plicity of the dienophilic fragment might simplify interpretation of the experimental results. Kinetic analysis, C^{14} tracer studies, product isolation, and structure proof are in accord with the first assumption but will be described more fully at another time. C^{13} and O^{18} isotope effects were both determined at levels of natural abundance by consecutive mass spectral analyses of purified CO_2 obtained (a) after 5–10% reaction, (b) after ten half-lives, and (c) from a commercial cylinder.[9] The results in Table I, column 2, have been corrected for instrumental "mass discrimination" and O^{17} contribution to the $m/e = 45$ peak. Other corrections were evaluated but then ignored when they proved to be less than the experimental uncertainty. These include: instrumental background, incomplete mass resolution, isotopic fractionation and/or exchange during CO_2 purification, O^{17} fractionation during decarboxylation, and C^{13} content in the $C_8H_6O_3$ fragment.

TABLE I

| | Observed | Predicted | |
		IIIA	IIIB
k_{12}/k_{13}	1.032 ± 0.001	1.0298	1.0293
k_{16}/k_{18}	1.015 ± 0.002	1.0155	1.0222
$\nu^{\pm}/\nu^{\pm}_C$		1.0073	1.0068
$\nu^{\pm}/\nu^{\pm}_O$		1.0023	1.0000
$\nu^{\pm}/\nu^{\pm}_O{}'$		1.0290	1.0455
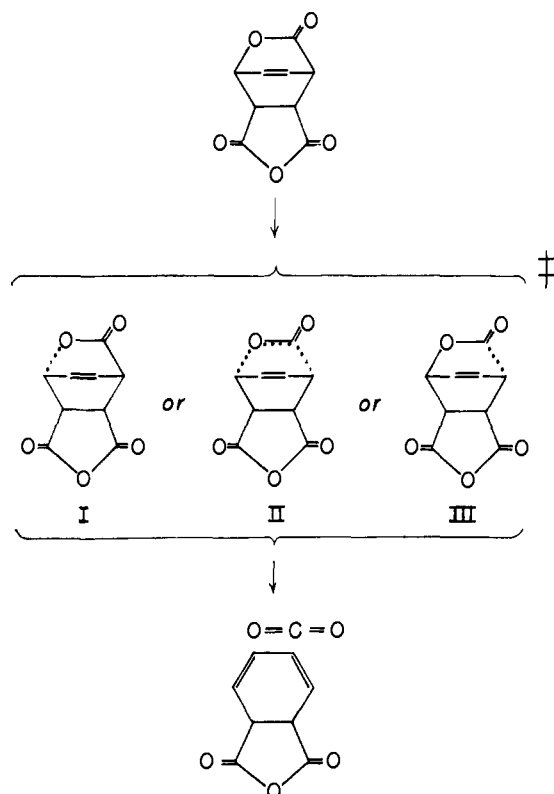
These results are most simply analyzed in terms of the idealized transition states I, II, and III. Thus, the observed k_{12}/k_{13} is sufficiently similar to those obtained in reactions where C–C cleavage is unambiguous[10] as to exclude I from further consideration.

II, however, requires more quantitative evaluation and, since we would have it encompass a wider range of possible structures, a more careful definition. This

(9) A Consolidated Engineering Corporation 21-401 mass spectrometer was used in its isotope ratio recording mode. Individual sample analyses were reproducible to ±0.02–0.05% for C and ±0.03–0.08% for O. Calculated isotope effects derive from five independent experiments for those of carbon and from three for those of oxygen. The solvent was dimethyl phthalate and the temperature was 130.1°.

(10) Malonic acid, 138°, 1.037; mesitoic acid 92°, 1.032; trichloroacetate ion, 70°, 1.034.[11a] By contrast: xanthate pyrolysis, 100°, 1.000.[7b]

is conveniently taken to be a common decomposition mode, the separation of rigid OCO' and $C_8H_6O_3$ along an axis joining their centers of mass. Mass dependence of the corresponding frequency $(\nu^{\pm})$ is thereby determined[12] and we may use the $\bar{\gamma}$-method[11b] and both our observed isotope effects to estimate the relative degrees of bond stretching at the two sites.[13]

$$\sum \frac{1/2(\Delta a^{\pm}_O + \Delta a^{\pm}_O{}')}{\Delta a^{\pm}_C} = \frac{\left(\frac{1}{12} - \frac{1}{13}\right)\left(\frac{k_{16}/k_{18}}{\nu^{\pm}/\nu^{\pm}_O} - 1\right)}{\left(\frac{1}{16} - \frac{1}{18}\right)\left(\frac{k_{12}/k_{13}}{\nu^{\pm}/\nu^{\pm}_C} - 1\right)}$$

Although it might have been anticipated that the ratio (of mean changes in force constants at oxygen to those at carbon) would be somewhat less than one,[14] the calculated value is -0.10 ± 0.09. Whether truly negative or zero, the result is sufficiently irreconcilable with the decomposition mode used to generate it as to preclude further realistic discussion of any such transition state.

Left only with III, defined by $\Delta a^{\pm}_O = \Delta a^{\pm}_O{}' = 0$, we need but choose an appropriate decomposition mode to predict k_{16}/k_{18} and so consider two possibilities: A, in which rigid OCO' and $C_8H_6O_3$ unfold about a stationary bridgehead pivot, during C–C cleavage, and B, in which O serves as pivot.[15] Prediction of k_{12}/k_{13} is inherently less reliable in this case since it requires the further ad hoc assignment of $\Delta a_C^{\pm}$ and net frequency change. The traditional[12b] values of -4.50 mdynes/Å. and 900 cm.$^{-1}$ were chosen both to avoid prejudice and to permit comparison with the evaluation of similar assumptions elsewhere.[16]

Table I clearly reveals IIIA to be the simplest description of the transition state consistent with both isotope effects. Obvious extensions of this technique to related systems are being pursued.

(11) (a) J. Bigeleisen and M. Wolfsberg, Advan. Chem. Phys., 1, 68 (1958); (b) ibid., 1, 18–26, 67 (1958).

(12) M. Wolfsberg, J. Chem. Phys., 33, 21 (1960).

(13) $\Delta a^{\pm}_C$, $\Delta a^{\pm}_O$, and $\Delta a^{\pm}_O{}'$ are the activation changes in diagonal cartesian force constants, at the carbonyl carbon, alkyl oxygen, and carbonyl oxygen, along any one of the three axes, and the sum is taken over all three axes. Subscripts following $\nu^{\pm}$ refer to the molecule bearing the heavier isotope at the position indicated. Zero time reaction and isotopic homogeneity of O and O', are implicitly assumed and can be justified under our conditions.

(14) Thermochemical data require that the CH_3–C bond in methyl acetate be weaker than the CH_3–O by some 2–14 kcal./mole.

(15) These provide the $\nu^{\pm}$ ratios by analogy with mechanical models. Cf. J. Bigeleisen and M. Wolfsberg, J. Chem. Phys., 21, 1972 (1953); ibid., 22, 1264 (1954); P. Yankwich and R. M. Ikeda, J. Am. Chem. Soc., 81, 1532 (1959).

(16) M. J. Stern and M. Wolfsberg, J. Chem. Phys., in press.

(17) Union Carbide Corporation Research Fellow, 1962–1963.

DEPARTMENT OF CHEMISTRY   M. J. GOLDSTEIN
CORNELL UNIVERSITY   G. L. THAYER, JR.[17]
ITHACA, NEW YORK

A New Boron Hydride Ion $B_9H_{14}^-$

Sir:

Decaborane is degraded in aqueous base to boric acid, hydrogen, and a new, stable boron hydride ion of the composition $B_9H_{14}^-$. The possibility that such an ion might exist has been discussed[1] and, in two instances, ultraviolet absorption maxima were observed[2] which we now suspect were due to its presence. Salts containing the anion have now been isolated and the anion has been characterized by analyses, by conversion to known compounds, and by determination of the stoichiometry of the preparative reaction.

(1) F. E. Wang, P. G. Simpson, and W. N. Lipscomb, J. Chem. Phys., 35, 1335 (1961); W. N. Lipscomb, Proc. Natl. Acad. Sci. U. S., 47, 1791 (1961).

(2) G. W. Schaeffer, J. J. Burns, T. J. Klingen, L. A. Martincheck, and R. W. Rozett, Abstracts of Papers, 135th National Meeting of the American Chemical Society, April, 1959, p. 44M; M. F. Hawthorne, A. R. Pitochelli, R. D. Strahm, and J. J. Miller, J. Am. Chem. Soc., 82, 1825 (1960).

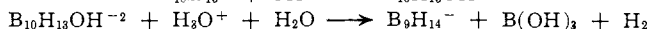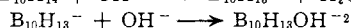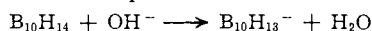Salts prepared by metathesis include cesium, triphenylmethylphosphonium, alkylammonium, and quaternary ammonium tetradecahydrononaborates$(1-)$. For example, CsB_9H_{14} was obtained in 65% yield (*Anal.* Calcd. for B_9CsH_{14}: B, 39.83; H, 5.77; mol. wt., 244. Found: B, 40.21; H, 5.17; mol. wt., 244) and $(CH_3)_4$-NB_9H_{14} in 85% yield (*Anal.* Calcd. for $C_4H_{26}B_9N$: C, 25.89; H, 14.12; B, 52.44; N, 7.55. Found: C, 25.39; H, 13.63; B, 52.24; N, 7.91).

A structural similarity between the B_9H_{14} anion and members of the B_9H_{13}(ligand) series of compounds[3] was demonstrated by the following transformations: Heating a suspension of $(CH_3)_3NHB_9H_{14}$ in benzene resulted in the elimination of hydrogen and the formation of $B_9H_{13}[(CH_3)_3N]$ in 67% yield. Similarly, treatment of $(CH_3)_4NB_9H_{14}$ with a solution of anhydrous hydrogen chloride in acetonitrile gave a 66% yield of B_9H_{13}-(CH_3CN).

Both inorganic bases such as sodium, potassium, and ammonium hydroxides as well as weak organic bases such as N-methyl- and N,N-dimethylformamide effectively degrade decaborane to the B_9H_{14} anion in aqueous solution. The course of the reaction, however, depends both on the quantity and the type of base used. Only reactions in aqueous hydroxide are summarized here. More detailed information will be reported at a later date.

When decaborane is stirred with one molar equivalent of aqueous sodium or potassium hydroxide for a period of about 12 hr., hydrogen is gradually evolved and the $B_9H_{14}^-$ ion is formed by way of an apparently complex series of reactions. With two molar equivalents of hydroxide, decaborane is quickly converted to a colorless, reasonably stable intermediate with no gas evolution. This intermediate undergoes very slow hydrolysis to $B_9H_{14}^-$. Acidification, however, effects the conversion rapidly and in high yield.

The second procedure has been studied in some detail and has been found to proceed in three discernible steps: (1) Decaborane first reacts with hydroxide to yield a yellow solution containing the $B_{10}H_{13}$ anion, identified by its ultraviolet absorption maxima at 265 and 330 mμ.[2] (2) Further reaction with hydroxide yields the intermediate anion which absorbs at 227 and 262 mμ. This ion has not been fully characterized but is believed to be a dianion of the composition $B_{10}H_{13}$-OH^{-2}, resulting from the addition of OH^- to $B_{10}H_{13}^-$. Analogous ions have been reported.[4] (3) The intermediate finally undergoes acidolysis to produce the B_9H_{14} anion ($\lambda_{max}^{H_2O}$ 271 mμ, ϵ 3980), boric acid, and hydrogen. The reaction sequence is shown in the equations

$$B_{10}H_{14} + OH^- \longrightarrow B_{10}H_{13}^- + H_2O$$
$$B_{10}H_{13}^- + OH^- \longrightarrow B_{10}H_{13}OH^{-2}$$
$$B_{10}H_{13}OH^{-2} + H_3O^+ + H_2O \longrightarrow B_9H_{14}^- + B(OH)_3 + H_2$$

The stoichiometry of the over-all process was ascertained by quantitative determination of the products and found to be in agreement with the sum of the above equations.

Acknowledgment.—This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by the Bureau of Naval Weapons, RMMP, under Contract No. NOrd 18728.

(3) B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, **1**, 626 (1962).

(4) W. H. Knoth and E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **20**, 66 (1961); B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, **1**, 622 (1962).

AMERICAN CYANAMID COMPANY   LAWRENCE E. BENJAMIN
STAMFORD LABORATORIES   STANLEY F. STAFIEJ
STAMFORD, CONNECTICUT   EDWARD A. TAKACS

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Bridged Polycyclic Compounds. XXIII. Some Carbonium Ion Reactions in Dibenzobicyclo[3.2.1]-octadiene Systems[1]

Sir:

Several examples are known demonstrating that the course of carbonium ion reactions of epimeric homoallylic compounds may be significantly different. In one system,[2,3] acetolysis of Ia resulted in complete retention of structure and configuration, forming acetate Ib, while its epimer Ic underwent Wagner–Meerwein rearrangement on hydrolysis in aqueous sodium bicarbonate, forming II. Ia solvolyzes 10^7 times faster than Ic. The reactivity and retention observed with Ia has been ascribed[2,3] to anchimeric assistance by the π-electrons of the double bond. The driving force for the solvolysis rearrangement was attributed to the formation of an allylic cation.
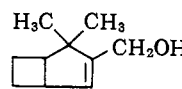
Similarly, it has been observed[4] that acetolysis of IIIa or deamination of IIIb led to unrearranged and retained IIIc or IIId, while the *syn-p*-toluenesulfonate IIIe solvolyzed with rearrangement to IV. No rate enhancement was observed with the *anti*-tosylate IIIa.
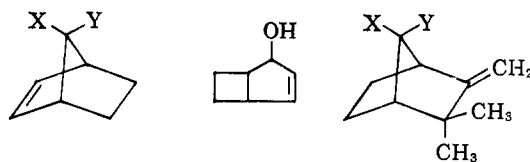
Ia, X = H, Y = OTs
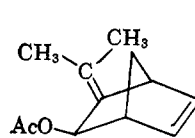Ib, X = H, Y = OAc
Ic, X = OTs, Y = H

II

IIIa, X = OTs, Y = H
IIIb, X = NH$_2$, Y = H
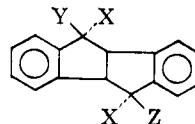IIIc, X = OAc, Y = H
IIId, X = OH, Y = H
IIIe, X = H, Y = OTs

IV

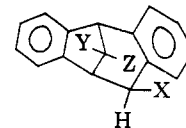Va, X = H, Y = OTs
Vb, X = H, Y = OAc
Vc, X = OTs, Y = H

VI

VIIa, X = OAc, Y = H, Z = I
VIIb, X = OAc, Y = H, Z = OAc
VIIc, X = OAc, Y = H, Z = NHAc
VIId, X = OH, Y = H, Z = NH$_2$
VIIe, X = OAc, Y = NHAc, Z = H
VIIf, X = H, Y = Cl, Z = H
VIIg, X = H, Y = H, Z = Cl

VIIIa, X = H, Y = Z = OAc
VIIIb, X = OAc, Y = Z = H
VIIIc, X = Y = Z = H
VIIId, X = H, Y = OAc, Z = H
VIIIe, X + Y = O, X + Z = O

IX

(1) Previous paper in series: S. J. Cristol and J. K. Harrington, *J. Org. Chem.*, **28**, 1413 (1963).

(2) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955).

(3) S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

(4) E. E. van Tamelen and C. I. Judd, *ibid.*, **80**, 6305 (1958).