[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

Proof of the Configuration of Bornyl Chloride; Observations on the Non-reactivity of Bornyl Dichloride

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Direct evidence on the configuration of bornyl chloride has been obtained by derivation from (*endo, endo*)-2,6-dichlorocamphane. The remarkable lack of reactivity of the latter in solvolysis and elimination reactions is discussed.

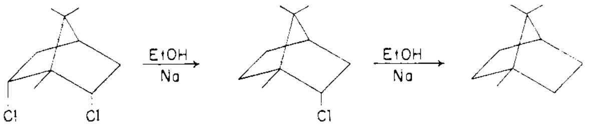
Introduction.—Many current concepts of reaction mechanism derive experimental foundation from studies of the stereochemistry of reactions in bicyclic systems[1]; in particular, cases involving bornyl and isobornyl tautomerides. Our knowledge of the absolute configuration of bornyl (*endo*) and isobornyl (*exo*) alcohols and esters, has consequently been the subject of considerable discussion.[2] The accepted assignments depend strongly on synthetic demonstrations by Asahina and co-workers[3] that a non-lactone forming hydroxyacid is intermediate in the stepwise reduction of isoketopinic acid to borneol. The observations of Toivonen[2b] have afforded strong confirmation of these assignments.

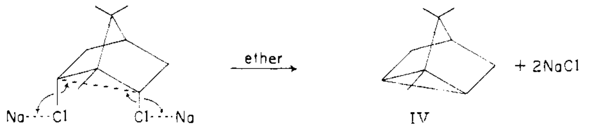
It has been pointed out[4] that our knowledge of the configurations of the corresponding halides is largely based on analogy; camphene reacts with aqueous sulfuric acid to give isoborneol, with sulfuric in carboxylic acid solution to give isobornyl esters and with hydrogen chloride to give isobornyl chloride. In each case the more rapidly formed isomer is assigned the isobornyl configuration. The similarity in solvolytic behavior is another factor that relates, by analogy, the configurations of the halides to that of isobornyl esters obtained from camphene.

It seemed highly desirable to have a direct determination of the halide configurations that did not depend on analogy. For this purpose the structure of the only known 2,6-dichlorocamphane (bornyl dichloride) isomer (I) recently established[5] as *endo–endo*, serves admirably. The reduction of one of the halogen atoms on the skeleton of this compound, under conditions which do not promote the equilibrium between bornyl and isobornyl chloride, should give one product, exclusively, depending on which of these tautomerides possesses the *endo* configuration.

Results and Discussion

The Reduction of Bornyl Dichloride.—The establishment of equilibrium between bornyl and isobornyl halides has been shown to be relatively slow and promoted by electrophilic reagents.[6] We, therefore, chose to explore only basic conditions of reduction. It is well known[7] that sodium, in excess of stoichiometric amounts, converts 2,6-dichlorocamphane in ether (or mixed solvents containing preponderantly ether) entirely to tricyclene in a rapid, near quantitative reaction. Obviously, bornyl chloride (II) is not an intermediate in this reaction since we have observed that under the same conditions it is reduced to camphane (III), unaccompanied by significant tricyclene formation. However, the use of a stoichiometric amount of sodium (one atom per mole of bornyl dichloride), highly diluted in the form of an *ca.* 2% amalgam, and suspended in a refluxing (basic) ethanol solution of the dihalide *yielded only bornyl chloride* in 50 hours. No tricyclene (IV) or camphane (III) was obtained and more than half of the charged dihalide had failed to react in this period. When the sodium was used in undiluted form camphane was the only recoverable product. We concluded from these observations that reduction in alcoholic solvent is a stepwise reaction of the carbon–halogen bond proceeding in turn from bornyl dichloride to bornyl chloride to camphane by some unspecified path favored by conditions of dilution and donor solvents. On the other hand, in ether (or other inert solvents) the process appears to be concerted in nature, wherein a single act of reduction involves both of the neighboring halogen bearing centers and ultimately gives tricyclene.





The identity of the bornyl chloride product of the reduction by sodium amalgam in alcohol was established by infrared and X-ray diffraction spectrum comparison with an authentic specimen of II. Furthermore, this product exhibited the usual chemical properties of II, (among others) being readily reduced to camphane whose infrared spectrum was identical with that of an authentic sample of III. This result would appear to indicate beyond question that bornyl chloride possesses the *endo* configuration II. It is possible also to assign the same configuration to bornyl bromide reasoning from the fact that 2,6-dibromocamphane,

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[1] (a) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, THIS JOURNAL, **74**, 113 (1952); (b) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, *ibid.*, **74**, 1127 (1952), and other references discussed in these articles.

[2] (a) See J. L. Simonsen, "The Terpenes," Cambridge Univ. Press, London, 1949, Second Edition, Vol. II, pp. 354–357, and numerous references cited in this discussion; (b) see particularly p. 362.

[3] A. Y. Asahina and T. Sano, *Ber.*, **69**, 343 (1936); B. Y. Asahina and M. Ishidate, THIS JOURNAL, **68**, 555 (1935).

[4] P. D. Bartlett and I. Pockel, THIS JOURNAL, **60**, 1585 (1938), and reference 2, particularly pages 346-348.

[5] H. Kwart, *ibid.*, **75**, 5942 (1953).

[6] H. Meerwein and K. van Emster, *Ber.*, **53**, 1821 (1920); **55**, 2506 (1922).

[7] See for example, O. Aschan, *ibid.*, **61**, 42 (1928).

formed from pinene in a manner analogous[8] to the formation of I, shows a very similar pattern of reactivity.

Observations on other Reactions of Bornyl Dichloride.—While seeking a method of reduction of bornyl dichloride unifunctionally under basic conditions we studied the effects of Grignard reagent in the presence of cobalt and iron salts as discussed by Kharasch and co-workers.[9] These authors have shown that bornyl chloride undergoes ready reduction by these means, principally to camphane and camphene. When we applied this procedure to the dichloride, reaction took place very smoothly and afforded among other products a readily separable fraction, VI, having physical properties suggestive of bornyl chloride. On infrared comparison this fraction showed every one of the bands, plus a few additional bands in excess of the 32 identified for pure bornyl chloride (see spectral data table). Furthermore, when this fraction was reduced with sodium and alcohol the product was identical with authentic camphane, but for four weak additional bands in the infrared (table) and a somewhat depressed melting point. Except for a persistent small impurity (probably a dichloride as indicated by the high halogen analysis) it would appear that the reduction of (I) with Grignard reagent in the presence of cobaltous chloride has proceeded to bornyl chloride. Other products were isolated in small amounts in this reaction, principally a high melting (245°) substance (VII) and a considerably lower melting one (VIII) having an almost identical analysis. The analysis and molecular weight determination, furthermore, is quite consistent with the structure of a dimerization product. We would suggest an unsymmetrical (*exo–endo*) dimeric structure for VII and a symmetrical (*exo–exo*) structure for VIII on the basis of the rule that symmetrical structures have the higher melting point and lower solubility in an isomeric pair.[10]

Another possible mode of degrading bornyl dichloride to bornyl chloride involved mono-dehydrochlorination, followed by catalytic reduction of the double bond. In these laboratories[11] it has been shown that elimination of hydrogen halide from the bicycloheptane (2,2,1) ring (when possible) by means of very strong base in non-solvolytic media occurs readily and without rearrangement. In the present investigation we have confirmed that, although considerable amounts of camphene (representing rearrangement) are formed on reaction of bornyl chloride with most of the usual bases employed for elimination (sodium hydroxide, quinoline, pyridine bases), bornylene is readily obtained with the use of potassium butylate or amylate.[12] However when bornyl dichloride is subjected to the identical reaction conditions nothing but unchanged starting material is recovered after more than 100 hours refluxing at *ca.* 100° or six hours at *ca.* 230° in a sealed tube. Furthermore, bornyl dichloride resisted elimination with bases as powerful as lithium diethylamine or lithium-N-methylaniline in ether. A similar disparity in the solvolytic reactivity of I and II also was noted. Bornyl chloride gives a ready precipitate of silver chloride with aqueous alcoholic silver nitrate. Prolonged refluxing of bornyl dichloride in the same medium is without effect.

Evidently enormous reduction in reactivity results from the introduction (specifically) of this second halogen in bornyl chloride. It will be noted that the second *endo*-halogen greatly increases the non-bonded interaction[13] and if mere release of strain were a driving factor[14] in either the solvolysis or elimination reactions of bornyl chloride we should have expected the contrary effect on the reactivity of bornyl dichloride. In the elimination reaction with strong base (E_2) the proton abstraction step might have been expected to occur as readily as in the case of bornyl chloride. It would seem, therefore, as if the second halogen in some fashion prevents the solvation of the (departing) chloride ion as required in the reaction mechanism.[15] In other 2,6-(bicyclo)dihalides examined in these laboratories[11] having the *exo–endo* and *exo–exo* relationships, elimination occurs very readily to form the dehydronorbornyl halides. Further, when the second halogen is on the same carbon as in 2,2-dichlorocamphene, elimination (with rearrangement) to chlorocamphene occurs even with bases as weak as acetate anion.[16] Apparently resistance to elimination in bornyl dichloride is an example of stereoelectronic retardation that requires further examination.

At first glance the lack of reactivity of bornyl dichloride toward silver ion appears to be comparable to the great reduction in solvolytic rate produced by chlorine substitution on *t*-butyl chloride.[17]

Experimental

2,6-Dichlorocamphane was prepared by a modification of the method of Tishchenko and Matveev.[18] One thousand grams of pure α-pinene (distilled over sodium, b.p. 155–156°) was charged in a carefully dried flask. Dry sodium bicarbonate (370 g.) was added with stirring. The mixture was cooled and maintained at −5 to −10° and vigorously agitated while a steady stream of chlorine[19] was introduced. It usually required about 9 hours to complete the addition

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[8] See for example, F. Flavitsky, *J. prakt. Chem.*, **45**, 119 (1892), and reference 7.

[9] M. S. Kharasch, F. Engelmann and W. H. Urry, THIS JOURNAL, **66**, 365 (1944).

[10] For a further discussion of these criteria see R. L. Shriner, R. Adams and C. S. Marvel in H. Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1st ed., 1938, Vol. 1, pp. 370 ff.; 2nd ed., 1943, Vol. I, pp. 444 ff.

[11] Unpublished results of L. Kaplan, J. S. Luloff and V. Rolleri.

[12] H. Meerwein and J. Jonssen, *Ber.*, **55**, 2533 (1922).

[13] C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

[14] W. Hückel, O. Neunhoeffer, A. Gercke and E. Frank, *Ann.*, **477**, 99 (1929); H. C. Brown, *Science*, **103**, 385 (1946); H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949); and P. D. Bartlett, paper before the 10th National Organic Symposium, Boston, Mass., June, 1947, p. 22 of abstracts.

[15] For a complete discussion of the factors in mechanisms of the elimination reaction we have reference to here, see paper by S. J. Cristol, Fourteenth National Organic Chemistry Symposium, Lafayette, Ind., June 13–16, 1955, pp. 6–12 of the abstracts.

[16] M. Meerwein and W. Wortmann, *Ann.*, **435**, 194 (1924).

[17] H. C. Brown, M. S. Kharasch and T. H. Chaso, THIS JOURNAL, **62**, 3438 (1940). For other instances of this effect see L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 154 and 208.

[18] D. Tishchenko and B. Matveev, *J. Gen. Chem.*, (*U.S.S.R.*), **20**, 896 (1950); *C. A.*, **44**, 9381 (1950).

[19] Prepared according to A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans Green Co., New York, N. Y., 1951, p. 180

of one equivalent of chlorine, as calculated on the basis of the amount of potassium permanganate used.

The reaction mixture was then poured into water, washed repeatedly and dried over calcium chloride. Fractional distillation afforded two main cuts; a large liquid fraction distilling in the range 25–65° at approximately 1 mm. and consisting mainly of unreacted pinene and possibly some monochlorinated side reaction products and a second fraction distilling in the range 65–100° at the same pressure. Product was recovered from the latter fraction in the form of a large mass of crystals which separated on standing overnight. Two recrystallizations from ethanol yielded 80 g. of very pure material m.p. 173° (uncor.), lit.[7] m.p. 173–174°.

Reduction of 2,6-Dichlorocamphane with Sodium Amalgam in Ethanol.—Six grams of 2,6-dichlorocamphane was dissolved in 80 ml. of dry ethanol. To this solution was added 88.6 g. of 1.84% sodium amalgam prepared according to Vogel.[20] The mixture was brought to reflux under vigorous stirring and maintained in this condition for 48 hours. At the end of this period water was added, the aqueous layer extracted with several portions of ether, and the combined extracts dried over potassium carbonate. Removal of solvent left a white solid which lent itself readily to purification in a vacuum sublimator at 35° and 10 mm. pressure. The yield of triply sublimed product was 1.75 g. melting 131–132° (uncor.). No depression of this melting point was observed on admixture with an authentic sample of bornyl chloride.

The infrared spectrum and X-ray diffraction pattern of the product were indistinguishable from those of an authentic specimen of bornyl chloride.[21]

X-RAY DIFFRACTION DATA

Lattice spacings d in Å.	Relative intensities
6.5	2
5.9	10
5.2	8
2.97	2

The Reduction of 2,6-Dichlorocamphane with Grignard Reagent.—This reaction was carried out by modifying the method applied by Kharasch, Engelmann and Urry for reduction of bornyl chloride.[9] The differences in procedure consisted mainly in reversal of the addition mode; here the Grignard solution was added to the bicyclic halide. Twenty grams of 2,6-dichlorocamphane dissolved in 250 ml. of dry ethyl ether was charged in a flamed out flask. A dry nitrogen atmosphere was maintained during the reaction. Anhydrous cobaltous chloride (0.63 g.) was added and the blue-tinted mixture cooled to 0° under stirring. Methylmagnesium bromide (40 ml., 2.6 *M*) in ether was added dropwise during the course of about an hour. During this time the temperature gradually rose to 20° and a steady evolution of gas was observed. The reaction mixture gradually turned dark brown. Stirring was continued for one hour and then gentle refluxing for five hours. After permitting the mixture to stand overnight it was poured into ice-water acidified with acetic acid. An ether-insoluble substance, VII, was filtered off (weighing 2.2 g.); it melted at 246° after two recrystallizations from carbon tetrachloride. The combined ether extracts were washed with sodium bicarbonate, water and dried over calcium chloride. Stripping off the solvent left an oily-crystalline mass which was subjected to vacuum sublimation.

At temperatures in the range of 35° and approximately 2 mm. a white solid was sublimed free from the mixture. On being twice recrystallized from ethanol–water mixtures, 2.3 g. was recovered which melted at 120° (uncor.). This fraction was identified by infrared spectral comparison to be very similar to bornyl chloride. Clearly, however (see infrared data) it contained some difficultly-separable impurities. *Anal.* Calcd. for bornyl chloride: Cl, 20.53; found, Cl, 21.25.

At 120° a second white solid sublimed. After two recrystallizations from ethanol–water mixtures this fraction weighed 7.6 g. and melted at 174° (uncor.). This substance was readily proven to be unreacted 2,6-dichlorocamphane.

Crystals of VIII formed now in the remaining oily residue in the vacuum sublimator. These weighed 4.0 g. after recrystallization, once from acetone and twice from *n*-amyl alcohol, and melted at 155° (uncor.).

The infrared spectra of the Grignard reduction product VI differs from known bornyl chloride in that it possesses the following additional bands. Pure bornyl chloride (in Nujol) has 32 bands in the region 2–16 μ.

Relative % absorption	Wave length in microns	Average width of band in microns
17.0	3.25	0.05
5.0	6.35	.15
25.0	7.48	.05
9.0	8.85	.08
13.0	9.40	.05
30.0	10.70	.20
24.5	12.80	.18
28.0	13.90	.20
25.0	15.10	.15

Anal. (VIII) Calcd. for $C_{20}H_{32}Cl_2$: C, 69.94; H, 9.38; Cl, 20.67. Found: C, 70.10; H, 9.45; Cl, 20.70. *Anal.* (VII) Calcd. for same as (VIII). Found: C, 69.38; H, 9.65; Cl, 20.41. Calcd. for both mol. wt., 343. Found: mol. wt. (ebullioscopic in carbon tetrachloride), VII, 341; VIII, 331.

The Reduction of Grignard (Reduction) Product with Sodium in Ethanol.—The procedure of Semmler[22] yielded product m.p. 133–135°. Continued recrystallization produced no increase in the melting point. On comparison of infrared spectral data with camphane prepared above, this sample showed the following additional four bands. Pure camphane (in Nujol) shows a spectrum with 18 bands in the region of 2–16 μ.

Relative % absorption	Wave length in microns	Average width of band in microns
11.0	3.30	0.05
12.0	9.00	.08
15.0	11.00	.08
22.5	13.90	.10

Dehydrohalogenation Experiments.—A variety of reagents and conditions were attempted for effecting dehydrohalogenation in bornyl chloride and 2,6-dichlorocamphane with varying results. These are summarized in the following table.

Reagent used	Approx. temp. of reflux, °C.	Time of heating, hr.	Response of product isolated to test
	2,6-Dichlorocamphane		
Lithium-N-methylaniline[23] in ether	45	20	Neg. $KMnO_4$[25] Neg. Br_2 in CCl_4
Lithiumdiethylamine[24] benzene	90	15	Neg. $KMnO_4$[25] Neg. Br_2 in CCl_4
Potassium *t*-alcoholate in *t*-butyl or amyl alcohol	100 230	100 6 6	Neg. $KMnO_4$[25] Neg. Br_2 in CCl_4
	Bornyl chloride		
Lithiumdiethylamine in benzene	90	15	Pos. $KMnO_4$ Pos. Br_2 in CCl_4 Neg. $AgNO_3$ in EtOH
Potassium *t*-alcoholate in *t*-butyl or amyl alcohol	100 230	38 6	Pos. $KMnO_4$ Pos. Br_2 in CCl_4 Neg. $AgNO_3$ in EtOH

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[20] Reference 18, p. 190.

[21] We are grateful to Dr. W. E. Fox of the Hercules Experiment Station for the X-ray diffraction data.

[22] F. W. Semmler, *Ber.*, **33**, 777, 3424 (1900).

[23] K. Ziegler, L. Jacob, H. Wolthan and A. Wenz, *Ann.*, **511**, 64 (1934).

[24] A. C. Cope and B. D. Tiffany, THIS JOURNAL, **73**, 4158 (1951).

[25] Shown subsequently to be unreacted 2,6-dichlorocamphane.