, this reduction represents an apparent exception to the general rule of *exo* attack<sup>11</sup> on simple norbornane derivatives. Examination of a Dreiding stereomodel of ketone (IX), however, provides an adequate explanation for this course of reduction. It is clear that the phenyl groups can not maintain a coplanar relationship with the enone moiety because of the pronounced non-bonded repulsions shown in (XII) at positions "a", "b", and "c". The *ortho*-hydrogen at "c" exercises the most immediate influence at the site of reduction,



(XII)

⌋ = proton below plane

⌋ = proton above plane

and rotation of phenyl group B can take place such that the proton at "c" occupies space *exo* or *endo* with respect to the carbonyl group. On the same grounds which validate the general rule of *exo* approach<sup>11</sup>, it may be argued that the favored rotamer of (IX) is that shown in structure (XII) in which the relevant proton at "c" occupies an *exo* position. The rotation of phenyl group B in this direction out of the plane of the olefinic double bond would be accompanied by rotation of phenyl group A in the corresponding direction as illustrated in (XII). This argument in favor of the conformation (XII) is strengthened by noting that rotation of the phenyl rings in the

opposite direction would bring the *ortho*-hydrogen at position "a" even closer to the bridgehead proton than it is in the coplanar conformation. The overall effect, then, is a shielding of the *exo* side of the carbonyl group by the proximate phenyl group thus forcing the reduction to occur from the *endo* side with predominate production of (VIIb). Recalling our earlier postulate that the carbinol (VII) was formed from (VI) via a carbonium ion, we may note that subtle differences in the two substrates (the ketone and the carbonium ion) such as the differing extent of non-bonded interaction at position "c" (less in the ion) and the possible degree of participation of the 1,6-bond\*, as well as the difference in bulk of the attacking reagents, must operate to produce the differing stereochemical results in the two reactions. Obviously, further speculation on these points is best deferred until more experimental data becomes available.

Other products isolated from the original reaction mixture were identified as benzopinacol and benzhydrol in 6 and 4% yield, respectively, based on the quantity of benzophenone used. Although alternate explanations are available, the simplest explanation for the formation of these products may well involve the probable presence in the reaction mixture of unreacted amylsodium and sodium metal. In addition, the presence of a trace (less than 1%) of the ketone (IX), most likely formed by oxidation during work-up, was inferred from gas-chromatographic and infrared analysis of certain fractions eluted from the alumina column.

In conclusion, it appears to us that the ability of sodium alkyls to metalate relatively inert substrates may be more advantageously exploited by including the expedient of metal-metal exchange reactions. For example, an olefin could be metalated by treatment with an alkylsodium reagent and the product converted to the corresponding lithium or magnesium derivative by reaction with the appropriate metal halide. In this way the more nucleophilic<sup>2,12</sup> (and more soluble) but less basic organometal compound is made available for additional transformations. Although this possibility was pointed out twenty-five years ago by Gilman and Swiss<sup>13</sup>, it seems not to have attracted widespread attention<sup>14,15</sup>. We hope to examine the application of this procedure, not only to (I), but also to other alkenylsodium reagents.

#### EXPERIMENTAL PART

Infrared spectra were determined on Perkin-Elmer Model 137, Model 237, or Baird Model B spectrometers, ultraviolet measurements were made with a Perkin-Elmer Model 202 instrument, and nuclear magnetic resonance spectra were recorded on a Varian Associates A60 spectrometer using tetramethylsilane as an internal standard. The melting points (Fisher-Johns block) and boiling points are uncorrected. Micro-analyses were performed by Dr. A. BERNHARDT, Mulheim, Germany. Gas chromatography was carried out using a Wilkens Aerograph instrument, with helium as carrier gas and equipped with a 5 ft  $\times$   $\frac{1}{4}$  in. column packed with 20% SF-96 silicone on firebrick.

#### *Reaction of 2-sodionorbornene (I) with benzaldehyde*

A suspension in 250 ml pentane of (I), preformed from a mixture of 0.094 mole norbornene and 0.09 mole amylsodium which had been stored at room temperature

\* See footnote\*\* on p. 264.

for six weeks, was added to a solution in pentane of 41 g (0.39 mole) benzaldehyde. This addition was carried out over fifteen minutes while the contents of the flask were stirred, maintained in an atmosphere of nitrogen, and cooled in an ice bath. The reaction mixture was maintained for an additional half hour at ice bath temperature, then three hours at room temperature before hydrolysis was effected with saturated aqueous ammonium chloride solution. The layers were separated and the aqueous layer, after being extracted with ether, was made strongly acidic with hydrochloric acid. Extraction of this acid solution with ether provided, after drying (Drierite) and evaporation of the solvent, 1.35 g white solid, m.p. 120–122°, alone or admixed with an authentic sample of benzoic acid. The infrared spectra (KBr) of the two samples were indistinguishable. The organic layer was dried over Drierite and the solvent was evaporated to leave 42 g reddish brown oil. Distillation of the oil was commenced at 40–50° (0.05–0.1 mm) and continued while the temperature of the pot was slowly raised to 100°. The distillate (9.9 g) was mainly benzaldehyde (infrared and gas-chromatographic comparison) but contained 10–15% benzyl alcohol (gas-chromatographic comparison). A portion of the residue was distilled (bulb to bulb) at 100° (air bath) (0.05 mm) providing an oil with  $\nu_{max}$  (film) 1724 and 1684  $\text{cm}^{-1}$  and which gave a positive test with 2,4-dinitrophenylhydrazine reagent. Gas-chromatographic analysis showed the presence of two major constituents. The remainder of the residue (28.9 g) was fractionated through a 60 × 0.7 cm spiral wire column. Seven fractions were collected (total, 16.4 g) at narrow intervals over the temperature range 108.5–117° (0.18–0.2 mm). Infrared and gas-chromatographic analyses indicated that the higher boiling component (90% of the last two fraction, b.p. 116–117°) gave rise to the band at 1684  $\text{cm}^{-1}$ . The higher boiling constituent was identified as benzyl benzoate by infrared and gas-chromatographic comparisons with an authentic sample, and was calculated to represent approximately 78% of the total distillate. Since a second passage through the fractionating column did not increase the purity of the lower boiling constituent, a sample was collected directly from a gas-chromatography column and redistilled for analysis, b.p. 80° at 0.05 mm (bath temperature) (Lit.<sup>16</sup> b.p. 155–8° at 10 mm),  $\lambda_{max}$  (95% ethanol) 242, 278, 319  $\mu$  ( $\epsilon$ , 14,000, 1450, 182). (Found: C, 83.64; H, 7.71.  $\text{C}_{14}\text{H}_{16}\text{O}$  calcd.: C, 83.96; H, 8.05%.)

An authentic specimen of *endo*-2-norbornyl phenyl ketone (III) was prepared as follows. To 1.25 ml (2.5 mmole) phenyllithium solution (2 M) in benzene–ether (75:25) (Foote Mineral Co.) was added slowly with cooling 4 ml dry ether containing 140 mg (1 mmole) *endo*-norbornane-2-carboxylic acid<sup>2</sup>. The reaction mixture was then heated at reflux temperature for 2 h before it was hydrolyzed with saturated aqueous ammonium chloride solution. The aqueous layer was extracted with ether and the combined organic layers then washed with 2 N sodium bicarbonate solution, water, then dried over magnesium sulfate. The residue remaining after removal of the solvent was analyzed by gas chromatography and, although several minor constituents were evident, the major product from this reaction had a retention time and infrared spectrum indistinguishable from those of the product derived from (I).

#### *Reaction of 2-sodionorbornene (I) with benzophenone*

A solution in ether (300 ml) containing 17.5 g (0.096 mole) benzophenone was added to a reaction mixture which had been prepared originally from a suspension in pentane of amylsodium (0.096 mole) and 9.6 g (0.102 mole) norbornene. (The nor-

bornene metallation mixture had been in storage for approximately six months.) After the addition was completed (45 min), the mixture was heated to reflux temperature and stirring was continued for 4.5 h. An inert atmosphere was maintained within the flask all during the reaction. Hydrolysis was then effected with saturated aqueous ammonium chloride solution and the layers separated. The aqueous layer was extracted with ether and the combined organic layers were dried over Drierite. Removal of the solvent left an oily residue which, when diluted with Skelly-Solve B and refrigerated, deposited in two crops a total of 0.82 g crystalline solid. This material was recrystallized from an ether-Skelly-Solve B mixture and had m.p. 186–187° alone or admixed with an authentic sample of benzopinacol. An infrared comparison confirmed this identification. The solvent was removed from the mother liquors leaving 16.8 g residue. Attempts to obtain a pure product by crystallization or distillation of portions of this residue were unsuccessful. Accordingly, the remainder of the residue (14 g) was chromatographed on alumina (550 g, Merck, acid washed). The column was made up in isohexane and the materials were eluted with isohexane and mixtures of isohexane containing increasing amounts of ether. Fractions of 500 ml were collected and the products obtained are described below in the order of their elution from the column.

(a) *The initial fractions* provided a series of oils which contained over a dozen constituents as judged by gas- and thin-layer-chromatographic analysis. No pure materials were obtained.

(b) *Benzopinacol, the ketone (IX), and the carbinols (VII)*. Fractions number 53–60 were eluted with isohexane containing 4% ether and, when combined, provided 201 mg yellow semi-solid. No pure material could be obtained by recrystallization and rechromatography of this material; however, gas chromatography (234°, 120 ml/min) showed the presence of benzopinacol (9%), the carbinols (VII) (72%), and a third compound having a retention time identical with that of the ketone (IX) (see below). In addition, the mixture showed a weak carbonyl band in the infrared at 1718 cm<sup>-1</sup>. Elution was continued with the same solvent mixture and from fractions 61–64 was obtained 520 mg tan semi-solid. Crystallization and recrystallization from ether-hexane mixtures afforded 110 mg benzopinacol, m.p. 182–186°, alone or admixed with an authentic specimen. From the mother liquors, 410 mg yellow oil was obtained which was shown to consist of 17% benzopinacol, 72% of the carbinols (VII), and 11% of the ketone (IX) by gas-chromatographic analysis. Again, a weak carbonyl band at 1718 cm<sup>-1</sup> was present in the infrared spectrum of the oil.

(c) *The carbinols (VII)*. Fractions number 65–93 were eluted with the same solvent mixture and, having nearly identical infrared spectra, were combined to give 5.8 g yellow oil. This oil crystallized from an ether-hexane mixture and after several recrystallizations, 3.9 g white crystals were obtained, m.p. 59–71°;  $\nu_{max}$  (KBr) 3584, 3425, 2959, 2865, 1597, 1572, 1490, 1443, 1335, 1290, 1096, 1073, 1056, 1010, 780, 754, 737, and 701 cm<sup>-1</sup>;  $\lambda_{max}$  (95% ethanol) 251 ( $\epsilon$  10,500). Repeated recrystallization did little to improve the melting point. Microanalysis were performed on two different samples. (Found: C, 86.99, 87.12; H, 7.39, 7.12. C<sub>20</sub>H<sub>20</sub>O calcd.: C, 86.92; H, 7.29%.)

Gas-chromatographic analysis (235°, 116 ml/min) of the various crystalline crops as well as the mother liquors indicated two components to be present in the approximate ratio 4:1. The retention times for the major and minor constituents were 13 and 8.25 min, respectively.



(d) *Benzhydrol*. Fractions 94–99 (isohexane–4% ether) provided 800 mg yellow oil which was shown gas-chromatographically to contain 42% of the mixture (4:1) of carbinols (VII), 56% benzhydrol, and small amounts of unidentified compounds. Fraction 100–106, eluted with an isohexane–6% ether mixture, yielded 494 mg yellow semi-solid which, after several recrystallizations from acetone–hexane mixtures, afforded pure benzhydrol, m.p. 66–67°. The infrared spectrum of this material was indistinguishable from that of an authentic sample and a mixture melting point was undepressed.

*Oxidation of the carbinols (VII). 3-Benzhydrylidenebornan-2-ol (IX)*

A solution of (VII), (100 mg) in petroleum ether, b.p. 30–60° (15 ml) was stirred for 40 h at room temperature in the presence of 1.1 g manganese dioxide (Beacon Chemical Industries, activated). The reaction mixture was filtered and the solid washed several times with hot acetone. The combined filtrates were evaporated to provide 89 mg yellow crystals, m.p. 136–139°. A single recrystallization from an acetone–hexane mixture afforded a sample (83 mg) with m.p. 139–140°;  $\nu_{max}$  (KBr) 2959 (doublet), 2861, 1718, 1603, 1493, 1443, 1211, 1094, 917, 775, 743, 704, 696  $\text{cm}^{-1}$ ;  $\lambda_{max}$  (95% ethanol) 230, 305  $\text{m}\mu$  ( $\epsilon$  8500, 8200). Gas-chromatographic analysis showed only one peak. (Found: C, 87.41; H, 6.54; O, 5.95; mol. wt., 262.  $\text{C}_{20}\text{H}_{18}\text{O}$  calcd.: C, 87.56; H, 6.61; O, 5.83%; mol. wt., 274.)

*Attempted exchange experiment with (IX)*

A solution of (IX) (60 mg) in deuteromethanol (2 ml) containing a catalytic amount of sodium methoxide was heated at reflux temperature for thirty minutes. After the solution had stood an additional hour at room temperature, the bulk of the solvent was removed with a nitrogen jet. The residue was treated with 2 ml deuterium oxide and extracted with ether. Removal of the ether (after drying over magnesium sulfate) gave 58 mg of recovered starting material. The melting point, infrared spectrum, and NMR spectrum of the recovered material was unchanged.

*Reduction of ketone (IX)*

A solution of (IX) (60 mg) in 2 ml tetrahydrofuran was added to 49 mg sodium borohydride in 2 ml tetrahydrofuran. The mixture was heated at reflux for two hours but the yellow color of the ketone did not disappear. Upon addition of 2 ml methanol, the mixture became homogeneous and the yellow color was quickly discharged. The mixture was allowed to stand at room temperature for ten hours before it was hydrolyzed with ice-cold 2 *N* sulfuric acid and extracted with ether. The ether layer was washed with 2 *N* sodium bicarbonate solution and water, dried over magnesium sulfate, and evaporated to give 50 mg white crystals, m.p. 113–134°;  $\nu_{max}$  (KBr) 3584, 3448 (shoulder), 2697 (doublet), 2874, 1597, 1572, 1493, 1443, 1309 (doublet), 1289, 1105, 1063 (doublet), 1029, 761, 746, and 699 (doublet)  $\text{cm}^{-1}$ ;  $\lambda_{max}$  (95% ethanol) 252  $\text{m}\mu$  ( $\epsilon$  10,600).

Several recrystallizations from acetone–hexane mixtures did not improve the melting range. Gas-chromatographic analysis showed the presence of two compounds in the ratio 9:1 having the same retention times as the two components (ratio 4:1) present in the original mixture of carbinols, (VII).

## ACKNOWLEDGEMENT

It is a pleasure to acknowledge helpful discussions with Drs. D. KNUTSON and A. J. SOLO.

## SUMMARY

When 2-sodionorbornene, prepared by the metalation of norbornene with amylsodium, reacts with benzaldehyde, the products formed are benzyl alcohol, benzoic acid, benzyl benzoate, and *endo*-2-norbornyl phenyl ketone. None of the anticipated 2-norbornenyl phenyl carbinol was found in the product mixture. Benzophenone reacts with 2-sodionorbornene to produce a mixture of *endo*- and *exo*-2-hydroxy-3-benzhydrylidenenorbornane in which the *exo* isomer is believed to predominate. Accompanying this mixture of carbinols is a trace of the corresponding ketone, 3-benzhydrylidenenorcamphor, as well as benzhydrol and benzopinacol. The *exo* carbinol is produced when the norcamphor derivative is reduced with sodium borohydride and a conformational argument is advanced to account for this result.

## REFERENCES

- 1 R. A. FINNEGAN, *J. Org. Chem.*, **30** (1965) 1333.
  - 2 R. A. FINNEGAN AND R. S. MCNEES, *J. Org. Chem.*, **29** (1964) 3234; *Chem. Ind. (London)*, (1961) 1450.
  - 3 J. E. FRANZ, C. OSUCH AND M. W. DIETRICH, *J. Org. Chem.*, **29** (1964) 2922.
  - 4 R. M. EVANS, *Quart. Rev.*, **13** (1959) 61.
  - 5 I. T. HARRISON, *Proc. Chem. Soc.*, (1964) 110.
  - 6 R. C. COOKSON AND S. MACKENZIE, *Proc. Chem. Soc.*, (1961) 423.
  - 7 P. G. GASSMAN AND P. G. PAPE, *J. Org. Chem.*, **29** (1964) 160.
  - 8 R. ZBINDEN AND H. K. HALL, JR., *J. Am. Chem. Soc.*, **82** (1960) 1215.
  - 9 P. LASZLO AND P. VON R. SCHLEYER, *J. Am. Chem. Soc.*, **86** (1964) 1171, and references therein.
  - 10 P. B. D. DE LA MARE, in P. DE MAYO, *Molecular Rearrangements*, Interscience, New York, 1963, p. 70.
  - 11 E. L. ELIEL, *Stereochemistry of Carbon Compounds*, McGraw-Hill, New York, 1962, pp. 303-304.
  - 12 W. I. O'SULLIVAN, F. W. SWAMMER, W. J. HUMPHLETT AND C. R. HAUSER, *J. Org. Chem.*, **26** (1961) 2306.
  - 13 H. GILMAN AND J. SWISS, *J. Am. Chem. Soc.*, **62** (1940) 1847.
  - 14 J. F. NOBIS, L. F. MOORMEIER AND R. E. ROBINSON, in *Metal-Organic Compounds, Advan. Chem. Ser.*, **23** (1959) 63.
  - 15 O. F. BEUMEL, JR., U.S. Pat. 3,155,736 (Nov. 3, 1964); *Chem. Abstr.*, **62** (1965) 1687h.
  - 16 N. K. KOCHETKOV AND A. YA. KHORLIN, *Zh. Obshch. Khim.*, **27** (1957) 3182; *J. Gen. Chem. USSR*, **27** (1957) 3217; *Chem. Abstr.*, **52** (1958) 8985b.
- J. Organometal. Chem.*, **4** (1965) 261-270