kyl–oxygen cleavage of *t*-butyl benzoate was obtained by Kuhn,[5] who suggested a more general approach using an ester labeled with an oxygen isotope. It is hoped that such an experiment can be conducted in this Laboratory in the near future.

Experimental

Materials.—Trichloroethyl and tribromoethyl benzoates were prepared by the aluminum chloride catalytic method.[10] Methyl *p*-nitrobenzoate, m.p. 95–96°, and methyl 3,5-dinitrobenzoate, m.p. 107–108°, were prepared by dissolving the acid chlorides in methanol and recrystallizing *in situ*. The remaining esters and acids were commercial C.P. reagents used without further purification other than careful drying. The 100% sulfuric acid was prepared by the method previously described.[2b]

Hydrolysis of Esters.—In a typical experiment a solution of ethyl benzoate (1.982 g., 0.0132 mole) in 10.0 ml. of 100% sulfuric acid was kept at 50° for one hour and then poured onto ice and water. The precipitated benzoic acid, identified by mixed melting point, weighed 0.916 g. (0.0075 mole, 57%) after recrystallization from 10 ml. of 1:3 methylene chloride–petroleum ether.

Freezing Point Measurements.—The apparatus used was essentially the same as that described by Newman, Kuivila and Garrett.[2b] The vessel was constructed to fit a platinum resistance thermometer (Leeds and Northrup, No. 8163-S) which had a ground glass joint sealed to its shield. A reciprocating stirrer of nichrome wire was used, with a mercury seal to keep out moisture. The latter was replaced in a second apparatus with a self-lubricating Teflon stopper which was machined to fit a ground glass joint. This change greatly simplified construction, and avoided the danger of introducing mercury into the sulfuric acid solution. In each determination, the solvent was 50 ml. (91.2 g.) of approximately 99.9% sulfuric acid. For heating cycles the whole apparatus was partially immersed in a constant temperature bath kept at 50 ± 1°.

The operational technique has been discussed by many authors.[3,11] A correction for supercooling (which was usually about 1°) was made according to the method of Gillespie, Hughes and Ingold.[11] The value for the cryoscopic constant determined by these authors[11] (5.98) was incorporated into the equation for "*i*" used by Hammett[2] and Newman.[3]

$$i = \frac{\Delta\theta}{m \times 5.98(1 - 0.0047\theta)}$$

The symbol m represents the molality of the solute, $\Delta\theta$ is the freezing point depression due to m, and θ is the total freezing point depression.

In a recent publication, Wyatt[12] questioned the invariance of the cryoscopic "constant," and thereby rendered all *i*-factor measurements suspect, at least in the second decimal. We have retained this third significant figure in Table V, although it might have been discarded on the basis of some experimental variations alone. For this report, all the *i*-values were checked by duplicate experiments.

WHITE OAK, SILVER SPRING, MD.

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[10] M. E. Hill, THIS JOURNAL, **76**, 2329 (1954).

[11] R. J. Gillespie, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2473 (1950).

[12] P. A. H. Wyatt, *ibid.*, 1175 (1953).

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY]

The Boric Acid Dehydration of Alcohols

BY GEORGE L. O'CONNOR[1] AND HAROLD R. NACE

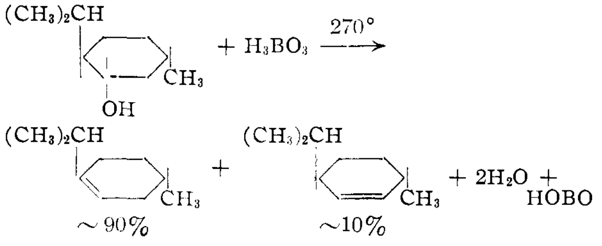
RECEIVED FEBRUARY 18, 1954

Evidence is presented that the dehydration of an alcohol by pyrolysis with boric acid takes place through a metaborate ester in which the eliminated groups have the *cis*-configuration. The preparation and properties of several metaborate esters are described and a mechanism for their pyrolysis is proposed.

Brandenberg and Galat[2] have recently recorded a new method for the preparation of olefins by the pyrolysis of equimolar amounts of boric acid and an alcohol. In the cases studied, excellent yields were obtained. The mechanism of the reaction was stated to involve two steps: (1) the formation of the orthoborate ester ($(RO)_3B$); and (2) the decomposition of this ester into olefin and boric acid. The authors pointed out that this reaction was analogous to the decomposition of acetate esters which also yields olefins.

A further study of this reaction has been carried out to extend its synthetic utility and to shed further light on its mechanism.

l-Menthol was studied first because of the elegant work of Hückel, *et al.*,[3] and Barton, *et al.*,[4] on the elimination reactions of this compound. When equimolar amounts of *l*-menthol and boric acid were heated at 150–180°, two moles of water were formed, and on raising the temperature to 270°, an 83–92% yield of a mixture of 9–13% of Δ^2-menthene and 91–87% of Δ^3-menthene was obtained.



Approximately 70% of the Δ^3-menthene formed by the boric acid elimination was racemized. In order to determine if this was characteristic of the reaction or if the Δ^3-menthene was racemized, following its formation, by metaboric acid, a sample of menthene obtained from *l*-menthyl S-methylxanthate by the Chugaev reaction, containing approximately 70% Δ^3-menthene and 30% Δ^2-menthene, was heated with metaboric acid at 270°. The Δ^3-menthene was partly racemized (10%) by this treatment and, therefore, it seems likely the racemization observed in this elimination is caused by the action of metaboric acid on the Δ^3-menthene after it has been formed. When a sample of pure Δ^2-menthene, obtained from *l*-menthyl chloride by elimination with sodium methoxide, was heated with metaboric acid at 270°, no racemization was observed.

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[1] Dow Chemical Company Fellow, 1952–1953.

[2] W. Brandenberg and A. Galat, THIS JOURNAL, **72**, 3275 (1950).

[3] W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

[4] D. H. R. Barton, A. J. Head and R. J. Williams, *J. Chem. Soc.*, 453 (1952).

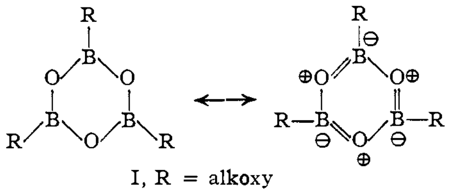
The predominance of Δ^3-menthene must be due to a *cis*-elimination while the Δ^2-isomer can arise by either a *cis*- or *trans*-elimination.

To test the theory of Brandenberg and Galat that orthoborate esters are the unstable intermediates in the dehydration, *l*-menthyl orthoborate was prepared, in quantitative yield, by heating under reflux three molar equivalents of menthol with one of boric acid in toluene. When the orthoborate was heated at 300° (30° above the usual reaction temperature) for several hours, no reaction took place. However, on the addition of two molar equivalents of boric acid to one of the orthoborate, the reaction proceeded normally at 270°.

Schiff[5] reported the formation of several metaborates by the treatment of orthoborates with boric acid or boric anhydride.

In order to determine whether metaborate esters are the unstable intermediates in the dehydration reaction, several of them were prepared and characterized. When equimolar amounts of *l*-menthol, cyclohexanol or *n*-butanol and boric acid were heated under reflux in toluene, two molar equivalents of water were formed, and the respective metaborates were obtained in practically quantitative yield. The *n*-butyl metaborate could not be obtained pure, however, since on distillation it partially disproportionated to yield a distillate consisting of *n*-butyl orthoborate and unchanged metaborate, and a residue which appeared to be boric anhydride. After several redistillations the disproportionation was complete.

The infrared spectra of the metaborates was examined in the 2–9 μ region and showed only C–H absorption. If the —B=O structure was present, it might be expected to have a strong absorption similar to the —C=O group. The absence of such absorption and the fact that Schiff metaborates appeared to be polymers led to molecular weight studies, which showed that the metaborates existed as trimers (I). It has been shown previously[6] that the analogous alkyl boric anhydrides (R–B–O) exist as trimers in a six-membered ring (II), and the electron diffraction studies[6b] suggest a resonance hybrid.



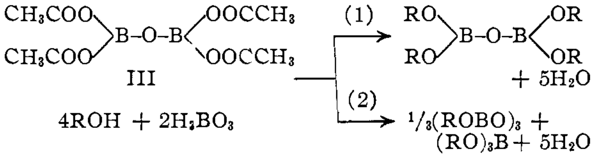
I, R = alkoxy
II, R = alkyl or aryl

Both the metaborate and orthoborate esters hydrolyze readily. If *l*-menthyl metaborate is allowed to stand it adds one molar equivalent of water to form *l*-menthoxyboric acid ($ROB(OH)_2$), which is still completely soluble in organic solvents, indicating that no free boric acid has been formed.

The preparation of the alkoxy boric acid was attempted since it is a possible intermediate in the formation of the metaborate. However, when equimolar amounts of *l*-menthol and boric acid were heated under reflux in benzene,[7] two molar equivalents of water were formed by the time all of the boric acid had reacted, and only the metaborate was formed.

It is interesting to note that boric acid will react with alcohols in ratios greater than 1:1 under the conditions used for the formation of the metaborates. In experiments using an excess of boric acid to cyclohexanol, it was found that the ratio of boric acid to alcohol in the product was approximately 4 to 3. The product obtained could be crystallized from benzene–petroleum ether mixtures and was found to contain a higher percentage of boron than the metaborate.

In view of the fact that the boric acid and alcohols react to give esters in the ratios 3:1, 1:1 and 4:3, it was desirable to investigate the product obtained from a 2:1 ratio since this might give rise to a compound of structure similar to the one obtained by the action of acetic anhydride on boric acid[8] (III). This reaction, however, proceeds by path (2) rather than (1).



When either menthyl or cyclohexyl metaborate trimer was heated to 270°, it readily decomposed, yielding Δ^2- and Δ^3-menthene, or cyclohexene, respectively, and metaboric acid. Below this temperature practically no decomposition occurred. The question now arises as to whether the metaboratet rimer is the unstable intermediate in this reaction or whether it exists in equilibrium with an unstable monomer. In an attempt to shed some light on this question, molecular weight determinations were made on the cyclohexyl compound cryoscopically at 80° in naphthalene and at 218° in anthracene. At the lower temperature, the metaborate is at rimer (with perhaps a trace of monomer present); however, at the higher temperature, the results show that it may be dissociated to the extent of 6%. It seems unlikely that the lower molecular weight at 218° was caused by decomposition to the olefin since no reaction appeared to take place below 260°. If an equilibrium does exist between the trimer and monomer at these higher temperatures, it is far on the side of the trimer.

On the basis of the available evidence, and by analogy to the mechanism of pyrolysis of other esters[9] a possible mechanism for the dehydration of alcohols by boric acid can be proposed. The predominance of Δ^3-menthene suggests that the metaborate (monomer or trimer) decomposes by a *cis*-elimination[10] through a cyclic transition state

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[5] H. Schiff, *Ann.*, Supp. V, 154 (1867).

[6] (a) H. R. Snyder, J. A. Kuck and J. R. Johnson, THIS JOURNAL, **60**, 105 (1938); (b) S. H. Bauer and J. V. Beach, *ibid.*, **63**, 1394 (1941).

[7] Benzene was used in place of toluene because boric acid does not lose water below 100°, and thus it might be possible to stop the reaction at the alkoxy boric acid stage.

[8] O. Dimroth, *Ann.*, **446**, 97 (1925).

[9] G. L. O'Connor and H. R. Nace, THIS JOURNAL, **74**, 5454 (1952); **75**, 2118 (1953), and references cited there.

[10] One of the referees has proposed that the Δ^3-menthene could be formed by a process other than a *cis*-elimination. The authors feel that it is unlikely, however, that an ionic or solvolytic mechanism would be favored in the melt present during the pyrolysis.

analogous to those proposed for other esters.[9]

The fact that the O—B=O linkage would be expected to be linear and thus less likely to form a cyclic transition state is not a major drawback to this mechanism because at the high temperatures required to bring about the reaction sufficient energy would be available for distortion of the O—B=O bond.

In order to determine the scope of this reaction, several alcohols were investigated. As already mentioned, *l*-menthol and cyclohexanol gave good yields of olefin (83–92%). Cholesterol and cholestanol also dehydrated readily by this procedure giving $\Delta^{3,5}$-cholestadiene and a 1:1 mixture of Δ^2- and Δ^3-cholestene, respectively, in good yields. With the bile acids, the results were not satisfactory, polymeric esters being obtained with methyl cholate and desoxycholate.

Experimental[11]

Dehydration of *l*-Menthol.—In a 50-ml. distilling flask were placed 15.6 g. (0.1 mole) of *l*-menthol and 6.2 g. (0.1 mole) of boric acid. The mixture was slowly heated in an oil-bath to 150–180°, while 4.0 ml. (0.22 mole) of water was collected. The temperature of the bath was then slowly raised to 270° where the menthenes began to distil. The major part distilled in 15 minutes and was complete after an hour. The mixture of menthenes was then fractionated at 15 mm., giving the following fractions in a typical run.

Fraction	B.p. (15 mm.)[a]	Wt., g.	$[\alpha]_D$
1	55–59	2.10	+53°
2	59–60	2.15	+53
3	60–60	2.15	+54
4	60–61	2.10	+46
5	61–62	2.18	+39
6	62–63	0.62	+35
7	Residue (menthol)	2.50	

[a] B.p. of Δ^2-menthene at 15 mm., 56°, Δ^3-menthene, 62°.[5]

The total weight of Δ^2- and Δ^3-menthene was 11.30 g. (92% yield based on recovered menthol) and it had $[\alpha]_D$ +50°. The analysis of the mixture of Δ^2- and Δ^3-menthene was carried out by saturating 20 ml. of a 1% solution of the total mixture of menthenes in chloroform with water and passing dry hydrogen chloride through the solution for 30 minutes. The turbidity of the solution and the excess hydrogen chloride were removed by the addition of anhydrous calcium chloride. The rotation after racemization was $[\alpha]_D$ +17° and was due to Δ^2-menthene $[\alpha]_D$ +132°, 13%, and Δ^3-menthene $[\alpha]_D$ +109°, 87%, of which 70% was originally racemized.

Racemization of Δ^3-Menthene by Metaboric Acid.—One gram of a Δ^2- and Δ^3-menthene mixture, $[\alpha]_D$ +127°, obtained by the Chugaev reaction, containing about 70% of the Δ^3-isomer, was heated for 1 hour with 0.5 g. of metaboric acid in a sealed tube at 270°. The rotation of the menthene was then $[\alpha]_D$ +115°.

Attempted Racemization of Δ^2-Menthene by Metaboric Acid.—One gram of Δ^2-menthene, $[\alpha]_D$ +132° (prepared from *l*-menthyl chloride by reaction with sodium methoxide) was heated with 0.5 g. of metaboric acid for 30 minutes in a sealed tube at 270°. After distillation the rotation of the Δ^2-menthene was unchanged.

***l*-Menthyl Orthoborate.**—A solution of 4.68 g. (0.03 mole) of *l*-menthol in 50 ml. of toluene was refluxed 3 hours with 0.62 g. (0.01 mole) of boric acid under a continuous water separator. Removal of the toluene gave 4.76 g. (100%) of *l*-menthyl orthoborate, m.p. 150–152°. The analytical sample was crystallized from 1:1 acetone–ethyl acetate and had m.p. 150–152°.

Anal. Calcd. for $C_{30}H_{57}O_3B$: B, 2.27; Found: B, 2.25.

Pyrolysis of *l*-Menthyl Orthoborate.—A 50-ml. distilling flask containing 4.76 g. (0.01 mole) of *l*-menthyl orthoborate was slowly heated in an oil-bath to 300° and held at 300° for 1 hour without any material distilling. A sample of the residue in the flask was crystallized from acetone–ethyl acetate, m.p., 150–152°.

Pyrolysis of *l*-Menthyl Orthoborate with Boric Acid.—A 50-ml. distilling flask containing 4.76 g. (0.01 mole) of *l*-menthyl orthoborate and 1.24 g. (0.02 mole) of boric acid was slowly heated in an oil-bath. Water distilled from the reaction mixture at 150° and Δ^2- and Δ^3-menthene at 270°; the major part distilled in 15 minutes and was complete in one hour. The mixture of menthenes was fractionated yielding 3.5 g. (92%) of Δ^2- and Δ^3-menthene, b.p. 55–63° at 15 mm.

***l*-Menthyl Metaborate Trimer.**—A mixture of 15.6 g. (0.1 mole) of *l*-menthol, 6.2 g. (0.1 mole) of boric acid and 100 ml. of toluene was heated under reflux with a constant water separator. After 3 hours all of the boric acid had reacted to give a clear homogeneous solution with the formation of 4.0 ml. (0.22 mole) of water. The major part of the toluene was removed by distillation and the menthyl metaborate allowed to crystallize. The product was dried at 100° and 2 mm. for several hours. The yield was 18.0 g. (99%) of white needles, m.p. 113–115°, very soluble in the usual organic solvents.

Anal. Calcd. for $(C_{10}H_{19}OBO)_3$: B, 5.98; mol. wt., 546; Found: B, 6.04; mol. wt., 530.

Pyrolysis of *l*-Menthyl Metaborate Trimer.—A 50-ml. distilling flask containing 5.5 g. (0.01 mole) of menthyl metaborate trimer was slowly heated in an oil-bath. Only a few drops of material distilled under 260° and at 270° menthene distilled readily for one hour (the major part distilled in 15 min.). The mixture of menthenes was fractionated to yield 3.7 g. (89%) of Δ^2- and Δ^3-menthene, b.p. 55–63° (15 mm.).

***l*-Menthoxyboric Acid.**—*l*-Menthyl metaborate trimer (1.82 g.) was ground to a fine powder, placed in a watch glass, and allowed to stand in the air for several hours. At the end of this time, the product had gained 0.18 g. and was still completely soluble in organic solvents. The m.p. of the *l*-menthoxyboric acid was 132–135°.

Anal. Calcd. for $C_{10}H_{19}OB(OH)_2$: B, 5.44; mol. wt., 200. Found: B, 5.45; mol. wt., 205.

Cyclohexyl Metaborate Trimer.—A mixture of 25.0 g. (0.25 mole) of cyclohexanol, 15.5 g. (0.25 mole) of boric acid and 100 ml. of toluene was heated under reflux with a constant water separator. After 3 hours all the boric acid had reacted, yielding a clear solution and 9.0 ml. of water. About 50 ml. of the toluene was distilled and the solution allowed to cool, whereupon the cyclohexyl metaborate trimer crystallized as long white needles. The product was dried at 100° (2 mm.) for several hours. The yield was 30.0 g. (95%), m.p. 165–167°. A sample was recrystallized from a 1:1 mixture of benzene–petroleum ether, m.p. 165–167°.

Anal. Calcd. for $(C_6H_{10}OBO)_3$: B, 8.62; mol. wt., 378. Found: B, 8.65; mol. wt., 375 at 80° in naphthalene; 363 at 218° in anthracene.

In other runs it was found that if the toluene was replaced with benzene the time required was 7 hours but equally good yields of cyclohexyl metaborate trimer were obtained.

Pyrolysis of Cyclohexyl Metaborate Trimer.—A 50-ml. distilling flask containing 6.5 g. (0.017 mole) of cyclohexyl metaborate trimer was slowly heated in an oil-bath. Below 260° only a few drops of material distilled and at 260–270° cyclohexene distilled. The product was fractionated to yield 3.9 g. (90%) of cyclohexene, b.p. 82–84°.

Reaction of Cyclohexanol with Excess Boric Acid.—A mixture of 25.0 g. (0.25 mole) of cyclohexanol, 23.2 g. (0.375 mole) of boric acid and 200 ml. of xylene or toluene (the reaction was found to take place faster and more completely in xylene) was heated under reflux with a constant water separator. Solution of the boric acid appeared to be complete after about 10 hours but refluxing was continued 8 hours longer, the solution was filtered hot, and the boric acid air-dried. The unreacted boric acid (2.1 g.) recovered corresponded to a 4:3 ratio of boric acid and cyclohexanol in the product. The filtrate was allowed to cool, and 100 ml. of petroleum ether was added. The product was dried at 100° (2 mm.) for several hours. The yield was 33 g., m.p. 140–143°. A sample was recrystallized from 1:1 benzene–petroleum ether, m.p. 141–143°.

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[11] All melting points are corrected.

Anal. Calcd. for $C_{18}H_{34}O_8B_4$: B, 10.25. Found: B, 10.05.

n-**Butyl Metaborate Trimer.**—This compound was prepared from 0.1 mole of *n*-butyl alcohol and 0.1 mole of boric acid in toluene as above, yielding 3.8 ml. of water. The toluene was distilled and the clear residue fractionated, yielding two main fractions: I, b.p. 72–80° (2 mm.) and II, b.p. 95–100° (2 mm.), and a white residue, presumably boric anhydride. Fraction I was largely *n*-butyl borate and II was a mixture of *n*-butyl borate and metaborate.

Anal. Calcd. for $(C_4H_9O)_3B$: B, 4.68. Found for fraction I: B, 4.78.

Anal. Calcd. for $(C_4H_9OBO)_3$: B, 10.9. Found for fraction II: B, 8.5.

Redistillation of fraction II resulted in complete conversion of the metaborate to *n*-butyl borate, b.p. 80–83° (2 mm.) (B = 4.70) and boric anhydride.

Dehydration of β-Cholestanol.—One gram (2.6 mmoles) of β-cholestanol and 0.16 g. (2.6 mmoles) of boric acid were heated together in a test-tube at 300° in an oil-bath for 2 hours. The product was taken up in ether, washed with water and dilute base and dried over anhydrous sodium sulfate. The ether was evaporated and the residue taken up in 25 ml. of petroleum ether and chromatographed over 10 g. of aluminum oxide (Merck and Co., Inc., "suitable for chromatographic absorption") in a column 1 × 12 cm. The Δ^2- and Δ^3-cholestene were easily eluted with petroleum ether to yield 850 mg. (89%) of Δ^2- and Δ^3-cholestene, m.p. 64–68°, $[\alpha]_D$ +64° (chloroform). Conversion of a sample to the dibromides as previously reported[8] gave $[\alpha]_D$ +43° (chloroform), which corresponds to 53% of Δ^2-cholestene.

Dehydration of Cholesterol.—Cholesterol was dehydrated as above in 80% yield to $\Delta^{3,5}$-cholestadiene, m.p. 78–79°, $[\alpha]_D$ −108° (chloroform).

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Reformatsky Reaction with Ethyl Bromofluoroacetate[1]

BY E. T. MCBEE, O. R. PIERCE AND D. L. CHRISTMAN

RECEIVED JULY 16, 1954

Ethyl bromofluoroacetate reacts with zinc and carbonyl compounds to yield α-fluoro-β-hydroxy esters. Although the reaction is more sluggish than corresponding condensations with ethyl bromoacetate, the yields are comparable. The use of fluorine-containing ketones in the condensation is a new extension of the Reformatsky reaction.

Discussion

The Reformatsky condensation with ethyl bromofluoroacetate serves as a novel synthesis of esters and acids containing an α-fluorine atom, a type of compound obtained previously only by oxidative[2] or replacement methods.[3] These latter methods do not appear to have as wide an applicability as the method reported here since condensations with bromofluoroacetate can be effected with nearly all types of aldehydes and ketones (Table I). While the reactions are more sluggish than with ethyl bromoacetate, the yields of desired products are comparable when using solvents such as toluene or xylene. In contrast to activation of the metal used as condensing agent by amalgamation,[4] the zinc in the present investigation was purified only by washing with 2% hydrochloric acid, water, alcohol and acetone.[5] Each condensation gave the desired product possessing an α-fluorine atom. This is unlike the results obtained by Miller and Nord[6] with ethyl dichloroacetate, ethyl dibromoacetate and ethyl trichloroacetate, where the condensation products in all but one case were devoid of halogen. No catalyst was used with ethyl bromofluoroacetate, whereas cupric chloride or mercuric chloride are required for condensations with the esters of dichloro-, dibromo- and trichloroacetic acid.

Although ethyl bromofluoroacetate gave little or no condensation with fluorinated ketones, the same ketones with ethyl bromoacetate gave fair yields of the hydroxy esters.[7] Since fluorinated ketones are readily available,[8] they can thus be used in the Reformatsky reaction with ethyl bromoacetate to give a variety of products containing a perfluoro group.

In a number of reactions, ethyl acetate and ethyl fluoroacetate were isolated from the reaction mixtures. The removal of bromine has been explained[9] by metal exchange between the zinc compound and the enol forms of aldehydes or ketones. This explanation cannot apply in reactions with compounds such as benzaldehyde, which cannot enolize. In the Reformatsky reaction with methyl γ-bromocrotonate and benzaldehyde, the condensation occurs alpha as well as gamma and the hydrolysis products contain unchanged benzaldehyde as well as methyl crotonate.[9c,10] From these results an ionic intermediate was postulated, which can account for the bromine-free esters observed.

The sluggishness of the polyhalogen esters in the condensation can be explained by comparison of ethyl bromoacetate with ethyl bromofluoroacetate. In I, the polarization of the C–Br bond causes partial induced charges. The partial positive charge on the carbon atom in II is enhanced due to the

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[1] This paper represents part of a thesis submitted by D. L. Christman to the Graduate School, Purdue University in partial fulfillment of the requirments for the degree of Doctor of Philosophy.

[2] A. L. Henne and C. J. Fox, THIS JOURNAL, **76**, 479 (1954).

[3] (a) J. C. Bacon, C. W. Bradley, E. I. Hoegberg, P. Tarrant and J. T. Cassaday, *ibid.*, **70**, 2653 (1948); (b) E. Gryszkiewicz-Trochimowski, A. Sporzynski and J. Wnuk, *Rec. trav. chim.*, **66**, 413 (1947); (c) H. McCrombrie and B. C. Saunders, *Nature*, **158**, 382 (1946).

[4] (a) G. Darzens and A. Levy, *Compt. rend.*, **204**, 272 (1937); (b) G. Darzens, *ibid.*, **203**, 1374 (1936); (c) G. Darzens, *ibid.*, **151**, 883 (1910); see also E. R. Blout and R. C. Elderfield, *J. Org. Chem.*, **8**, 29 (1943).

[5] R. L. Shriner, "Organic Reactions," Vol. I, Chapter 1, John Wiley and Sons, Inc., New York, N. Y., 1942.

[6] R. E. Miller and F. F. Nord, *J. Org. Chem.*, **16**, 728 (1951).

[7] Recently D. E. Rivett, *J. Chem. Soc.*, 3710 (1953), reported the condensation of ethyl bromoacetate and ethyl ethoxalylfluoroacetate to give ethyl monofluorocitrate.

[8] D. D. Meyer, Ph.D. Thesis, Purdue University, 1954.

[9] (a) M. S. Newman, THIS JOURNAL, **64**, 2131 (1942); (b) A. S. Hussey and M. S. Newman, *ibid.*, **70**, 3024 (1948); (c) F. R. H. Jones, D. G. O'Sullivan and M. C. Whiting, *J. Chem. Soc.*, 1415 (1949).

[10] A. S. Dreiding and R. J. Pratt, THIS JOURNAL, **75**, 3717 (1953); and J. English, Jr., J. D. Gregory and J. R. Trowbridge II, *ibid.*, **73**, 615 (1951), report similar α- and γ-additions.