Secondary Deuterium Kinetic Isotope Effects in Radical-Forming Reactions. II. The Decomposition of t-Butyl Perpivalate

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Abstract: Measurement of the rates of decomposition of t-butyl perpivalate and its deuterated analog show the secondary deuterium kinetic isotope effect on the formation of t-butyl radical is 1.02 per deuterium. The theories proposed to explain these isotope effects are compared using the present data and that for the formation of t-butyl cation.

While the effect of substitution of deuterium for hydrogen on the rates of a large number[2] of reactions leading to cationic intermediates have been determined, almost no attention has been given to these effects in radical-forming processes. The earliest report of such an isotope effect in a radical reaction was that for the autoxidation of cumene which indicated the magnitude of k_H/k_D to be 1.10.[3] The effects have also been measured[4] for radical addition to olefins but the interpretation in these cases is complicated by opposing α and β effects which operate simultaneously. In a study directed mainly at determining the magnitude of α isotope effects in concerted acyl peroxide cleavage, a preliminary measurement of the effect of partial β deuteration on the rate of decomposition of t-butyl perhydratropate was also reported.[5] Here the isotope effect was found to be quite small ($k_H/k_D \sim 1.02$). This small[6] isotope effect for the formation of α-phenethyl radical in the converted decomposition of the corresponding perester was at odds with that reported for the formation of cumyl radical and also at odds with some theories[2] of the origin of these isotope effects in general. It was thus decided to measure the β deuterium secondary kinetic isotope effect on the formation of t-butyl radicals in the decomposition of t-butyl perpivalate.

It has previously been shown[7] that the decomposition of this compound is concerted. Therefore, t-butyl radical character is present in the over-all rate-determining transition state. Since nine deuterium atoms can be incorporated, a reduction in the relative error of the measurements was anticipated. In addition, a comparison of the isotope effects for formation of radicals and cations of the same formal structure should be helpful in providing a distinction between the theories proposed to account for these isotope effects. The isotope effect on the solvolysis of t-butyl chloride has been determined by several groups.[8]

While these studies were in progress, a report of the β isotope effect on the formation of α-phenethyl radical in the decomposition of the corresponding azo compound appeared.[9] The isotope effect observed in this case was in agreement with that estimated for the decomposition of the perhydratropate but with greatly increased accuracy.

Results

Deuterated pivalic acid was obtained from t-butyl chloride-d_9 by a Grignard sequence. The peresters were obtained by the Bartlett[7] method and purified by column chromatography. Their deuterium content was estimated by a quantitative nmr technique. Purity was judged by their nmr and infrared spectra and by reproducibility of the rate constants upon repurification.

The rates were measured in purified solvents by disappearance of the infrared carbonyl adsorption (k_{IR}) at 1772 cm^{-1} and by pseudo-first-order[10] and zero-order disappearance[11] of galvinoxyl (k_G) using its visible absorption at 770 mμ. The results of these studies are summarized in Table I.

The stated errors are for completely reproduced experiments in which each compound was resynthesized from a different batch of t-butyl chloride. Decompositions in different batches of purified solvent and the decomposition of the undeuterated perester obtained from a commercial batch of pivalic acid all showed rate behavior within the stated uncertainty. The rate constants were obtained from a linear least-squares treatment of the data.[12] All rate plots were linear for at least three half-lives.

The rate constants obtained by the infrared method were invariably higher than those observed by the galvinoxyl method. Both the presence of a good radical scavenger and the low perester concentrations used in the galvinoxyl method should tend to decrease the relative importance of any radical-induced paths for destruction of perester. The difference in the rates obtained by the two methods might, therefore, be a consequence of some induced decomposition remaining

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(4) A. P. Stefani, M. Szwarc, and M. Feld, ibid., 84, 4451 (1962); W. A. Pryor, R. W. Henderson, R. A. Patsiga, and N. Carroll, ibid., 88, 1199 (1966).
(5) T. Koenig and W. Brewer, Tetrahedron Letters, 2773 (1965).
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(7) P. D. Bartlett and R. R. Hiatt, J. Am. Chem. Soc., 80, 1398 (1958); P. D. Bartlett and D. M. Simmons, ibid., 82, 1753 (1960).

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Table I. Rates[a] of Decomposition of t-Butyl Perpivalate and t-Butyl Perpivalate-d_0

Perester	Temp, °C	$k_{IR} \times 10^4$ sec^{-2}	k_{H_9}/k_{D_9}	$k_G \times 10^4$ sec^{-1}	k_{H_9}/k_{D_9}	n^e
H$_9$[b]	60.56	0.419 ± 0.010	1.16 ± 0.03	0.400 ± 0.015	1.24 ± 0.04	1.07
D$_9$[b]	60.56	0.361 ± 0.003		0.324 ± 0.005		1.14
H$_9$[b]	74.04	2.27 ± 0.056	1.14 ± 0.03	1.93 ± 0.036	1.22 ± 0.03	1.17
D$_9$[b]	74.04	1.995 ± 0.027		1.57 ± 0.032		1.16
H$_9$[c]	60.56			0.626 ± 0.021	1.25 ± 0.03	0.68
D$_9$[c]	60.56			0.505 ± 0.010		0.56
H$_9$[d]	60.56			0.650 ± 0.012	1.23 ± 0.02	
D$_9$[d]	60.56			0.527 ± 0.010		

[a] Averages of from 3 to 11 runs. Linear least-squares treatment of individual runs gives standard deviations of less than 2% for three half-lives in all cases. Stated uncertainties are average deviations. [b] Chlorobenzene. [c] 90% Aqueous dioxane. [d] A second batch of 90% aqueous dioxane. [e] Moles of galvinoxyl decolorized per mole of peroxide.

Table II. Zero-Order Rates of Decomposition of t-Butyl Perpivalate at 60.56°

$[G]_0$, $M \times 10^3$	$[P]_0$, $M \times 10^3$	n^a
3.14	4.42	0.878
3.14	8.84	0.833
3.14	26.5	0.730
3.41	32.8	0.722
3.14	35.4	0.709
3.32	58.9	0.687

[a] Assuming a k_G of 4.188 × 10^{-5} sec^{-1}.

under the conditions of the infrared measurement. The data of Table II support this interpretation.

A clearly defined increase in n, the moles of radicals trapped/mole perester consumed, with decreasing initial perester concentration was observed by the zero-order[11] galvinoxyl method. Since the products of the reaction include a large amount of polymer, the details of this radical-induced path are obscured. However, we believe the data of Table II establish that such a path exists and therefore that the galvinoxyl rates are more nearly correct. The intervention of such a radical-induced path would tend to decrease the isotope effect if it is isotopically insensitive. This would explain the lower magnitude of the isotope effect obtained by the infrared method.

The gaseous products of the decomposition were examined briefly, and the results are summarized in Table III.

Table III. Gaseous Products of Decomposition at 60.56°

Product	Yield, moles/mole Chlorobenzene	90% aqueous dioxane
Carbon dioxide	0.908	0.874
Isobutane	0.134	0.381
Isobutylene	0.109	0.477
Methane	0.103	0

In chlorobenzene, the yields of carbon dioxide, isobutylene, and isobutane are comparable to those obtained previously.[7] The yields of these hydrocarbons are higher in the aqueous dioxane. The t-butyl alcohol obtained from decomposition of the deuterated perester in aqueous dioxane was shown to contain no deuterium. This indicates that none of the ionic processes such as

carboxy inversion[13] or t-butyl cation formation[14] are likely in this case.

Discussion

The results of the preceding section indicate that k_H/k_D for the formation of t-butyl radical from the corresponding perester is 1.02. This value is slightly higher than that observed for the formation of α-phenethyl radical ($k_H/k_D = 1.017$) in the decomposition of the corresponding azo compound.[8] Though the isotope effect is small, it is much larger than effects calculated for transition states which do not involve perturbations of the C–H force constants.[9,15] It is, however, much smaller than the effect ($k_H/k_D \sim 1.11$) observed for formation of t-butyl cation under a variety of conditions.[8] The fact that the isotope effect is nearly the same in the more basic aqueous dioxane shows the polar character, necessitated for the transition state of concerted decomposition of ring-substituted t-butyl perphenylacetates ($P = -1.09$),[16] is apparently not pronounced enough to cause carbonium ion type isotope effect to be admixed in this case. This result is in accord with the small solvent effect on the over-all rate of decomposition. The data at the second temperature in chlorobenzene indicate the small observed isotope effects are not a result of proximity to an isokinetic temperature.

Theories of the β Effect. Though these isotope effects have been known for a number of years, there is no general agreement on the details of their origin. The theories proposed to explain them include pure steric effects,[17] large decrease in C–H bending frequency in the hyperconjugatively stabilized transition states,[18] decreased stretching frequency in the hyperconjugatively stabilized transition states,[19] hyperconjugative effects plus solvation,[20] and decreased zero-point energy due to hyperconjugation and anharmonicity.[21] The latter theory is a quantitative one in which isotope effects have been identified with the loss in resonance energy due to the decrease in the average C–D bond length

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(16) P. D. Bartlett and C. Rüchardt, J. Am. Chem. Soc., 82, 1756 (1960).
(17) H. C. Brown and G. J. McDonald, ibid., 88, 2514 (1966); H. C. Brown, M. Azzaro, J. Koelling, and G. J. McDonald, ibid., 88, 2520 (1966).
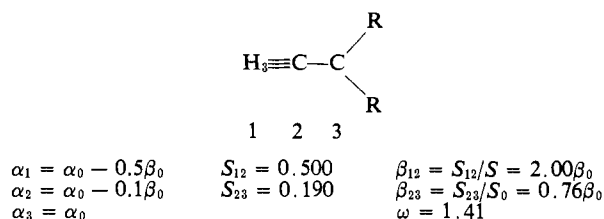(18) A. Streitwieser, R. Jagow, R. Fahey, and S. Suzuki, ibid., 80, 2326 (1958).
(19) E. S. Lewis, Tetrahedron, 5, 143 (1959).
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(21) A. Ron, E. A. Halevi, and R. Pauncz, J. Chem. Soc., 630 (1960).

and bond angle as calculated by molecular orbital methods.[22]

Most of these theories have the concept of hyperconjugative stabilization of radicals and cations as a common beginning point. In order to compare the predictions of these various theories for radical- and cation-forming processes, molecular orbital calculations for the ethyl, isopropyl, and t-butyl radicals and cations were carried out using essentially the parameterization of Colpa and DeBoer.[23,24] In these calculations, the three hydrogen 1s and methyl carbon atomic orbitals are transformed into pseudo-group orbitals, one of which, in each case, has the proper symmetry for linear combination with the 2p vacancy at the central carbon.

$$H_3 \equiv C - C \Big\langle \begin{matrix} R \\ R \end{matrix}$$

$$\begin{matrix} 1 & 2 & 3 \end{matrix}$$

$$\alpha_1 = \alpha_0 - 0.5\beta_0 \qquad S_{12} = 0.500 \qquad \beta_{12} = S_{12}/S = 2.00\beta_0$$
$$\alpha_2 = \alpha_0 - 0.1\beta_0 \qquad S_{23} = 0.190 \qquad \beta_{23} = S_{23}/S_0 = 0.76\beta_0$$
$$\alpha_3 = \alpha_0 \qquad\qquad\qquad\qquad\qquad \omega = 1.41$$

The results of the calculations with these parameters, are summarized in Table IV.

Table IV. Molecular Orbital Results

Species	DE^a	ΔDE^b	Den.^{c}	$\Delta P_{12}{}^d$	$\pi_{12,12}{}^e$	$k/k'{}^f$
$C_2H_5{}^+$	0.6967	216	0.592	0.072	0.454	1.96
$C_2H_5 \cdot$	0.1025	54	0.860	0.025	0.077	1.11
$C_3H_7{}^+$	0.9190	288	0.468	0.048	0.283	2.27
$C_3H_7 \cdot$	0.2020	102	0.758	0.022	0.067	1.20
$C_4H_9{}^+$	1.1088	330	0.404	0.037	0.203	2.38
$C_4H_9 \cdot$	0.2952	144	0.678	0.020	0.055	1.26

^{a} The delocalization energy in units of β_0, the bond integral for benzene. ^{b} Decrease in delocalization energy (in cal/mole) for the deuterated compound due to increased S_{12} assuming $\beta_0 = 60$ kcal/mole. ^{c} Spin or positive charge density at the central carbon for the radicals or cations, respectively. ^{d} Decrease in bond order per C–H bond, i.e., $1 - [(2 + P_{12})/3]$. ^{e} Self-polarizability of the π C=H bond. ^{f} Total calculated isotope effect for the fully β-deuterated intermediates at 300°K.

Ideally, these calculations should predict the resonance energy and spin density for the radicals and resonance energy and charge density for the cations. The calculated resonance energy is in fair agreement with experiment[27] for the radicals, but somewhat low for the cations in the gas phase assuming β_0 is 60 kcal/mole. The delocalization of both spin[28] and charge appears to be overemphasized when compared to esr[29] and nmr[30] results for the species in solution.[31]

(22) We are grateful to Professor Halevi for helpful discussions concerning the interpretation of his theory.

(23) J. P. Colpa and E. DeBoer, Mol. Phys., 7, 333 (1963).

(24) An excursion into the variation in parameters and methods of iteration including those of Chesnut,[25] Halevi,[21] and Mulliken[26] indicates none of the conclusions made here would be significantly altered by a different choice.

(25) D. B. Chesnut, J. Chem. Phys., 29, 43 (1958).

(26) N. Mueller and R. Mulliken, J. Am. Chem. Soc., 80, 3489 (1958).

(27) J. Franklin and H. Tumpkin, J. Chem. Phys., 20, 745 (1952).

(28) The application of the McLachlan perturbation formula to wave functions obtained here gives an increase in calculated spin density at the central carbon which makes the agreement with the esr measurements better: A. D. McLachlan, Mol. Phys., 3, 233 (1960).

(29) R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 39, 2147 (1963).

(30) G. Olah, E. Baker, J. C. Evans, W. Tolgyesi, J. McIntyre, and I. Bartein, J. Am. Chem. Soc., 86, 1360 (1964).

The calculated changes in resonance energy for the deuterated intermediates, listed in the third column of the table, are arrived at by increasing S_{12} by 0.0025 according to the arguments of Halevi[2,21] but without consideration of the inductive effect of deuterium. The change for the t-butyl radical is close to the observed isotope effect. The similarity calculated by this method for the radical- and cation-forming processes is, however, too great even without consideration of the greater electropositivity of deuterium.[32]

In order to examine the molecular orbital predictions of the relative isotope effects due to changes in vibrational frequency, several assumptions are necessary. (a) Streitwieser's[18] simplification of the complete equation for calculation of isotope effects in terms of vibrational frequencies is used.

$$\ln k_H/k_D = (0.187/T)\Sigma(\nu - \nu^{\pm}) \qquad (1)$$

(b) The differences between transition and intermediate states and between gas phase and solution are neglected in the beginning but discussed later. (c) The drastic[33] assumption is made that all of the vibrational frequencies which are important in determining the magnitude of the isotope effect will vary in proportion to the change in the C–N stretching force constant. This last assumption allows a simplification of (1) to

$$\ln k_H/k_D = (0.187/T)\Delta\gamma_{eff} \qquad (2)$$

where $\Delta\gamma_{eff}$ is the effective frequency change on going from initial to transition state which is assumed to be proportional to the change in force constant for C–H stretching. The problem now becomes one of relating the molecular orbital wave functions to change in force constant for C–H stretching since

$$\Delta\gamma_{eff} = \gamma_{eff}(1 - \sqrt{F'/F_0})$$

where γ_{eff} is an effective frequency and F' and F_0 are the force constants for the C–H stretching in the transition and beginning states, respectively.

It can be seen immediately that the isotope effects for the radical- and cation-forming processes will be too similar in magnitude if one assumes the changes in force constants to be proportional to changes in bond order.[34] Salem[35] has shown, in fact, that the bond order terms for changes in force constants cancel and that the actual changes should be porportional to the self-polarizability of the bond. Adapting this method to the present problem gives

$$F'/F_0 = 1 + C\pi_{12,12}\beta_0 \qquad (3)$$

(31) Application of Simpson's truncated perturbation method to these molecules, parameterizing with the measured resonance energies and estimated heats of formation of the ethyl radical and cation structures, gives charge and spin densities which are very close to those calculated here. This method, however, predicts no electronic transitions for the t-butyl cation below 220 mμ: W. T. Simpson and C. W. Looney, ibid., 76, 6285 (1954).

(32) A more refined version of this type of calculation gives better agreement: S. Ehrenson, private communication.

(33) In general, this is indeed a drastic assumption, but in terms of molecular orbital theory, it has some merit. For example, as the C≡H3 π bond weakens, the C–C π bond must strengthen. The effect also appears to be dominated by the stretching mode change.

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The infrared spectrum of *t*-butyl cation in solution has recently been measured and a normal mode analysis carried out.[30] The set of frequencies obtained from this analysis predicts an equilibrium isotope effect for formation of the cation which is nearly identical with the kinetic isotope effect observed for the solvolysis of *t*-butyl chloride.[36] These data provide a method of parameterizing eq 3 so that self-polarizability can be used to predict secondary isotope effects. The F'/F_0 ratio used in this normal mode analysis is 0.885 and k_{H_9}/k_{D_9} for solvolysis of *t*-butyl chloride at 25° is 2.38. These data give

$$\ln k_H/k_D = (482/T)(1 - \sqrt{1 - 0.572\pi\beta}) \quad (4)$$

where the constants have been taken into account and π is the self-polarizability of the C≡H$_3$ π bond. The last column of Table IV gives the calculated isotope effect of all the compounds shown using this parameterization. The observed total isotope effect for formation of the *t*-butyl radical is very close to the value calculated here.

The relatively small isotope effect now established for radical formation is thus in agreement with the extent to which hyperconjugation stabilizes such molecules. The calculated self-polarizability of the C≡H$_3$ π bond in the α-phenethyl radical is nearly identical with that for *t*-butyl and thus an identical isotope effect would be predicted by the present theory. We believe the lower value for this isotope effect observed by Seltzer is due to a decrease in the relative endothermicity of azo compound compared to perester decomposition and that the isotope effect in the perhydratropate decomposition will be closer to that observed for the perpivalate. This point is being tested presently.

The good quantitative agreement for the *t*-butyl radical and cation systems should be viewed cautiously because of the assumptions made. Two complications with assumption b are apparent. One is the difference in degree of planarity of the transition states for radical- and cation-forming processes. Preliminary calculations using the extended Hückel method[37] indicate that the isotope effect should be reduced for nonplanar transition states. These calculations also indicate that radicals experience relatively less stabilization on planarization than do carbonium ions. The importance of this possibility is being examined by studies of bridged compounds.

Alternatively, it can be argued that the isotope effect for radical reactions should be more nearly calculable by molecular orbital theory since radical reactions in solution are not very different from the corresponding process in the gas phase. The calculated charge density on the central carbon of isopropyl cation is less than that estimated from its nmr spectrum[30] taken under conditions quite similar to those for the infrared measurements which in turn were fit by the normal mode analysis. Thus, calculated delocalization is greater than observed for carbonium ions so that an underestimate of the isotope effect for the radical process should have resulted from parameterization using carbonium ion data.

This situation is resolved if the solvent is postulated to furnish an attractive interaction with the polarized β protons of the hyperconjugatively stabilized carbonium ion. The consequent broadening of the vibrational potential for these C–H bonds would result in a lowering of the effective force constant when considering the cations as independent entities. This is essentially a restatement of the effect as described by Shiner[20] and one which can be tested since its logical consequence is a similar isotope effect for cation formation in the gas phase. This argument could explain the relative insensitivity of the isotope effects for *t*-butyl cation formation in different solvents.

While we favor the last hypothesis as the best single explanation for β isotope effects in cation formation, the very approximate nature of the present treatment makes the argument considerably less than compelling. A more reasonable view is that the net isotope effects can be a result of several of the postulated origins. However, we would hope that the present treatment might be useful as an empirical guide to the expected magnitudes of such isotope effects. Accordingly, Table IV contains calculated isotope effects for each species and these predictions are presently being tested.

The steric origin[17] of these isotope effects has been neglected here. The argument that these effects are due to inordinately large changes in bending frequency[18] has also been neglected (a breakdown of assumption c). The infrared spectrum of the *t*-butyl cation showed no particular indication of this origin.

Experimental Section

Proton nuclear magnetic resonance spectra were determined on a Varian A-60 spectrometer. Infrared measurements were made using a Beckman IR-7 instrument. Ultraviolet and visible spectral measurements were made on Cary 14 or Cary 11 spectrophotometers. Mass spectra were determined using a modified Consolidated Electrodynamic 26-614 residual gas analyzer.[38] Gas-liquid partition chromatography was carried out using an Aerograph Autoprep instrument.

Materials. Chlorobenzene was purified by shaking with 98% sulfuric acid, then with water, and drying over magnesium sulfate followed by a 2-hr reflux over phosphorus pentoxide. Finally, it was distilled from phosphorus pentoxide and then from potassium hydroxide, bp 130.5–130.9°.

Dioxane (reagent grade) was passed through a column of Woelm neutral alumina, refluxed over sodium for 24 hr, distilled, and passed through a column of neutral alumina. It was used immediately to prepare the 90% dioxane-water solutions which were stored in the dark, under nitrogen, at 0° until used.

t-Butyl hydroperoxide (Matheson Coleman and Bell) was distilled with the first third being discarded. The second third was retained, bp 32–35° (15 mm).

Galvinoxyl was prepared by the method of Kharasch.[39] Purification was by recrystallization in small amounts of absolute ethanol under nitrogen to a constant extinction coefficient of 595 at 776 mμ in benzene solution (lit.[40] 607 mμ). Pivalic acid was obtained from Matheson Coleman and Bell.

Peresters. The peresters were prepared from the corresponding acid chlorides by the method of Bartlett.[7] Pivalic acid-d_9 was obtained by a Grignard sequence.[41] The pivaloyl chloride was obtained by adding 90% of the calculated equivalents of thionyl chloride to the pivalic acid. After refluxing for 0.5 hr, a small aliquot was removed and the acid content determined by its nmr spectrum. Small increments of thionyl chloride were added until

(36) J. C. Evans and G. Y. -S. Lo, *J. Am. Chem. Soc.*, **88**, 2118 (1966).

(37) R. Hoffman, *J. Chem. Phys.*, **39**, 1397 (1963). The program for these calculations was the one obtainable from Quantum Chemistry Program Exchange with minor modifications.

(38) Funds for the purchase of this instrument were partially furnished through grants from the National Science Foundation and National Institutes of Health.

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(40) P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2956 (1962).

(41) A. Streitwieser and H. S. Klein, *ibid.*, **85**, 2759 (1963).

the acid chloride/acid ratio was greater than 20. The acid chloride was then used directly for the perester synthesis.

The peresters were purified by passing them through a column of Woelm activity 1 basic alumina at 0° using ether eluent. This effectively removes all traces of t-butyl hydroperoxide. Before each kinetic run the compounds were rechromatographed and all traces of ether removed by pumping under high vacuum. Peroxide contents as determined by iodometric titration were not reproducible (83–92%). A purity of 100% was assumed on the basis of the nmr and infrared spectra and the reproducible kinetic behavior.

The pivalic acid-d_9 and pivaloyl chloride-d_9 were shown to contain less than 1% hydrogen using the nmr spectrum of a solution containing weighed amounts of compound and dioxane. The perester contained less than 2.6% hydrogen in the pivaloyl fragment as judged by the total nmr peak areas in the t-butyl region compared to dioxane in known concentration.

Kinetic Methods. The infrared method for measuring the rates utilized the disappearance of the carbonyl stretching band of the perester at 1772 cm^{-1}. The products of the reaction do not absorb at this frequency. Beer's law behavior was verified for this solvent–perester system. About 0.1-ml aliquots of about 0.1 M solutions of perester were added to 15 small tubes of Pyrex glass. The tubes were sealed and immersed in a constant temperature bath regulated to ±0.03°, removed at timed intervals, and quenched in ice. The tubes were stored at 0° until the infinity points were taken (ten half-lives). The analyses for duplicate runs were carried out together.

The pseudo-first-order galvinoxyl method utilized the disappearance of the galvinoxyl absorption at 767 mμ. The galvinoxyl solutions (10^{-3} M) containing less than a radical equivalent (n × perester concentration) in Pyrex culture tubes were carefully degassed and sealed under vacuum. Beer's law behavior and the effective path length were determined for each tube. The reaction tubes were immersed in the oil baths for timed intervals, removed and quenched, read in the spectrophotometer, and reimmersed in the bath for a new time increment. Blank solutions of galvinoxyl in chlorobenzene were completely stable over the length of the runs. The blank galvinoxyl solutions in aqueous dioxane showed 14% decomposition over the eight half-life time periods. The runs in this solvent were therefore corrected, point by point, for the behavior of the blank solution. All of the rate plots were linear for more than three half-lives. The zero-order galvinoxyl studies were the same except for the initial perester concentrations.

Product Studies. The gaseous products from the decomposition were collected from breakseal flasks into a calibrated vacuum line. The total gas yield was thus obtained. The composition of the gas mixture was estimated by the sensitivities of the mass spectrometer to the components of the mixture. The t-butyl alcohol from the decomposition of the deuterated perester in aqueous dioxane was separated by glpc using a 30 ft × $^5/_8$ in. column packed with 30% SE-30 on Chromosorb W. Its mass spectrum was identical with that of authentic t-butyl alcohol.

The Coupling Reactions of 1-Chlorocyclopentene, 1-Chlorocyclohexene, and 1-Chlorocycloheptene with Phenyllithium. The Question of Cycloallenic Intermediates[1]

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Abstract: In previous work it was postulated that the coupling reactions of 1-chlorocyclopentene and 1-chlorocyclohexene with phenyllithium in ether at 150°, which yield 1-phenylcyclopentene and 1-phenylcyclohexene, proceed *via* an elimination–addition mechanism involving short-lived cycloalkyne intermediates. An alternative mechanism utilizing cycloallenic intermediates was not rigorously ruled out, however. In the present study the reactions of 1-chloro-2-methylcyclopentene, 2-chloro-3-methylcyclopentene, 1-chloro-2-methylcyclohexene, 2-chloro-3-methylcyclohexene, 1-chlorocyclopentene-2,5,5-d_3, 1-chlorocyclohexene-2,6,6-d_3, 1-chlorocycloheptene, and 1-chlorocycloheptene-2,7,7-d_3 with phenyllithium have been examined. In addition, isotopic rate constant ratios, k_H/k_D, were obtained from competition experiments employing 1-chlorocycloalkenes and 1-chlorocycloalkenes-2,n,n-d_3 (n-membered ring). Rate constant ratios for the five-, six-, and seven-membered rings were 3.36 ± 0.40, 5.34 ± 0.40, and 7.16 ± 0.40, respectively. The results of these studies provide compelling evidence that the coupling reactions of 1-chlorocyclopentene, 1-chlorocyclohexene, and 1-chlorocycloheptene with phenyllithium take place predominantly, if not exclusively, by way of an elimination–addition mechanism involving cycloalkyne intermediates.

In 1944, Wittig and Harborth[3] reported that 1-phenylcyclohexene was formed in 5% yield upon heating 1-chlorocyclohexene and phenyllithium in ether at 100°. Later, it was suggested[4] that this reaction might, in a manner analogous to the coupling reactions of aryl halides with aryllithium reagents,[5] proceed *via* an elimination–addition mechanism involving a cyclohexyne intermediate. In an effort to delineate the

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