the butadiene moiety would determine the 6 and 7 substituents in the naphthalene product.

Electrochemistry.—Qualitatively the reduction and oxidation potentials of I correlate with the electron-donating effects of methyl groups (Table III). The peak potential (E_{peak}) for the oxidation of I exhibits a large amount of solvent dependence. The reference electrode used in these studies was an aqueous saturated calomel electrode (sce). Use of the sce introduces an unknown liquid–liquid junction potential between the sce and the electrolytic solution. Differences in the junction potential between the sce and the various solvent systems probably account for the major portion of solvent dependence of I.[4a]

TABLE III

MOLECULAR ORBITAL ENERGIES OF NAPHTHALENIC COMPOUNDS WITH THEIR REDUCTION AND OXIDATION POTENTIALS[f,g]

	Naphthalene	Dimethyl-naphthalene	Tetramethyl-naphthalene
LUMO[a,c]	−0.6180	−0.6480	−0.6770
HFMO[b,c]	+0.6180	+0.5617	+0.5083
Reduction potential	−2.58	−2.68	−2.71
Oxidation potential	+1.72[e]	+1.56[d]	1.44[d]

[a] Lowest unoccupied molecular orbital. [b] Highest filled molecular orbital. [c] These values in units of β_0. [d] These values are cyclic voltametry peak potentials taken at 0.5 V/sec. [e] Estimated from $E_{1/2}$ of +1.70 at a rotated platinum disk as determined in R. D. Rieke, W. E. Rich, and T. H. Ridgway, *J. Amer. Chem. Soc.*, **93**, 1962 (1971). [f] Data for the LUMO of naphthalene and dimethylnaphthalene are from ref *e*. The energies for the remaining MO's were determined as in ref *e*. [g] Data in volts *vs.* sce.

Experimental Section

Cyclic voltametric (CV) experiments were performed with a solid state three-electrode instrument. The cell used has been described elsewhere.[4b] The platinum bead electrode used for the oxidation work was pretreated with aqua regia for 2 min, washed with distilled water, and dried before each experiment. Melting points were taken on an oil bath type instrument and are uncorrected. Nuclear magnetic resonance spectra were recorded for solutions in carbon tetrachloride with tetramethylsilane internal reference on a JEOL-C-60-HL instrument. Gas chromatography was done with a Hewlett-Packard 5750 on a 6.5 ft × 0.25 in. 20% SE-30 on Chromosorb W column. Infrared spectra were obtained with a Perkin-Elmer 257 spectrometer.

Chemicals.—Spectro Grade acetonitrile (Matheson Coleman and Bell) was dried by addition of Al_2O_3 which had been dried at 400° for 24 hr. *n*-Butyronitrile was stirred with $KMnO_4$ and anhydrous Na_2CO_3 and heated to 70°. Fast distillation at 15 mm gave BN with an impurity evident in the uv spectrum which could not be removed by fractionation. However, this BN was acceptable, giving limits of +1.7 to −1.6 on platinum. Propylene carbonate was prepared by the method of Nelson and Adams.[5] Spectro Grade dimethylformamide obtained from Matheson Coleman and Bell was refluxed over copper sulfate through a Soxhlet containing Linde 4A molecular sieves under vacuum, not allowing the pot temperature to rise above 50°. The DMF was then distilled under vacuum into a receiver cooled to −78°, where it was stored under N_2.

Tetraethylammonium perchlorate (TEAP) was purchased from Eastman and purified by a standard procedure.[6] Tetra-*n*-butylammonium perchlorate (TBAP) was made according to a published procedure.[7]

All AN solutions were 0.1 *M* in TEAP, PC solutions were 0.25 *M* in TEAP, and BN solutions were 0.1 *M* TBAP.

In all experiments I was 1 mmol and was purified by gc.

2,3,6,7-Tetramethyl-4a,5,8,8a-tetrahydro-1,4-naphthaquinone (III).—Quinone II was prepared as described by Fieser and Ardao[2] and allowed to react with 2,3-dimethylbutadiene as has been described,[2] yielding III (73–84%), mp 104.5–105° (lit.[2] mp 103–104°), ir 1671 cm^{-1} (CH_2Cl_2).

2,3,6,7-Tetramethyl-2,3,4a,5,8,8a-hexahydro-1,4-naphthoquinone (IV).—Compound III (35.9 g, 0.165 mol) was dissolved in HOAc (180 ml) and added to a vigorously stirred suspension of activated[8] zinc dust in H_2O (100 ml). After 8 min the suspension was filtered, cooled, and diluted with H_2O to give a crop of white needles (7.0 g). The solution was then neutralized with $NaHCO_3$ and saturated with NaCl. A solid appeared at the top of the solution, and was skimmed off and extracted with acetone; the acetone was stripped off and the product was dried *in vacuo*, yielding IV (total of 21.9 g, 79%, 0.1 mol): mp 129–130° (CCl_4); ir 1708 cm^{-1} (CH_2Cl_2); mass spectrum *m/e* 220.1462 (calcd for $C_{14}H_{20}O_2$, 220.1553).

2,3,6,7-Tetramethyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene (V).—Diketone IV (28.9 g, 0.13 mol) was treated with hydrazine hydrate (115 ml, 99%) in diethylene glycol (500 ml) until all IV had dissolved. KOH (120 g) in diethylene glycol (480 ml) was added and the mixture was refluxed for 1 hr. The condenser was removed and the solution temperature was allowed to rise to 185°, at which point the condenser was replaced and the solution was refluxed for 5 hr, cooled, and extracted with petroleum ether (bp 30–60°) which was stripped off, leaving light yellow oil V (17.0 g, 67%, 0.089 mol). This product was chromatographed through a 2 × 15 cm column of Al_2O_3 with hexane, yielding a colorless liquid: nmr τ 8.175, 8.47, 8.68, 8.93, 9.05, 9.13, 9.25 (peaks overlap too much to allow valid integration); ir (neat) 2960 (w), 2904 (m), 1455 (w), 1378 (w) cm^{-1}; mass spectrum *m/e* 192.1884 (calcd for $C_{14}H_{24}$, 192.1878).

2,3,6,7-Tetramethylnaphthalene (I).—Octahydrodecalin V (3.54 g, 18 mmol) was mixed with sulfur (2.45 g, 76 mmol) and heated at 235° for 5 min. The reaction mixture was cooled and extracted with petroleum ether, which was evaporated and the residue was chromatographed on a 2 × 50 cm column of alumina (Merck) to yield I (1.51 g, 45%, 8.2 mmol). The product was light yellow, indicating an impurity: mp 188–190° (lit.[1] mp 191.0–191.5°); nmr τ 7.66 (12 H, methyl), 2.63 (4 H aromatic) (lit.[9] 7.64); mass spectrum *m/e* 184.1254 (calcd for $C_{14}H_{16}$, 184.1252).

Registry No.—I, 1134-40-3; III, 38312-84-4; IV, 38312-85-5; V, 38312-86-6.

Acknowledgment.—Partial support of this research by the National Science Foundation is gratefully acknowledged.

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[4] (a) R. P. Van Duyne, Ph.D. Dissertation, University of North Carolina at Chapel Hill, 1970, p 110. (b) See Table III, footnote *e*.

[5] R. Nelson and R. Adams, *J. Electroanal. Chem.*, **13**, 184 (1967).

[6] C. K. Mann, "Electroanalytical Chemistry," Vol. 3, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1969, p 133.

[7] Reference 6, p 132.

[8] K. Tsuda, E. Ohki, and S. Nozoe, *J. Org. Chem.*, **28**, 783 (1963).

[9] F. F.-H. Yew, R. J. Kiuland, and B. J. Mair, *Anal. Chem.*, **36**, 843 (1964).

The Reaction of Bromomethylenecyclopropane with Potassium *tert*-Butoxide

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In continuation of our study of rearrangement reactions of terminal halo olefins,[1] we report here the reaction of bromomethylenecyclopropane (1) with potas-

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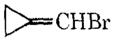
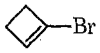
[1] K. L. Erickson, *J. Org. Chem.*, **36**, 1031 (1971); K. L. Erickson, J. Markstein, and K. Kim, *ibid.*, **36**, 1024 (1971), and references cited therein.

sium *tert*-butoxide. This compound completes the series of exocyclic vinyl halides.

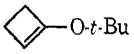
Of particular interest was whether **1** would give rise to the ring-enlarged bromide, 1-bromocyclobutene (**2**), in analogy to the bromomethylenecyclobutane system,[2] or whether it would produce instead the ring-enlarged enol ether, 1-*tert*-butoxycyclobutene (**3**), the reaction course followed by the larger ring bromomethylenecycloalkanes.[3]



1

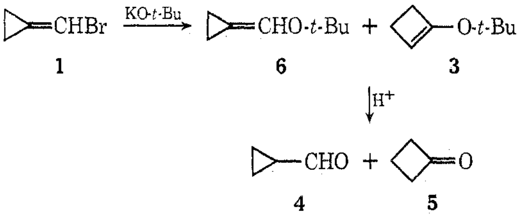


2



3

Bromomethylenecyclopropane (**1**) was prepared by bromination–dehydrobromination of methylenecyclopropane.[4,5] When **1** was treated with neat potassium *tert*-butoxide at 100°, an immediate reaction occurred. The volatile products consisted of a 1.3:1.0 mixture of cyclopropanecarboxaldehyde (**4**) and cyclobutanone (**5**). No 1-bromocyclobutene (**2**) (independently synthesized) was detected. Since the volatile products were isolated by collection on an acid-washed vapor phase chromatography column, the carbonyl compounds, rather than the *tert*-butyl enol ethers, were obtained. Spectral data on the crude products verified the presence of enol ethers.



1-*tert*-Butoxymethylenecyclopropane (**6**) most likely arises by either a displacement or an addition–elimination reaction. Several mechanisms are possible for the formation of the ring-expanded product, 1-*tert*-butoxycyclobutene (**3**). The carbenoid–cycloalkyne pathway established for the larger ring homologs[3] would involve cyclobutyne here, a somewhat unattractive intermediate. The cleavage–recombination mechanism proposed for the rearrangement of bromomethylenecyclobutane to 1-bromocyclopentene,[1] if operative here, would lead to 1-bromocyclobutene (**2**), which then needs to be converted to enol ether **3**. However, 1-bromocyclobutene appears to be stable to the reaction conditions. If **1** is not purified by vapor phase chromatography, it contains small amounts of 1-bromocyclobutene (and 1-bromo-2-methylpropene). This impure material, when treated with potassium *tert*-butoxide, gives product mixtures still containing **2**, while product mixtures from pure **1** show no detectable 1-bromocyclobutene. 1-*tert*-Butoxymethylenecyclopropane (**6**) by ring opening and reclosure could give rise to **3** directly, but it is difficult to understand why **6** would rearrange to **3** if **1** does not rearrange to **2**.

Bässler and Hanack[5] have reported the production of cyclobutanone from bromomethylenecyclopropane (**1**) under solvolytic conditions (60 or 80% aqueous ethanol at 130–150°) in the presence of triethylamine, and these authors postulate a vinyl cation intermediate. While such a cation is possible under their reaction conditions, it is highly unlikely in neat potassium *tert*-butoxide. In fact, these authors have not ruled out the possibility of the solvolysis reaction proceeding *via* a carbene–cycloalkyne or some alternate pathway. However, it does appear that a strong base is needed for ring enlargement to occur in our case. When potassium *tert*-butoxide is replaced by potassium hydroxide, the only volatile product found is cyclopropanecarboxaldehyde (**4**).

Failure to observe any 1-bromocyclobutene (**2**) in the potassium *tert*-butoxide reaction mixture indicates that the ring enlargement of halomethylenecycloalkanes to 1-halocycloalkenes is restricted to halomethylenecyclobutyl systems. The reason for this specificity is not yet known.

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer. The nmr spectra were obtained with a Jeolco Model C-60H spectrometer using tetramethylsilane as an internal standard. Vapor phase chromatographic analyses were performed with a Varian Aerograph Model 90-P3 unit. The column used was a 10 ft × 0.25 in., 20% Carbowax 20M on 60/80 Chromosorb W A/W DMCS at 100° unless otherwise noted.

Reaction of Bromomethylenecyclopropane (1) with Potassium *tert*-Butoxide. General Procedure.—Sample sizes of vinyl bromide ranged from 0.15 to 1.50 g; a 20% excess of base was used.

Potassium *tert*-butoxide was placed in a nitrogen-flushed round-bottom flask with a side arm stoppered by a serum cap. A nitrogen inlet was attached, atop which were placed two condensers. In earlier runs, a Dry Ice cooled trap was connected to the system to collect escaping volatile products, but this was found to be unnecessary.

The reaction vessel was heated to 100°, and the vinyl bromide was injected beneath the surface of the hot butoxide. Heating was continued for an additional 10–20 min, and then the mixture (dark brown) was cooled. Water was added, and extraction of this aqueous mixture with pentane or ether followed. The solvent was removed by distillation through a Vigreux column, and the residue was flash distilled. Vpc examination showed one predominant peak which was identified as a 1.3:1.0 mixture of cyclopropanecarboxaldehyde (**4**) and cyclobutanone (**5**) (combined yield ~30%). Identification was made by comparison of ir and nmr spectra and vpc retention times with those of authentic samples. There were several minor products of insufficient quantity for further study; however, none of these appeared to be 1-bromocyclobutene, as evidenced by the absence of ir absorption at 11.75 μ where **2** displays a very intense band.

Inorganic bromide determinations on the aqueous phase of the reaction mixture gave consistent values of ~83%. Polymeric material (nonbromine containing) was produced.

Reaction of Bromomethylenecyclopropane (1) with Potassium Hydroxide.—The above procedure was followed employing powdered potassium hydroxide in place of potassium *tert*-butoxide. Work-up afforded cyclopropanecarboxaldehyde (**4**) as the only identifiable volatile product, 2,4-dinitrophenylhydrazone mp 181–183° (lit.[6] mp 185.5–186.5°). No cyclobutanone was produced.

1,2-Dibromocyclobutane. A. From *trans*-Cyclobutane-1,2-dicarboxylic Acid.—To a stirred slurry of 11.65 g (0.052 mol) of red mercuric oxide and 15 ml of CCl_4 in a 100-ml round-bottom flask equipped with a condenser and drying tube and protected from light was added a slurry of 20 ml of CCl_4, 5.0 g (0.035 mol) of *trans*-cyclobutane-1,2-dicarboxylic acid, and 5.54 g (0.035 mol) of bromine. The mixture was stirred at 25° for 2 hr, during which time the induction period expired, and a vigorous reaction ensued. The mixture was then heated at 45° for 3 hr. Bromine was added in 1-g lots as the color faded. The mixture was cooled and filtered, and the salts were washed with fresh CCl_4. The

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[2] K. L. Erickson, B. E. Vanderwaart, and J. Wolinsky, *Chem. Commun.*, 1031 (1968).

[3] K. L. Erickson and J. Wolinsky, *J. Amer. Chem. Soc.*, **87**, 1142 (1965).

[4] R. Köster, S. Arora, and P. Binger, *Synthesis*, 322 (1971).

[5] T. Bässler and M. Hanack, *Tetrahedron Lett.*, 2171 (1971).

[6] L. I. Smith and E. R. Rogier, *J. Amer. Chem. Soc.*, **73**, 4047 (1951).

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).

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Boric Acid Catalyzed Tishchenko Reactions

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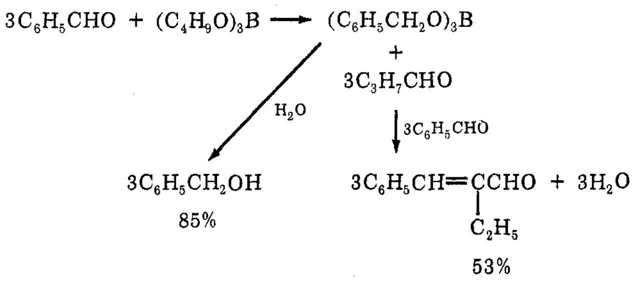
A recent article has described the use of boric acid catalysts for the aldol condensation of aldehydes and ketones.[1] It has now been found that boric acid is also an effective catalyst for the dismutation of certain aldehydes to the corresponding esters *via* a Tishchenko type reaction.[2] Aldehydes 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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[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).

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