ml. of dry tetrahydrofuran was added to a slurry of 2 g. (0.026 mole) of lithium aluminum hydride in 150 ml. of dry tetrahydrofuran. This mixture was stirred overnight at room temperature and then was boiled under reflux for 2 hr. The mixture was poured on ice and hydrochloric acid, and the organic product was extracted with ether. After these extracts were washed and dried, they were concentrated to yield 2.7 g. (70%) of a yellow solid. Recrystallization from pentane produced white plates, m.p. 98–99°.

Anal. Calcd. for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.75; H, 9.11; N, 13.97.

Fenchylnitramine. To a solution of 9.8 g. (0.185 mole) of potassium borohydride in 100 ml. of ethanol was added 9.8 g. (0.05 mole) of pernitrosofenchone.[37] The mixture was boiled under reflux for 2 hr., then poured into dilute hydrochloric acid and extracted with methylene chloride. Concentration of the organic extracts left 4.2 g. (40%) of a white solid which crystallized from pentane, m.p. 107–108°.

Anal. Calcd. for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.27; H, 9.29; N, 14.06.

Pinacolylnitramine. A solution of 5.0 g. (0.0347 mole) of pernitrosopinacolone[38] in 15 ml. of ethanol was added slowly to 2.0 g. (0.036 mole) of potassium borohydride in 15 ml. of water. This addition was carried out at ice bath temperatures over a 1-hr. period because it was very exothermic. After the addition was complete, 10 ml. of water was added and the mixture was saturated with potassium carbonate. The mixture was extracted with methylene chloride. The organic product was isolated and distilled to yield 2.7 g. (53%) of a colorless oil, b.p. 80–82° (2 mm.), n^{20}_{D} 1.4672.

Anal. Calcd. for $C_6H_{14}N_2O_2$: C, 49.29; H, 9.65; N, 19.17. Found: C, 49.14; H, 9.53; N, 19.44.

Methyl-α-(t-butylvinyl)nitramine. To a solution of 1.6 g. (0.07 g.-atom) of sodium in 25 ml. of anhydrous methanol was added 9.35 g. (0.065 mole) of pernitrosopinacolone[38] dissolved in 25 ml. of dry methanol and 20.0 g. (0.14 mole) of methyl iodide at ice bath temperatures. After the addition, the ice bath was removed and the mixture stirred at room temperature for 15 min., then under reflux for 4 hr. Excess methyl iodide and methanol were removed by distillation, 50 ml. of water was added, and the mixture was extracted with ether. The dried ether extracts were concentrated, and the residue was freed of the last traces of solvent in a desiccator. There was obtained 4.1 g. (40%) of solid product that was crystallized from hexane, m.p. 35–37° (lit.[13] m.p. 39°).

HUNTSVILLE, ALA.

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[37] F. Tiemann and F. Mahla, *Ber.*, **29**, 2807 (1896).

[38] R. Scholl and G. Born, *Ber.*, **28**, 1361 (1895).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

Rearrangement in Borate Pyrolysis

O. L. CHAPMAN AND G. W. BORDEN

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Pyrolysis of the borates of 3,3-dimethyl-2-butanol, borneol, cyclohexylcarbinol, and cyclobutylcarbinol gives rearranged products in every case. The formation of rearranged products is not consistent with the previously proposed *cis*-elimination mechanism and is interpreted on the basis of ionization of the borate esters.

Borate pyrolysis has been shown to be a useful method for the preparation of olefins.[1–3] The pyrolysis proceeds satisfactorily at temperatures well below those required for acetate pyrolysis and comparable to those employed for xanthate pyrolysis. The reaction is simple to carry out and gives excellent yields of olefins. The preparation of the borate esters is straightforward and from the experimental viewpoint superior to the preparation of xanthate esters. Mechanistically, the reaction has been considered a *cis* elimination analogous to the acetate and xanthate pyrolyses.[1,2,4] Our interest in utilization of borate pyrolysis led to an investigation of the structural integrity of the reaction in systems prone to carbonium ion rearrangements. We have examined the products of pyrolysis of the borates of 3,3-dimethyl-2-butanol, borneol, cyclohexylcarbinol, and cyclobutylcarbinol. Rearranged products predominate (94–100%) in each case.

The experimental method employed in this study was that used by O'Conner and Nace.[1] Equimolar quantities of the alcohol and boric acid were warmed slowly to 120–140°, and the water which distilled was separated. The solid borate on further heating melted, then decomposed in the range 250–290°. The olefins which distilled were collected in a Dry Ice trap. The crude olefinic product was analyzed by vapor phase chromatography. The peak areas were read from the simultaneous trace of a mechanical integrator. Each product was separated by preparative scale vapor phase chromatography and identified by comparison of infrared absorption and vapor phase chromatographic retention time with an authentic sample.

Pyrolysis of the borate of 3,3-dimethyl-2-butanol (I) gave three olefins (92–96% yield) which were identified as 3,3-dimethyl-1-butene (II, 0.3%) 2,3-dimethyl-1-butene (III, 25.9%) and 2,3-dimethyl-2-butene (IV, 73.7%). Authentic 3,3-dimethyl-1-butene (II) was prepared by pyrolysis of 3,3-dimethyl-2-butyl acetate.[5] The product from

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[1] G. L. O'Connor and H. R. Nace, *J. Am. Chem. Soc.*, **77**, 1578 (1955).

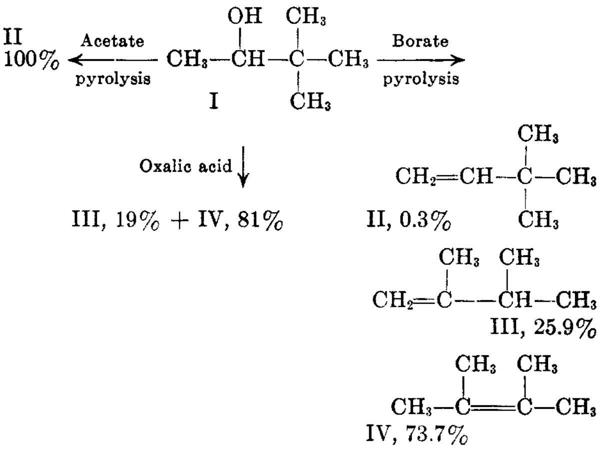
[2] S. Dev, *J. Ind. Chem. Soc.*, **33**, 769 (1956).

[3] W. Brandenberg and A. Galat, *J. Am. Chem. Soc.* **72**, 3275 (1950).

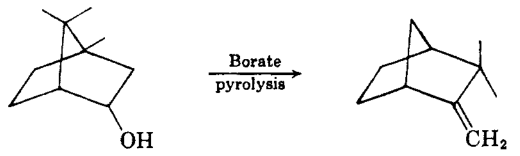
[4] For an excellent review of *cis* eliminations see C. H. DePuy and R. W. King, *Chem. Revs.*, **60**, 431 (1960).

[5] F. C. Whitmore and H. S. Rothrock, *J. Am. Chem. Soc.*, **55**, 1106 (1933).

the acetate pyrolysis was shown to be homogeneous by vapor phase chromatography. A mixture of 2,3-dimethyl-1-butene (III, 19%) and 2,3-dimethyl-2-butene (IV, 81%) was obtained by oxalic acid dehydration of I.[5] This mixture was separated by vapor phase chromatography, and the components were identified by their NMR spectra. The NMR spectrum of 2,3-dimethyl-1-butene (III) showed a six-proton[6] doublet ($J = 6.5$ c.p.s.) at 8.90 τ (isopropyl methyls), a one-proton multiplet at 7.77 τ (isopropyl C—H), a three-proton resonance at 8.32 τ (CH_3—C=C—) and a two-proton resonance at 5.23 τ ($>C=CH_2$). The NMR spectrum of 2,3-dimethyl-2-butene (IV) showed only an intense singlet at 8.38 τ.

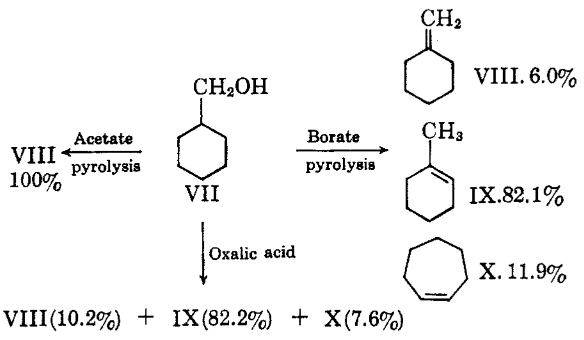


Pyrolysis of the borate of borneol (V) gave camphene (VI) in 69% yield. The low yield was due in part of the tendency of borneol to sublime from the reaction vessel during borate formation.

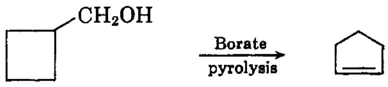


V VI

Cyclohexylcarbinol (VII) on pyrolysis of the borate gave methylenecyclohexane (VIII, 6.0%), 1-methylcyclohexene (IX, 82.1%) and cycloheptene (X, 11.9%).[7] Cyclohexylcarbinol was dehydrated with oxalic acid to obtain an indication of the product ratios in a simple carbonium ion process. This dehydration gave VIII (10.2%), IX 82.2%), and X (7.6%). Pyrolysis of cyclohexylcarbinyl acetate gave exclusively methylenecyclohexene (VIII).[8]

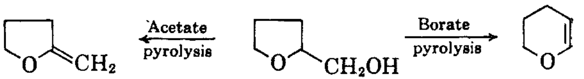


Pyrolysis of the borate of cyclobutylcarbinol (XI) gives a single olefinic product identified as cyclopentene (XII).



XI XII

During the course of our work, an instance of rearrangement in borate pyrolysis was reported by Baumgartner and Wilson.[9] Pyrolysis of the borate of tetrahydrofurfuryl alcohol (XIII) gave dihydropyran (XIV). In contrast, pyrolysis of the acetate gives the normal olefin.[9]



XV XIII XIV

The results described above leave no doubt that the principal products of these borate pyrolyses are formed in carbonium ion type rearrangements. This fact severely limits the potential applications of borate pyrolysis in synthesis.

The rearranged products obtained in the pyrolysis of the borates of I, V, VII, XI, and XIII raise interesting questions concerning the mechanism of this reaction. Rearrangement might proceed by any of three processes: (1) isomerization of the alcohol before or during borate formation, (2) isomerization of an olefin produced by *cis* elimination or (3) ionization of the borate. Isomerization before or during borate formation has been excluded as a possibility in the case of 3,3-dimethyl-2-butanol (I) and cyclohexylcarbinol (VII). The borates from each of these alcohols on dissolution in methanol gave unchanged starting alcohol. If the borate pyrolysis were a *cis* elimination as previously suggested,[1] the rearrangement must involve boric acid–catalyzed isomerization of the olefin initially produced. Ring expanded products such as XII and XIV would not be expected to predominate in acid-catalyzed isomerization of the exocyclic olefins anticipated from *cis* elimination in the borates of XI and XIII. It might be argued, however, that the ring expanded olefins are formed

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(6) Proton counts were made by scanning the spectrum with a Varian Associates electronic integrator.

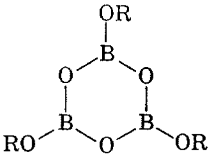
(7) Samples of methylenecyclohexane and 1-methylcyclohexene were furnished by Professor C. H. De Puy.

(8) H. E. Baumgarten, F. A. Bower, and T. T. Okamoto, *J. Am. Chem. Soc.*, **79**, 3145 (1957); R. Ya. Levina and N. N. Mezentsova, *Org. Khim.*, **7**, 241 (1950) [*Chem. Abstr.*, **49**, 3847*i* (1955)].

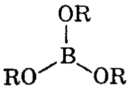
(9) G. J. Baumgartner and C. L. Wilson, *J. Am. Chem. Soc.*, **81**, 2440 (1959).

by a direct ionization mechanism while the other products are formed by isomerization of the exocyclic olefins. This cannot be the case, for pyrolysis of the borates of XI and XIII gives virtually exclusively the ring expanded products XII and XIV. In the case of VII the product ratios in the borate pyrolysis are very comparable to the product ratios in the acid-catalyzed dehydration of VII, strongly suggesting a common course for these reactions. We conclude that the products formed in borate pyrolysis are the result of ionization of the borate ester. The borate melt should be a sufficiently polar medium to permit ionization at elevated temperatures.[10] The ionization of the borate may involve ion pairs or more completely separated ions. In any event the olefins are derived from a carbonium ion sufficiently free to rearrange.

The species which ionizes is of some interest. This is most likely the metaborate or the metaborate trimer. Metaborates decompose thermally at about 270°.[1] Orthoborates, in contrast, are thermally stable well above 333°.[11] O'Connor and Nace have shown that heating equimolar quantities of cyclohexanol and boric acid gives the trimer of cyclohexyl metaborate, and that at 218° (melting point of anthracene) no more than 6% monomeric cyclohexyl metaborate is present.[1] It seems unlikely, at first, that a metaborate trimer (XVI) would ionize more readily than an orthorborate (XVII).

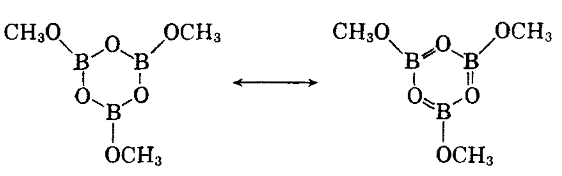


XVI



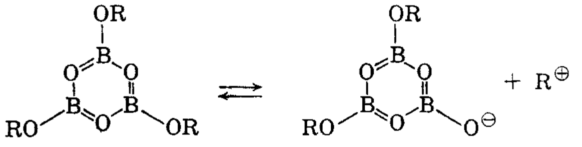
XVII

The planar structure of the B_3O_3 ring in trimethyl boroxole as determined by electron diffraction[12] suggests that the resonance from XVIIIb[13] is significant in the description of methyl metaborate trimer.



XVIIIa XVIIIb[13]

The ionization of a metaborate trimer to the anion and a carbonium ion then appears in a more favorable light. The anion of the borate trimer is isoelectronic with phenoxide ion, and indeed similar resonance structures may be written for the metaborate trimer anion. The stabilization of the metaborate trimer anion is not great but easily accounts for the more facile ionization of metaborate trimers relative to orthoborates.



EXPERIMENTAL

Pyrolysis of 3,3-dimethyl-2-butyl borate. A mixture of 3,3-dimethyl-2-butyl alcohol (10.0 g., 0.098 mole) and boric acid (6.06 g., 0.098 mole) was slowly heated to 120°. The water which distilled during this time was collected. The mixture was refluxed gently for 1 hr., and the temperature of the heating bath was slowly raised to 260°. At this temperature the olefins began to distill. After 1 hr. the reaction was complete; the yield was 7.6–7.9 g. of crude olefin (92–96%). The crude olefin product was analyzed by vapor phase chromatography on a 2 meter Perkin-Elmer R column at 52°.

Run/Product	II	III	IV
1	0.4	25.1	74.5
2	0.5	24.9	74.6
3	0.1	27.8	72.1
Average	0.3	25.9	73.7

Pyrolysis of 3,3-dimethyl-2-butyl acetate. Pure 3,3-dimethyl-2-butyl acetate was dropped slowly through a Vycor tube packed with glass helices maintained at 500°. The product was collected in a Dry Ice-cooled trap. The product was separated from acetic acid by trap-to-trap distillation in a vacuum line. The yield of 3,3-dimethyl-1-butene (homogeneous in vapor phase chromatography) was 4.5 g. (90%).

Oxalic acid-catalyzed dehydration of 3,3-dimethyl-2-butanol. A mixture of 3,3-dimethyl-2-butanol (8 g.) and oxalic acid (30 g.) was slowly heated to 100–110°. A mixture of water and olefins distilled. The yield of crude olefin (after drying over anhydrous magnesium sulfate) was 6.3 g. (94%). The crude olefin was analyzed by vapor phase chromatography. The products were identified by infrared and NMR spectra.

Run/Product	III	IV
1	16	84
2	21	78
Average	19	81

Pyrolysis of bornyl borate. A mixture of borneol (20 g., 0.13) mole) and boric acid (8 g., 0.13 mole) was heated until water no longer distilled. During this period some borneol (4. g.) sublimed up the distilling head, and it was necessary to change distillation heads before pyrolysis of the borate. When the bath temperature reached 260°, olefin began to distill. The crude product (11 g.) was dried over anhydrous sodium sulfate. The infrared spectrum of the product was identical to that of authentic camphene. Vapor phase

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(10) This point has been considered previously (see footnote 10, ref. 1).

(11) The orthoborate of XIII is only partially pyrolyzed at 500° to XIV.[9]

(12) S. H. Bauer and J. Y. Beach, *J. Am. Chem. Soc.*, **63**, 1394 (1941); see also J. A. Kuck and J. R. Johnson, *J. Am. Chem. Soc.*, **60**, 105 (1938); J. Goubeau and H. Keller, *Z. Anorg. Chem.*, **267**, 1 (1951).

(13) In XVIIIb it is a moot point where the charges should be placed. The B—O bond is definitely polarized so that boron is positive relative to oxygen. When oxygen donates electrons to boron (—B═O—), it is difficult to tell whether the donation approaches, equals or exceeds the magnitude of the original polarization.

chromatography showed the camphene to be at least 96% pure.

Pyrolysis of cyclohexylcarbinyl borate. A mixture of cyclohexylcarbinol (5 g.) and boric acid (2.7 g.) was heated slowly to 140°, and the water which distilled was separated. The bath temperature was then raised to 290°. At this temperature the olefinic product began to distill. The yield of olefinic product was 3.8 g. (91%). Analysis of the olefin mixture by vapor phase chromatography on a two meter Perkin-Elmer R column at 100° gave the results shown below. The two analyses are based on separate experiments and are not duplicate analyses of the same mixture. The olefins were separated by preparative scale vapor phase chromatography and identified by comparison of infrared spectra with the spectra of authentic samples.[6]

Run/Product	VIII	IX	X
1	5.9	82.3	11.8
2	6.1	81.9	12.0
Average	6.0	82.1	11.9

Oxalic acid dehydration of cyclohexylcarbinol. A mixture of cyclohexylcarbinol (5 g.) and oxalic acid (30 g.) was slowly heated to 135°. At this temperature water and olefinic product distilled. The yield of olefinic product (after drying) was 3.9 g. (92%). This mixture (analyzed as above) contained methylenecyclohexane (10.2%), 1-methylcyclohexene (82.2 %) and cycloheptene (7.6%).

Pyrolysis of cyclobutylcarbinyl borate. A mixture of cyclobutylcarbinol (0.8 g.) and boric acid (0.58 g.) was slowly heated to 140° and maintained at this temperature until water no longer distilled. The bath temperature was then slowly raised to 245–255°. At this temperature the olefinic product distilled smoothly. The product was shown to be a single olefin by vapor phase chromatography (Perkin-Elmer R column, 34°). The infrared spectrum of the product was identical to that of authentic cyclopentene.

Formation and hydrolysis of cyclohexylcarbinyl borate. A mixture of cyclohexylcarbinol (5 g.) and boric acid (2.7 g.) was slowly heated to 140°, and the water which distilled was separated. The bath temperature was then raised to 290° and maintained at this temperature for 10 min. The mixture was cooled and 100 ml. of methanol and 3 ml. of water were added. This solution was refluxed on the steam bath for 3 hr., and the methanol was removed. The residue was dissolved in ether and dried over anhydrous sodium sulfate. Removal of the ether and distillation of the residue gave unchanged cyclohexylcarbinol identical in infrared absorption with an authentic sample.

Formation and hydrolysis of 3,3-dimethyl-2-butyl borate. A mixture of 3,3-dimethyl-2-butanol (10 g.) and boric acid (6 g.) was heated slowly to 120°, and the water which distilled was separated. The bath temperature was then raised to 250° and maintained for 10 min. at this temperature. After cooling, the borate was dissolved in 100 ml. of methanol and 3 ml. of water. This solution was refluxed for 1 hr., and the methanol was removed. The residue was taken up in ether and dried over anhydrous sodium sulfate. Removal of the ether and distillation of the residue gave unchanged 3,3-dimethyl-2-butanol identical in infrared absorption to the starting alcohol.

Acknowledgment. The authors acknowledge their indebtedness to Professor C. H. De Puy for many lively discussions of ester pyrolysis.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LOYOLA UNIVERSITY]

Ring Size Effects in the Neophyl Rearrangement. II. The Decarbonylation of (1-Methylindanyl)acetaldehyde[1,2]

JAMES W. WILT AND CHARLES A. SCHNEIDER

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(1-Methylindanyl)acetaldehyde (IV) has been prepared and characterized. Its decarbonylation under free radical conditions led to 1,1-dimethylindane (V) and 2-methyltetralin (VI) in good yield. The 35% rearrangement found is significantly less than that observed in the parent system of β-phenylisovaleraldehyde. The decrease in rearrangement percentage is attributed to the planar, fixed attitude of the molecule which retards attainment of the Ar_1-3 type transition state. The existence of a bridged radical as a reaction intermediate in this reaction has been rendered unlikely by a kinetic investigation. The effect of excess peroxide on the rearrangement was also investigated.

The rearrangement exhibited by neophylaldehydes during homolytic decarbonylation has been attributed primarily to steric effects.[2] In an earlier study from this laboratory,[2] two compounds, albeit sterically similar, gave appreciably different rearrangement percentages in this reaction. It was felt that these two substances, (1-phenylcyclopentyl)-acetaldehyde and (1-phenylcyclohexyl)acetaldehyde, differed in their abilities to achieve the requisite transition state for rearrangement because of hindered rotation of the phenyl group in the cyclopentyl analog. Molecular models indicated interference of the *ortho* hydrogens of the aromatic ring by an adjacent cyclopentyl ring hydrogen.[3]

To lend support to the earlier contention as well as to learn more of the steric requirement for rearrangement in neophyl systems, a study was needed of a model compound which would have the

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[1] This report is taken from the M. S. thesis of C. A. S., Loyola University, February 1961.

[2] For Paper I and references, see J. W. Wilt and Bro. H. Philip, F. S. C., *J. Org. Chem.*, 25, 891 (1960).

[3] An additional reason for the different rearrangement abilities of the 1-phenylcyclohexyl- and 1-phenylcyclopentylcarbinyl radicals studied earlier[2] might be the relief of the axial strain of the carbinyl group and hydrogens 1,3- to it in the former. We thank Profs. W. H. Urry and N. C. Yang of the Department of Chemistry of the University of Chicago for this suggestion.