thebaine ratios are 20:1 and 25:1 for 5-day seedlings and the budding plant, respectively. The reticuline: thebaine molar ratios are 1:10 and 1:20 for the two age groups, respectively. Thus, the condition necessary to establish reticuline as the thebaine precursor has been met.

<div align="center">TABLE I</div>

<div align="center">RETICULINE–THEBAINE RELATIONSHIPS IN BIOSYNTHESIS
WITH $^{14}CO_2$</div>

Plant age (days)	5	5	120
$^{14}CO_2$ absorbed (mc.)	2.4	3.8	3.0
Duration of exposure (hr.)	2.5	2.75	1.0
Total alkaloid activity (d.p.m./mc./per hr. exposure per g. plant)	7.0×10^4	5.4×10^4	1.5×10^4
Total thebaine d.p.m./ reticuline d.p.m.	4:1	6:1	3:1
Thebaine sp. act. (d.p.m./ μmole)	4×10^5	9×10^4	4×10^5
Reticuline sp. act.[a] (d.p.m./μmole)	8×10^6	5×10^6	1×10^7
Thebaine concn. in plant (μmoles/g.)	0.1	0.1	0.012
Reticuline concn. in plant (μmoles/g.)	0.01	0.01	0.0006
Carrier reticuline added (μmoles)	3	0	2.7
Thebaine/reticuline molar ratios[a]	10:1	10:1	20:1

[a] Calculations are based on the maximum reticuline concentration.

Even if the mass of reticuline present was so low as to escape detection by g.l.c., one would expect to see a radioactivity peak for reticuline of the same magnitude as for thebaine, unless the rate of reticuline turnover is different from that of thebaine, because the reticuline:thebaine specific activity ratio must be at least equal to their inverse mass ratio.[11] Indeed, analysis of the alkaloids from 5-day seedlings exposed to $^{14}CO_2$ as above, but with no carrier added, showed a large activity, but no mass, peak for reticuline. Thebaine showed similar activity but with a substantial mass peak. Since the ratio of the *total* activities of thebaine:reticuline was from 3 to 6:1, and both compounds are known to be recovered to the same extent, it is clear that reticuline is more rapidly turned over than thebaine. This illustrates the potential of the gas chromatographic method with simultaneous mass and activity measurement, used in conjunction with $^{14}CO_2$ feeding of plants, to detect small amounts of active metabolites and to compare specific activities of related compounds.

Further support for the view that all the carbons of reticuline are incorporated into thebaine is given by the fact that the fraction of activity in the O- and N-methyl groups is substantially the same for thebaine (20%) and reticuline (17%) from a 5-day seedling experiment.

The early appearance of high concentrations of thebaine and the high rate of incorporation of radioactivity into the total alkaloid fraction as well as into thebaine and reticuline both in seedlings and in mature

(11) Assuming the *de novo* synthesis of reticuline and thebaine is small, and an average value of activity is incorporated into both alkaloids during the period of $^{14}CO_2$ exposure.

plants should place beyond doubt the intimate involvement of these alkaloids in the economy of the plant.[12] Our findings also constitute positive evidence for the operation of the same biosynthetic relationships (*i.e.*, $CO_2 \rightarrow$ reticuline $\rightarrow$ thebaine $\rightarrow$ codeine $\rightarrow$ morphine) in seedlings as in mature plants.[13,14]

(12) J. W. Fairbairn and G. Wassel, *Phytochemistry*, **3**, 253 (1964), present additional evidence for active metabolic roles for the morphine-type alkaloids, as suggested by the re-feeding experiments of F. R. Stermitz and H. Rapoport.[2]

(13) J. Massicot, *Ann. Pharm. Franc.*, **19**, 44 (1961), suggested that different metabolic pathways for the morphine-type alkaloids exist in seedlings compared with mature plants.

(14) D. Neubauer, *Planta Med.*, **12**, 43 (1964), presented negative though complementary evidence to support this view.

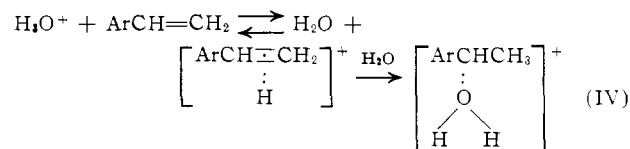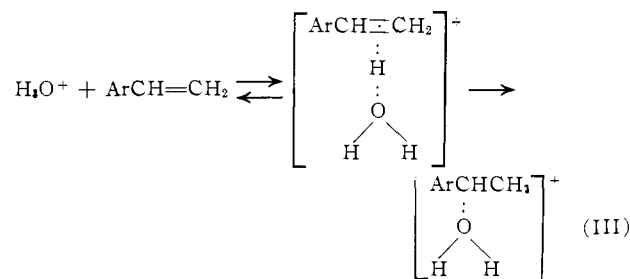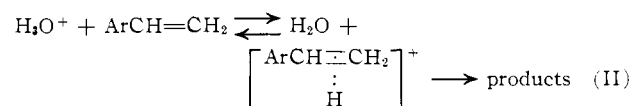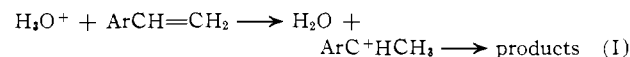(15) U. S. Public Health Service Postdoctoral Fellow.

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<div align="center">The Hydration of Styrenes</div>

Sir:

We have obtained evidence consistent with the rate-determining step in the hydration of styrenes being a proton transfer to styrene to form a carbonium ion (mechanism I). Rate-determining rearrangement of an "unencumbered" π-complex between olefin and a proton is excluded (mechanism II).[1]

$$H_3O^+ + ArCH{=}CH_2 \longrightarrow H_2O + ArC^+HCH_3 \longrightarrow \text{products} \quad (I)$$

$$H_3O^+ + ArCH{=}CH_2 \rightleftharpoons H_2O + \left[\begin{array}{c} ArCH{\dot{=}}CH_2 \\ \vdots \\ H \end{array} \right]^+ \longrightarrow \text{products} \quad (II)$$

$$H_3O^+ + ArCH{=}CH_2 \rightleftharpoons \left[\begin{array}{c} ArCH{\dot{=}}CH_2 \\ \vdots \\ H \\ \vdots \\ O \\ H \diagdown H \end{array} \right]^+ \longrightarrow \left[\begin{array}{c} ArCHCH_3 \\ \vdots \\ O \\ H \diagdown H \end{array} \right]^+ \quad (III)$$

$$H_3O^+ + ArCH{=}CH_2 \rightleftharpoons H_2O + \left[\begin{array}{c} ArCH{\dot{=}}CH_2 \\ \vdots \\ H \end{array} \right]^+ \xrightarrow{H_2O} \left[\begin{array}{c} ArCHCH_3 \\ \vdots \\ O \\ H \diagdown H \end{array} \right]^+ \quad (IV)$$

The following results have been obtained: (1) Values of the first-order rate constant for hydration, k_{obsd}, and of [Sty]/[ROH] at equilibrium were determined spectrophotometrically in 5–7 M perchloric acid (covering about a 15% range of acid strength) for styrene and four *para*-substituted styrenes. Due to lack of space, only those values of k_{obsd} ($k_{obsd} = k_{hydr} + k_{dehydr}$) and K ($K = k_{dehydr}/k_{hydr}$) obtained in the lowest and highest perchloric acid molarities in each case are listed in Table I. The ratio [Sty]/[ROH] = K was small and showed little sensitivity to perchloric acid molarity or temperature. Consequently, errors in

(1) R. H. Boyd, R. W. Taft, Jr., A. P. Wolf, and D. R. Christman, *J. Am. Chem. Soc.*, **82**, 4729 (1960), and earlier references.

TABLE I

RATE AND EQUILIBRIUM RESULTS FOR THE HYDRATION OF STYRENES AT 25°

Compd.	HClO$_4$, M	$10^4 k_{obsd}$	$100 \times K^a$	H_0 slope^b	H_R' slope^c	$k_H/k_D{}^d$
C$_6$H$_5$CH=CH$_2$	4.59	0.566	2.3	1.23^e	0.71	2.27
	7.41	85.5	2.6			3.29
C$_6$H$_5$CD=CH$_2$	5.72	4.15^f	1.8			
C$_6$H$_5$CH=CD$_2$	5.72	3.95^f	. . .			
p-CH$_3$OC$_6$H$_4$CH=CH$_2$	0.102	0.091	2.6	1.27	0.62	. . .
	3.53	50.1	3.2			1.93
p-CH$_3$C$_6$H$_4$CH=CH$_2$	3.53	1.68	2.1	1.33	0.64	2.43
	5.50	36.7	2.5			2.24
p-ClC$_6$H$_4$CH=CH$_2$	4.60	0.200	2.5	1.24	0.69	2.29
	7.41	29.5	2.5			4.00
p-NO$_2$C$_6$H$_4$CH=CH$_2$	6.93	0.161^g	8.5^g	1.23	0.70	1.95
	9.39	21.6^g	11.7^g			2.21
p-CH$_3$OC$_6$H$_4$C=CH$_2$ │ CH$_3$	0.102	9.68				2.23

^{a} K = [Sty]/[ROH] at equilibrium. ^{b} $-$d log $k_{hydr}/$dH_0. ^{c} $-$d log $k_{hydr}/$dH_R', where H_R' = H_R $-$ log a_{H_2O}. ^{d} Ratio of k_{hydr} in HClO$_4$ to that in DClO$_4$. ^{e} Average slope of curved plot ranging in slope from 1.13 to 1.33. ^{f} For styrene in the same HClO$_4$ molarity, k_{obsd} = 4.06 × 10^4 sec.$^{-1}$. ^{g} Determined at 50°.

evaluating K led to very small errors in k_{hydr}, but large errors in k_{dehydr}. (2) Plots of log k_{hydr} against either $-H_0$ or $-H_R'$ are linear except for styrene, which gave somewhat curved plots (see Table I). (3) A plot of log k_{hydr} in 3.83 M HClO$_4$ against σ^+ is linear with slope ρ = -3.42 ± 0.08 and r = 0.999. The linear H_0 plots were used to extrapolate log k_{obsd} for some of the styrenes to a common acidity. (4) There is no exchange in the forward hydration of styrene-β,β-d_2, as evidenced by complete retention of deuterium after 15% reaction. (5) No detectable secondary isotope effect was found in the hydration of styrene-α-d (k^H/k^D = 0.97 ± 0.03) or styrene-β,β-d_2 (k^H/k^D = 1.02 ± 0.03). (6) An appreciable positive solvent isotope effect was observed in the hydration of all the styrenes (see Table I). (7) The hydration of p-methoxy-α-methylstyrene showed general acid catalysis in dilute formic acid–formate ion buffers (Table II). The catalytic expression is: k_{obsd} = 0.0955·[H$_3$O$^+$] + (6 × 10^{-4})[HCO$_2$H].

TABLE II

HYDRATION OF p-METHOXY-α-METHYLSTYRENE IN FORMATE BUFFERS AT 50°

[HCO$_2$H], M	[HCO$_2$Na], M	[NaClO$_4$], M	$10^5 k_{obsd}$
0.0200	0.0100	0.0900	6.03 ± 0.04
0.0600	0.0300	0.0700	7.42 ± 0.04
0.1000	0.0500	0.0500	8.24 ± 0.08
0.1400	0.0700	0.0300	9.65 ± 0.07

The simplest mechanism consistent with all the known facts is mechanism I. The lack of exchange in the hydration of styrene-β,β-d_2 shows that any intermediate species in which the β-hydrogens are equivalent, e.g., the unencumbered carbonium ion, must be irreversibly formed in the forward direction. The magnitude of ρ indicates a fairly large degree of carbonium ion character in the transition state.

Mechanism I is consistent with the appreciable solvent isotope effects and the finding of general-acid catalysis in the hydration of p-methoxy-α-methylstyrene. It also is consistent with the observation of Grunwald that the racemization and O^{18} exchange rates of α-phenylethyl alcohol are much larger than

the dehydration rate, with k_{exch}/k_{rac} being 0.82.[2] Rate-controlling rearrangement of an unencumbered π-complex[1] (mechanism II) is excluded by the finding of general catalysis and possibly also the relatively large solvent isotope effects (cf. ref. 3 and 4). The rate-determining rearrangement of an encumbered π-complex to an encumbered carbonium ion (mechanism III) or the rate-determining attack of water on a nonencumbered π-complex to form an encumbered carbonium ion (mechanism IV) cannot strictly be excluded. In these mechanisms, suggested by Taft,[1] the transition state of the rate-determining step would have the same formal composition as that in mechanism I.

The magnitudes of the solvent isotope effects are generally comparable to those found in other assigned rate-determining proton transfers to carbon, such as σ-complex formation in aromatic hydrogen exchange,[5] deboronation,[6] and deformylation.[7] There is a tendency for the solvent isotope effect to increase, for any particular styrene, as perchloric acid molarity is increased. This may be a reflection of decreased water solvation of H$_3$O$^+$ relative to the transition state as a_{H_2O} decreases (cf. ref. 5b).

From the values of $-$d log $k_{hydr}/$dH_0 and $-$d log $k_{hydr}/$dH_R' (Table I), it is seen that the acidity dependence of the hydration rates lies roughly half-way between H_0 and H_R'. No systematic variation of these slopes with para substituent is apparent. The fact that the H_0 plots are linear cannot be given any special significance (cf. ref. 1, 4, and 8). However, the steepness of the acidity dependence of the rates indicates that the transition state is relatively weakly solvated by water.[1,4,8] In terms of mechanism I this could be a reflection of (1) a fairly large degree of

(2) E. Grunwald, A. Heller, and F. S. Klein, J. Chem. Soc., 2604 (1957).

(3) C. A. Bunton and V. J. Shiner, Jr., J. Am. Chem. Soc., 83, 42, 3207, 3214 (1961).

(4) C. G. Swain and E. R. Thornton, ibid., 83, 3844 (1961).

(5) (a) J. Schulze and F. A. Long, ibid., 86, 331 (1964); (b) A. J. Kresge and Y. Chiang, ibid., 84, 3976 (1962); (c) V. Gold, R. W. Lambert, and D. P. N. Satchell, J. Chem. Soc., 2461 (1960).

(6) H. G. Kuivala and K. Nahabedian, J. Am. Chem. Soc., 83, 2159 (1961).

(7) W. M. Schubert and P. C. Myhre, ibid., 80, 1755 (1958).

(8) W. M. Schubert and R. H. Quacchia, ibid., 85, 1278 (1963), and references therein.

proton transfer having occurred in the transition state (*i.e.*, low degree of positive character of the O–H protons) and, concommitantly, (2) a good distribution of positive charge in the organic portion of the transition state. The transition state in the hydration of aliphatic olefins appears to be more strongly solvated since the acidity dependence of the rates is less steep ($-\mathrm{d} \log k_c/\mathrm{d}H_0$ is around unity for a number of alkenes[1]). Perhaps this is due to the proton having been transferred to a lesser extent in the transition state; *i.e.*, the transition state has greater oxonium ion character. This would be consistent with the small solvent isotope effects found.[1] On the other hand, the small isotope effect in the hydration of aliphatic olefins has been attributed to nearly complete proton transfer in the transition state.[3] In that event, proton transfer in the transition state of styrene hydration may be less complete. The steeper acidity dependence of styrene hydration then could be attributed to a more efficient distribution of the positive charge in the organic portion of the transition state.

The lack of a detectable isotope effect in the hydration of styrene-β,β-d_2 and of styrene-α-d is consistent with mechanism I. The α-C–D isotope effect would be minimized by the α-carbon being trigonal in the transition state as well as the ground state. In mechanism I, the change that occurs at the β-carbon resembles that of σ-complex formation in aromatic substitution. Secondary isotope effects in the latter reaction also are absent or very small.[9]

(9) E. A. Halevi, "Secondary Isotope Effects," in "Progress in Physical Organic Chemistry," Vol. 1, Interscience Publishers, Inc., 1963, p. 109, and references therein.

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The Molecular Symmetry of Iodopentaborane

Sir:

The compounds formed by the direct attack of elemental iodine on pentaborane(9) in excess pentaborane-(9) at 70°[1] has been shown to be 1-iodopentaborane-(9); that is, the iodine atom is bonded to the apical boron of the tetragonal boron pyramid as shown in Fig. 1.

Since the compound is sensitive to air, single crystals were grown from the melt in thin-walled Pyrex capillaries. The unit cell is monoclinic with $a = 11.24$, $b = 10.03$, $c = 13.14$ Å., and $\beta = 110°5'$. $Z = 8$ and the space group is C2/c.

The structure was solved by the heavy atom technique using partial three-dimensional data obtained on a Buerger precession camera at $-25°$. The R value with individual isotropic temperature factors is 13.0 for the 529 reflections.

The space group places no symmetry requirements on the molecule. However, the measured bond distances and bond angles show that within experimental

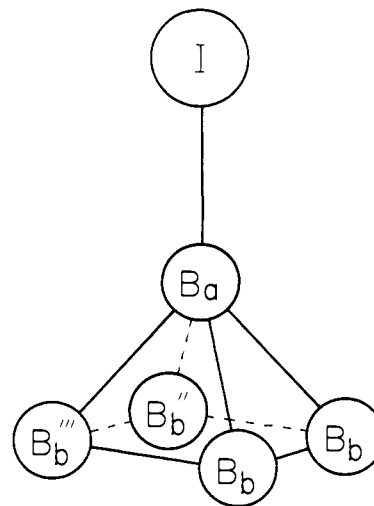(1) L. H. Hall, W. S. Koski, and V. V. Subbanna, *J. Am. Chem. Soc.*, **86**, 1304 (1964).

Fig. 1.—Molecular structure of B_5H_8I: bond distances are B_a–I = 2.20 ± 0.03, B_a–B_b = 1.71 ± 0.05, B_b–B_b = 1.84 ± 0.05 Å.; bond angles are $\angle B_b$–B_a–$B_b{}' = 65.0 ± 1.5°$, $\angle I$–B_a–$B_b = 130.5 ± 1.5°$, and $\angle B_b$–I–$B_b = 30.0 ± 1.0°$. The listed errors are estimated errors.

error the molecule nearly possesses a four-fold axis. The boron(apical)–boron(basal) average bond distance is 1.71 Å. with values ranging from 1.70 to 1.72 Å. The boron(basal)–boron(basal) average bond distance is 1.84 Å. with values ranging from 1.78 to 1.95 Å. A complete discussion will be presented in a later paper.

These results confirm the n.m.r. work of Schaeffer, *et al.*,[2] who concluded that the monoiodide of pentaborane(9) is apically substituted. It is to be noted that the boron–iodine bond distance in B_5H_8I, 2.20 Å., is somewhat longer than the boron–iodine distance in BI_3, 2.10 Å.[3]

(2) R. Schaeffer, J. N. Shoolery, and R. Jones, *ibid.*, **80**, 2670 (1958).
(3) M. A. Ring, J. D. H. Donnay, and W. S. Koski, *Inorg. Chem.*, **1**, 109 (1962).
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Blocked Rotation in Hexaisopropylbenzene. Evidence for Cyclobutadiene Intermediates in the Trimerization of Diisopropylacetylene by Dicobalt Octacarbonyl[1,2]

Sir:

The Fisher–Hirschfelder model of hexaisopropylbenzene (see Fig. 1) can only be constructed with great difficulty because of the requirement that each isopropyl group exactly interlock with its neighbors on either side. This can only be accomplished if (as shown) all of the

(1) Crowded Benzene Compounds. III. Ref. 3 and 4 are parts I and II in this series.
(2) This work was supported at various stages by NIH Grant CA-05512 and NSF Grant GP-2014, for which we are most grateful.
(3) E. M. Arnett, M. E. Strem, and R. A. Friedel, *Tetrahedron Letters*, No. 19, 658 (1961).
(4) E. M. Arnett and M. E. Strem, *Chem. Ind.* (London), 2008 (1961).