CCl_4 filtrate was distilled through a Vigreux column to remove the solvent, and then the residue was flash distilled, giving poor yields of the dibromide.

B. From Cyclobutene.—Cyclobutene was prepared by dehydrochlorination of chlorocyclobutane. Two grams (0.022 mol) of chlorocyclobutane (Ash-Stevens, Inc.) was injected onto 2.85 g (0.025 mol) of sublimed potassium *tert*-butoxide it 100°. The apparatus used was that described for the reaction of 1 with potassium *tert*-butoxide. The product gas was led directly into a pentane solution of bromine and pyridine[7] cooled to $-80°$. The mixture was allowed to warm to room temperature. It was washed with water, 5% $NaHSO_3$, 10% HCl, and water and dried, and the pentane was removed. Distillation of the residue afforded 1.2 g, bp 60–79° (15 mm), of a four-component mixture from which the desired dibromide (major product) was isolated by vpc (10 ft × 0.125 in., 20% SE-30 on 60/80 Chromosorb W A/W DMCS at 130°).

1-Bromocyclobutene (2).—This material was prepared by the dehydrobromination of 1,2-dibromocyclobutane as described in the literature.[8,9] When passed through the gas chromatograph, 1-bromocyclobutene appeared to undergo some ring opening to 2-bromo-1,3-butadiene. The nmr of vpc-collected material showed additional vinyl hydrogen absorption, and the ir displayed additional bands at 8.30, 10.27, and 11.24 μ. Intense absorption at these positions is observed in the ir of 2-bromo-1,3-butadiene.[10] Similar electrocyclic ring openings of cyclobutenes to butadienes on the vpc have been observed in our laboratory.[11]

Registry No.—1, 33745-37-8; potassium *tert*-butoxide, 865-47-4.

Acknowledgments.—We are grateful to Professors P. Abell and P. Maitte for providing us with ir spectra of 1-bromocyclobutene and 1,2-dibromocyclobutane.

[7] J. Wolinsky, R. Novak, and K. L. Erickson, *J. Org. Chem.*, **34**, 490 (1969).

[8] P. Abell and C. Chiao, *J. Amer. Chem. Soc.*, **82**, 3610 (1960).

[9] H. Normant and P. Maitte, *Bull. Soc. Chim. Fr.*, 1424 (1960).

[10] A. A. Petrov and G. I. Semenof, *Zh. Obshch. Khim.*, **27**, 928 (1957).

[11] K. L. Erickson, unpublished observations.

Boric Acid Catalyzed Tishchenko Reactions

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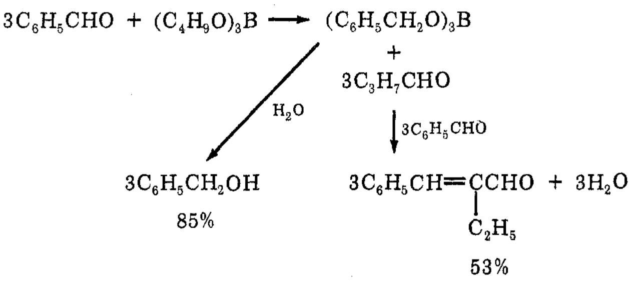
A recent article has described the use of boric acid catalysts for the aldol condensation of aldehydes and ketones.[1] It has now been found that boric acid is also an effective catalyst for the dismutation of certain aldehydes to the corresponding esters *via* a Tishchenko type reaction.[2] Aldehydes which may be used are those which are not readily susceptible to aldol condensation or to resinification.

When paraformaldehyde was heated with a catalytic quantity of boric acid in cyclohexane in an autoclave at 250° for 5 hr, essentially complete conversion of the formaldehyde was observed, and a 77% yield of methyl formate was isolated by distillation. Under similar conditions, isobutyraldehyde reacted more slowly. After 6 hr at 250°, a 74% aldehyde conversion was found and a 72% yield (based on reacted isobutyraldehyde) of isobutyl isobutyrate was obtained. Reaction temperatures of 200 and 225° gave comparable isobutyraldehyde conversions with somewhat reduced yields of ester. Table I summarizes results obtained with typical aldehydes.

When acrolein, furfural, or crotonaldehyde were treated under identical conditions only tars and resins were produced; this was somewhat surprising in view of the low acidity of boric acid. Lowering the reaction temperature to 150° in an attempt to prepare allyl acrylate from acrolein gave a low molecular weight solid polymer. The isolation of an appreciable amount of *n*-butyl butyrate from *n*-butyraldehyde is particularly noteworthy in view of the reported[1] production of only aldol condensation product from *n*-heptaldehyde under similar conditions.

In order to more fully define the scope of catalytic activity of boric acid, several additional experiments were conducted using benzaldehyde as the substrate. Addition of 25 ml of water to the boric acid catalyst completely destroyed the catalytic activity. Substitution of fused boric oxide for the boric acid resulted in a 17% benzaldehyde conversion after 6 hr at 250° with a 50% yield of benzyl benzoate. The use of tetrahydrofuran solvent also inhibited the reaction; under the same conditions only a 5% benzaldehyde conversion was realized. High temperatures are necessary for the disproportionation of the relatively unreactive benzaldehyde, since no reaction was observed after 18 hr reflux (180°) of neat benzaldehyde over boric acid. Activated alumina, in relatively large quantities, also functioned as a Tishchenko catalyst, albeit much more slowly. A 9% conversion was obtained after 8 hr at 250° and a 35% conversion and 78% yield of ester were obtained after 7 hr at 325°.

The use of *n*-butyl borate as a Tishchenko catalyst was also tested. The only products isolated were benzyl alcohol and α-ethylcinnamaldehyde. Reaction of benzaldehyde with *n*-butyl borate at atmospheric pressure is known[3] to give benzyl alcohol (after hydrolysis) and *n*-butyraldehyde; in this work using a closed system the butyraldehyde condensed with the excess benzaldehyde to form α-ethylcinnamaldehyde.



The Tishchenko reaction has been previously found to be catalyzed by strongly basic alkali metal alkoxides, the amphoteric aluminum alkoxides, and strong acids.[4] Although boric acid is an exceedingly weak acid, it appeared possible that, at the elevated temperatures used in this study, acid catalysis might indeed be occurring. However, neither acetic acid nor *p*-toluenesulfonic acid produced more than trace quantities of benzyl benzoate under similar conditions. An alternative explanation, which appears much more attractive, is based on the electrophilic nature of the

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[1] R. D. Offenhauer and S. F. Nelsen, *J. Org. Chem.*, **33**, 775 (1968).

[2] (a) W. Tishchenko, *Zh. Fiz. Khim.*, **38**, 355 (1906); (b) R. M. Wagner and H. D. Zook, "Synthetic Organic Chemistry," Wiley, New York, N. Y., 1953, p 494.

[3] V. K. Kuskov and A. N. Neverov, *Zh. Obshch. Khim.*, **29**, 1127 (1959); *Chem. Abstr.*, **54**, 1393 (1960).

[4] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, p 269.

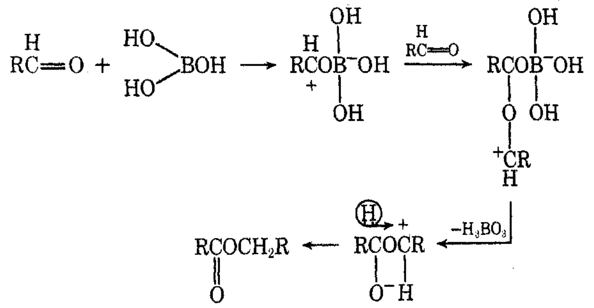
TABLE I[a]

$2RCHO \longrightarrow RCO_2CH_2R$

R	Registry no. (RCHO)	Mol	Conversion, %	Yield,[b] %	Bp, °C (mm)	Registry no. (RCO_2CH_2R)
H	50-00-0	5.83	100	77	32–33	107-31-3
$(CH_3)_2CH-$	78-84-2	3.13	74	72	144–145	97-85-8
$C_4H_9C(C_2H_5)H-$	123-05-7	1.95	52	90	113–115 (1.0)	7425-14-1
c-C_6H_9[d]	100-50-5	2.05	91	60	115–117 (0.5)	2611-00-9
C_6H_5	100-52-7	2.36	34	90	137–140 (0.2)	120-51-4
n-C_3H_7	123-72-8	3.54	82	12[c]	60–65 (12.0)	109-21-7

[a] Reactions were carried out for 6 hr at 250° using 20 g (0.32 mol) of boric acid in 200 ml of heptane or cyclohexane diluent. [b] Based on reacted aldehyde. [c] The total product contained 83% of 2-ethyl-2-hexenal and 17% of *n*-butyl *n*-butyrate. [d] 1-Cyclohex-3-enyl.

boron atom. Upon coordination with a carbonyl group and rehybridization from sp² to sp³ the boron atom would become tetracovalent and assume a formal negative charge.[5]



Addition of a second mole of aldehyde to the charged intermediate, loss of boric acid, and intramolecular hydride transfer would occur as depicted. This scheme would account for the observation that fused boric oxide is an inferior catalyst, since formation of a charged tetracovalent intermediate would become much more difficult. The decrease in rate of reaction using the relatively basic tetrahydrofuran solvent and complete inhibition by added water would be expected, since both would compete with the carbonyl group for coordination with the boron atom.

Experimental Section[6]

Disproportionation of Aldehydes over Boric Acid.—A 1-l. stainless steel Magnedrive[7] autoclave was charged with 20 g (0.32 mol) of boric acid, 200 ml of solvent, and the quantity of aldehyde shown in Table I. The autoclave was sealed, flushed with nitrogen, and heated at 250°. After cooling, the product was removed, filtered, and fractionated through a 0.75 × 36 in. helices packed column. The product esters were identified by comparison of their infrared and nmr spectra with those of authentic samples.

Boric Acid Catalyzed Reaction of *n*-Butyraldehyde.—A mixture of 255 g (3.54 mol) of *n*-butyraldehyde and 20 g of boric acid in 200 ml of heptane was heated for 6 hr at 250°. After filtration and fractionation there was obtained 45.9 g of unreacted *n*-butyraldehyde and 164.3 g of material, bp 60–65° (12 mm), which by glpc analysis (10 ft × 0.25 in. Carbowax 20M on Chromosorb P, 150°) was found to consist of 83% 2-ethyl-2-hexenal and 17% *n*-butyl *n*-butyrate.

Reaction of Benzaldehyde with *n*-Butyl Borate.—A mixture of 250 g (2.36 mol) of benzaldehyde, 21 g (0.091 mol) of freshly distilled *n*-butyl borate,[8] and 200 ml of dry cyclohexane was heated for 6 hr at 200°. The resulting product was washed with water, then with Na_2CO_3 solution, dried ($MgSO_4$), and filtered, and the cyclohexane was removed. The residue, weighing 257.3 g, was analyzed by glpc on a 10 ft × 0.25 in SE-30 on Chromosorb P column at 175° and was found to contain 9.8% of benzyl alcohol, 80.4% of benzaldehyde, and 9.1% of α-ethylcinnamaldehyde. Benzyl alcohol and α-ethylcinnamaldehyde were separated by preparative glpc and identified by comparison of infrared and nmr spectra with authentic samples.

Registry No.—Boric acid, 10043-35-3; 2-ethyl-2-hexenal, 645-62-5; *n*-butyl borate, 688-74-4.

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[5] H. Steinberg, "Organoboron Chemistry," Vol. I, Wiley, New York, N. Y., 1964, p 31.

[6] The aldehydes used were the best commercial grades and were purified by fractionation through a 36-in. helices packed column. Heptane and cyclohexane were Phillips Petroleum Co. Pure Grade materials and were used as received. Boric acid and fused boric oxide were obtained from Mallinckrodt.

[7] Autoclave Engineers, Inc., Erie, Pa.

[8] J. R. Johnson and S. W. Tompkins, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 106.

Communications

See Editorial, *J. Org. Chem.*, **38**, No. 19, 4A (1972)

1,3 Diradicals *via* Thermolysis of 1,2-Dioxolanes[1]

Summary: Stereochemical and kinetic results suggest direct deketonation of 1,2-dioxacyclopentanes on thermal activation affording 1-oxatrimethylene, which suffers a novel ring expansion.

Sir: From stereolabeling experiments[2] we rationalized that 1,2-dioxolan-3-ones **1** photodecarboxylate (eq 1) directly into the 1-oxatrimethylene diradical **2**, which serves as precursor to epoxide **4**, fragmentation ketone **5**, and the pair of rearrangement ketones **6** (~R_1) and **6′** (~R_2). However, in the thermal decomposition of **1** (eq 1), stereolabeling[3,4] and kinetic[5] experiments suggest that the 1,5-dioxa-2-oxopentamethylene diradical **3**

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[1] Paper XXVII in the Cyclic Peroxide Series. For previous paper, *cf.* W. Adam and H. C. Steinmetzer, *Angew. Chem.*, **84**, 590 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 540 (1972).

[2] W. Adam and G. Santiago Aponte, *J. Amer. Chem. Soc.*, **93**, 4300 (1971).