The magnitudes of the calculated β effects in the anion series were surprising to us. In the simple alkyl series the values are very similar to the corresponding radicals. Our prejudice, when we began this work, was that there would be very little isotope effect for anions but large effects for radicals. Substitution by aryl groups reduces the calculated isotope effects for anions more than for radicals so that some of our prejudice is borne out by the calculated results.

As mentioned previously, this particular molecular orbital method emphasizes hyperconjugation in a rather extreme way. The β-isotope effects calculated for "formation" of propene, 2,3-pentadiene, and cyclopentadiene are correspondingly appreciable. A test of the predicted 14% isotope effect on the "formation" of cyclopentadiene from its hypothetical localized precursor could be a retro-Diels–Alder reaction or equilibration of 1,1-d_2-cyclopentadiene with a Diels–Alder adduct.

While the present method of estimating these hyperconjugative effects is by no means completely satisfactory, it does seem to offer encouragement to pursue this line of investigation with more advanced molecular orbital formalisms. It would be worthwhile having a similar method for estimating the magnitudes of changes in stretching force constants for nonrotating β (as well as γ, δ, etc.) C–H groups. We are presently attempting to develop such a method.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this work and to Professor E. A. Halevi and Dr. M. Wolfsberg for helpful discussions.

Secondary Deuterium Isotope Effects in Radical-Forming Reactions. IV. Concerted Perester Decompositions

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Abstract: The secondary deuterium isotope effects on the rates of decomposition of *t*-butyl peresters of phenylacetic (**1**), hydratropic (**2**), α,α-dimethylphenylacetic (**3**), and pivalic acids have been determined by infrared, galvinoxyl, and double-labeling methods. The α effects for **1** and **2** are 1.03–1.06 per deuterium. The β effects for the series are 1.014–1.020 per deuterium. The implications of these effects with respect to the detailed mechanisms of the reactions are discussed.

Preliminary investigations[2] of secondary deuterium kinetic isotope effects on the decomposition of *t*-butyl perphenylacetate (**1**) and *t*-butyl perhydratropate (**2**) were carried out as control experiments to test the validity of our expectation that concerted decomposition rates would be sensitive to deuteration. This expectation was based on the idea that the benzylic carbon atoms of the peresters would approach sp^2 hybridization in the transition states. The bending frequencies associated with the α-hydrogen atoms might therefore be expected to be reduced.[3] The studies of Seltzer on the α effects in azo compound decomposition[4] as well as the β scission of cumyloxy radical[5] have indicated that these α effects are of the order of 1.10–1.15 per deuterium atom for these radical-forming reactions. The observed α effects in the preliminary studies were within this expected range while that for the decomposition of acetyl peroxide was much smaller. We therefore concluded that the small value for the latter reaction must be interpreted in terms of a nonconcerted process.

The β effect in the perhydratropate case was also examined and found to be much smaller than the value reported for the autoxidation[6] of cumene. Subsequently it was found that β effects in the formation of phenethyl[7] and cyanoisopropyl[8] radicals from the corresponding azo compound were also small. Similarly the β effect,[8] as estimated by direct kinetic methods, in the decomposition of *t*-butyl perpivalate was also small.[9] It has been demonstrated[9,10] that the ratio of the equilibrium β effects for the formation of radicals and cations of the same formal structure are in agreement with the predictions of molecular orbital theory.

During the course of these developments, the general picture for peroxide decompositions has been revolutionized by the demonstration of reversible oxy–oxy radical formation in a number of cases.[11,12] This perturbation of

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[1] National Defense Education Act Predoctoral Fellow, 1965–1968.

[2] T. Koenig and W. Brewer, *Tetrahedron Letters*, 2773 (1965).

[3] A Streitwieser, R. Jagow, R. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

[4] S. Seltzer and F. T. Dunne, *ibid.*, **87**, 2628 (1965).

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[6] C. E. Boozer, B. W. Ponder, J. C. Trisler, and C. E. Wrightman, *ibid.*, **78**, 1506 (1956).

[7] S. Seltzer and E. Hamilton, *ibid.*, **88**, 3775 (1966).

[8] S. Rummel, H. Huebner, and P. Krumbiegel, *Z. Chem.*, **7**, 351 (1967).

[9] T. Koenig and R. Wolf, *J. Am. Chem. Soc.*, **89**, 2948 (1967).

[10] T. Koenig and R. Wolf, *ibid.*, **91**, 2569 (1969).

[11] (a) J. Taylor and J. C. Martin, *ibid.*, **89**, 6904 (1967); (b) T. G. Traylor and H. Kiefer, *ibid.*, **89**, 6667 (1967); (c) W. Pryor and K. Smith, *ibid.*, **89**, 1791 (1967); W. Braun, L. Rajbenback, and F. R. Eirich, *J. Phys. Chem.*, **66**, 8591 (1962); (b) T. Koenig and M. Deinzer, *J. Am. Chem. Soc.*, **88**, 4518 (1966); T. Koenig and M. Deinzer, *ibid.*, **90**, 7014 (1968).

[12] T. Koenig, *ibid.*, **91**, 2558 (1969).

Table I. Infrared Rate Constants

Perester[a]	Solvent[b]	Temp, °C	$k_H \times 10^4$	$k_{\alpha\text{-D}} \times 10^4$	$k_{\beta\text{-D}} \times 10^4$	$(k_H/k_D)_\alpha$	$(k_H/k_D)_\beta$
1	Isooctane	95.18	3.527 ± 0.053	3.117 ± 0.035		1.13	
1	Isooctane	84.98	1.080 ± 0.010	0.947 ± 0.010		1.14	
1	Paraffin oil	84.98	1.150 ± 0.011	1.018 ± 0.032		1.13	
1	Chlorobenzene	84.98	1.945 ± 0.035	1.753 ± 0.025		1.11	
2	Isooctane	73.88	3.233 ± 0.085	3.147 ± 0.082	3.026 ± 0.038	1.03	1.07
2	Isooctane	60.58	0.660 ± 0.008	0.640 ± 0.006	0.603 ± 0.009	1.03	1.09
3	Isooctane	60.56	4.064 ± 0.061		3.616 ± 0.060		1.12
4	Isooctane	73.88	1.294 ± 0.048		1.142 ± 0.028		1.13

[a] Peresters concentration *ca.* 0.1 *M*. [b] Solvents contain 0.2 *M* styrene.

Table II. Galvinoxyl[a] Rate Constants

Perester	Solvent	Temp, °C	k_H	$k_{\beta\text{-D}}$	$(k_A/k_D)_\beta$[b]
3	Isooctane	60.56	3.059 ± 0.062	2.752 ± 0.025	1.11 ± 0.03
3	Isooctane	40.56	0.295 ± 0.011	0.256 ± 0.007	1.15 ± 0.05
4	Isooctane	73.88	0.882 ± 0.015	0.771 ± 0.009	1.14 ± 0.02
4	Isooctane	60.58	0.197 ± 0.007	0.162 ± 0.004	1.21 ± 0.05
4[c]	Chlorobenzene	60.56	0.400 ± 0.015	0.324 ± 0.005	1.24 ± 0.04
4[c]	Chlorobenzene	74.04	1.927 ± 0.042	1.569 ± 0.043	1.22 ± 0.06
4[e]	Chlorobenzene	60.56	0.402 ± 0.041	0.321 ± 0.073	1.25 ± 0.03
4[e]	Chlorobenzene	74.04	1.691 ± 0.053	1.505 ± 0.057	1.12 ± 0.06
4[d,e]	Dioxane (90%)	60.56	0.478 ± 0.007	0.424 ± 0.016	1.13 ± 0.05

[a] Galvinoxyl concentrations *ca.* 1 × 10^{-3} *M*. Perester concentrations *ca.* 2 × 10^{-3} *M*. [b] For the totally β-deuterated perester. [c] Data of ref 9. [d] With increased experience it is becoming evident that there are many more problems with the pseudo-first-order method than had previously been thought. Because of the dependence on the measurement of the absolute infinity point for each run, any factor which affects this value will drastically affect the rate constants themselves. Since the blank solutions in the pivaloyl runs in 90% aqueous dioxane and isooctane at 60.56° experienced significant decomposition over six half-lives, the infinity points for the runs under these conditions are very uncertain, with the result that the rate constants (and isotope effect) are not accurately determined by this method. The nonreproducibility of the rate constants for the decomposition of *t*-butyl perpivalate in chlorobenzene at 74.04°, even with stable blank solutions under these conditions, suggests that products from the reaction may be reacting further with the galvinoxyl to give over-all first-order kinetics with greatly reduced accuracy. This has also been observed in the decomposition of acetyl peroxide in isooctane at 74.04°, using the pseudo-first-order method (T. Koenig and R. Cruthoff, unpublished results). The pseudo-first-order results that give good, reproducible agreement of isotope effects with effects measured by the infrared or double-labeling method, such as for the cumyl perester at two temperatures and the pivaloyl perester at 73.88° in isooctane, indicate that the complications of extraneous galvinoxyl decomposition are at a minimum. [e] Data of ref 9, with adjusted infinity point.

the over-all mechanisms for these reactions has far-reaching consequences with respect to the interpretation of the observed rate constants for destruction of the compounds. We thus felt that further investigation of these peroxides was warranted.

Because of the complications involved in obtaining reproducible rate constants in radical reactions and because of the small value now expected for the β effects in radical formation, we have developed a competitive method[13] for estimating the isotope effects. This method involves measuring the oxygen-18 contents of the carbon dioxide formed from a mixture of deuterated and oxygen-18-enriched protio peroxides at short and infinite reactions. The values of the deuterium isotope effects are given by

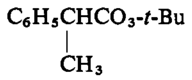
$$k/k' = \left(\frac{R_0{}^* - R_0{}^{\mathrm{m}}}{R_0{}^{\mathrm{m}} - R_0{}^{\mathrm{n}}}\right)\left(\frac{R_\infty{}^{\mathrm{m}} - R_\infty{}^{\mathrm{n}}}{R_\infty{}^* - R_\infty{}^{\mathrm{m}}}\right) \qquad (1)$$

where k/k' is the ratio of rate constants for protonated to deuterated starting material, the *R*'s are the 46/44 mass spectral peak intensity ratios of the carbon dioxide sample. The superscripts refer to deuterated (n), mixture (m), and oxygen-18-enriched (*) compounds and the subscripts refer to short (0) and infinite (∞) reaction times.

The application of this double-labeling method to the decomposition of acetyl peroxide, reconfirmed that the α effect was small in this case.[13] There was also an indication, in these studies, that the isotope effect on the over-all destruction of this peroxide was viscosity sensitive as would be expected if diffusive separation of the acetoxy–acetoxy pair contributed to the rate of the reaction in the forward direction.[12]

$C_6H_5CH_2CO_3$-*t*-Bu

1



$C_6H_5CH(CH_3)CO_3$-*t*-Bu

2

$C_6H_5C(CH_3)_2CO_3$-*t*-Bu

3

$(CH_3)_3CCO_3$-*t*-Bu

4

The present results deal with a more complete investigation of peresters (**1**–**4**) which were expected[14] to decompose in a concerted fashion leading directly to decarboxylation residue, carbon dioxide, and *t*-butoxy radical in a single step with no intervening intermediate. (This constitutes

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[13] T. Koenig and R. Cruthoff, *J. Am. Chem. Soc.*, **91**, 2562 (1969).

[14] P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958); P. D. Bartlett and D. M. Simons, *ibid.*, **82**, 1753 (1960).

Table III. Double-Labeling Results[a]

Compd	$R_0{}^n$	R_0	$R_0{}^*$	$R_\infty{}^n$	R_∞	$R_\infty{}^*$	k^*/k	n^*/n	$(k^{16}/k^{18})_n{}^b$	$(k^{16}/k^{18})^{*c}$
1	0.412	1.642	2.890	0.418	1.604	2.955	1.120	0.906	1.011	1.022
1		1.672			1.632		1.126	0.927		
1	0.413	1.689	2.878	0.415	1.659	2.943	1.109	0.942	1.005	1.022
2-α	0.551	2.105	3.526	0.546	2.089	3.555	1.044	1.064	1.009	1.008
2-β	0.415	2.065		0.419	2.039		1.060	0.987	1.009	
3	0.404	2.140	3.345	0.410	2.090	3.367	1.093	0.976	1.014	1.006
4	0.405	2.113	3.342	0.408	2.036	3.376	1.143	1.007	1.008	1.010

[a] R's, k^*/k, and n^*/n refer to eq 1. [b] Apparent oxygen-18 isotope effect using the deuterated compound. [c] Apparent oxygen-18 isotope effect using the enriched compound.

Table IV. Carbon Dioxide Yields

1	0.987	**3**	1.002
2	0.918	**4**	0.908

our operational definition of a concerted decomposition.) The concerted character of the perphenylacetate has recently been questioned[15] since it has been observed that the rates of destruction of this peroxide respond to changing viscosity in a manner which is similar to those for peroxides which clearly do not involve a concerted mechanism. Methods used here to estimate the isotope effects include conventional infrared and pseudo-first-order galvinoxyl rate measurements as well as the indirect double-labeling method.

Results

The peresters used in the present study were synthesized by the literature[14] method. They were purified by column chromatography at 0° over basic alumina. The infrared rate constants were determined using sealed ampoules which were heated for timed intervals and quenched in ice. The galvinoxyl rate constants were determined using the previously described[9] method. These kinetic data were analyzed using a linear least-squares computer program. The linearity was good for more than three half-lives in all cases. These results are summarized in Tables I and II. The double-labeling results were obtained by sealing the required solutions in breakseal flasks. These were heated for the required length of time in a constant-temperature bath and quenched in ice. The carbon dioxide was collected in a vacuum line and purified by bulb-to-bulb distillation. For compounds **1**–**3**, the carbon dioxide did contain traces of isooctane but it was shown that even large amounts of isooctane do not effect the 46/44 mass spectral ratio of tank or oxygen-18-enriched carbon dioxide.

The butylene from the pivalate poses more of a problem. The carbon dioxide samples from this perester were therefore purified by gas chromatography before mass spectral analysis. The results of these measurements are summarized in Table III. Each entry in the table is the result of a duplicate run. The actual values of the isotope effects are the average of more data than are listed.

The carbon dioxide yields were determined for each of the compounds by collecting the total product vapors in a calibrated vacuum line. The carbon dioxide contents of these gases were analyzed using mass spectrometry. These results are listed in Table IV.

Discussion

Preliminary experiments of the present study, as well as those in the earlier report,[2] followed the literature[14] procedure for the synthesis and purification of **1** and **2**. The material obtained in this way had reasonable spectral characteristics and gave reproducible infrared rate constants which were similar to those reported previously.[2,14] However, when these compounds were examined using the double-labeling method, the results were wildly irratic. When the peresters were purified by column chromatography over basic alumina at 0°, the observed rate constants were slightly decreased. The isotope effects estimated by the infrared and double-labeling methods were reproducible and in good agreement. The magnitudes of the isotope effects were significantly reduced. It thus appears that some impurity remains, with the previous purification, which can catalyze the decomposition of these compounds.

As was recognized in the preliminary communication, the operation of a very small amount of induced decomposition involving abstraction of the α-hydrogen atom,[16] could raise the apparent isotope effect significantly. Also a larger amount of impurity catalyst in the protio samples could serve to raise the observed isotope effects. These considerations are made less serious by the good agreement between the final results of the infrared and double-labeling methods. With the latter technique, the critical ratio is the result of the decomposition of a mixture of the two and has internal compensation for such complications.

The galvinoxyl method could not be used with these two peresters since the observed n (Δ[galvinoxyl]/[initial peroxide]) values were greater than 2.[17] This could be an indication that the peresters are still not pure. It could also be a reflection of the reaction of galvinoxyl with some of the products of the decomposition. Regardless of the explanation, these observations render the galvinoxyl method totally useless for the present purposes. These complications indicate that the observed values for the isotope effects for **1** and **2** should be considered as upper limit. No such complications were apparent for **3** and **4**

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(15) W. A. Pryor and K. Smith, Abstracts of Papers, the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April, 1968, Abstract P76.

(16) P. D. Bartlett and L. Gortler, *J. Am. Chem. Soc.*, **84**, 1864 (1962).

(17) See footnote *d* in Table II.

Table V. Summary of Total Isotope Effects[a]

Compd	Solvent	Temp, °C	$(k/k')_{\mathrm{Ir}}$	$(k/k')_{\mathrm{G}}$	$(k/k')\mathrm{O}^{18}$	$(k_{\mathrm{H}}/k_{\mathrm{D}})^{b}$	$k_{\mathrm{rel}}{}^{c}$
1-α	Chlorobenzene	84.98	1.11			1.055	
1-α	Isooctane	84.98	1.14		1.123	1.066	1.00
1-α	Paraffin oil	84.98	1.13		1.106	1.060	
2-α	Isooctane	73.99	1.03		1.044	1.046	5.6
2-β	Isooctane	73.88	1.07		1.062	1.020	
3-β	Isooctane	60.56	1.12	1.21	1.102	1.018	86
4-β	Isooctane	73.88	1.13	1.14	1.140	1.016	14.1

[a] The ratios k/k' refer to the completely deuterated compounds at the indicated positions. [b] Average isotope effect per deuterium atom. [c] Estimated or measured relative rate constants at 60.56° in isooctane. Relative to 0.0467×10^{-4} sec^{-1} for **1**.

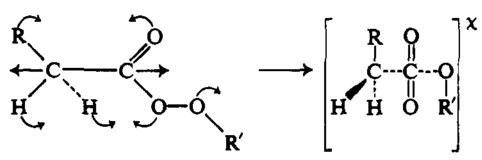
and the good general agreement of the data throughout the series is reassuring. Also the ratio of eventual yields of carbon dioxide (n^*/n) from the decomposition of the mixtures are all very close to unity. The yields of carbon dioxide are close to quantitative.

Though the values of the α effects for **1** and **2** are low, they are still much larger (per deuterium) than the corresponding effect observed in the decomposition of acetyl peroxide (<1.0110/D).[13] They are not so much larger than the α effects estimated for the decarboxylation of the acetoxy radical[13] (1.03/D). It could be argued that the small magnitudes of the α effects for **1** and **2** indicate partial nonconcerted decomposition as has been suggested by Pryor.[15] However, our estimate of the rate of destruction of **1** in paraffin oil was slightly larger than in isooctane. The α effect in the more viscous medium did not increase as would be expected if the importance of the diffusive separation of phenylacetoxy-*t*-butoxy radical pairs were being reduced. We therefore believe that it is unlikely that there is any return of phenylacetoxy-*t*-butoxy pairs. It also seems improbable that the rate constants for formation and return of oxy–oxy radical pairs or the concerted decomposition rate constant should always be *totally* insensitive to large changes in solvent viscosity. Thus small variations in the observed rate of destruction of a peroxide could appear to be correlated with viscosity functions without demanding reversible radical-pair formation.

This does not mean that we rule out the contribution of an unknown amount of nonconcerted decomposition of **1** and **2**. The process could be completely nonconcerted (which would explain the low $k_{\mathrm{H}}/k_{\mathrm{D}}$) and still not be subject to return if the free energy of activation for return were significantly larger than that for decarboxylation. Even for a very low potential energy of activation for return, the free energy of activation could be appreciably positive because of the entropy changes associated with the formation of a single molecule from a radical pair.

The possibility of completely nonconcerted decomposition of **2** and **3** seems unlikely since the values of $k_{\mathrm{H}}/k_{\mathrm{D}}$ for the α effect are somewhat larger than one would expect if there were no reorganization of the α-C–H group. Furthermore, in the case of **2**, the β effect is comparable in magnitude to that observed[4] in the decomposition of azobis-α-phenylethane (in which the α effect is 1.12 per deuterium atom). Also the oxygen-18 isotope effects are significantly lower than those reported for acetyl peroxide.[18a] This is in accord with expectations of a transition state with more carbon dioxide character.

These considerations lead us to propose the following rationalization of the low value of the α effects for **1** and **2**. The atomic motions leading to the transition state for concerted decomposition, could be represented as in **5**.



5 **6**

In a transition state, leading to a radical pair with carbon dioxide in close proximity to the alkyl radical, the bending motion of the α-hydrogen atoms might not be reduced as much as would obtain in a separated pair of the same valency. When nitrogen intervenes, as in an azo compound decomposition, the restriction of the bending motion of the α-hydrogen atoms should not be so "severe" though it would remain as a factor in the magnitude of the α effect. The operation of the hyperconjugative interaction of the β-C–H bonds with the developing radical center would not be subject to steric restriction though it should respond to the residual bond character between the intervening group and the radical center (C–C or C–N).

This rationalization does not violate the other kinetic criteria[14] of concerted decomposition of the perester. It also is in accord with the observed activation volume recently measured[18b] for **1**. The total expansion of such a transition state might very well be smaller than for a single-bond homolysis if the attractive part of the single-bond potential surface is considered to resemble a Morse function.

Similar motions could be involved in nonconcerted decompositions. If so the acyloxy radicals, which could have a *long* lifetime on a vibrational time scale, would not have the structure analogous to a carboxylate anion but would be expected to have wider O–C–O bond angles and longer C–C bonds. Such a situation would resolve the problem of the magnitude of the carbon-13 and oxygen-18 isotope effects in the decomposition of acetyl peroxide.[18a]

The observed β effects, summarized in Table V, for **2**, **3**, and **4** in isooctane further strengthen the previous conclusion that such isotope effects are small for radical-forming processes. The observed values are appreciably

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(18) (a) M. Goldstein, *Tetrahedron Letters*, 1501 (1964); (b) R. Neuman and J. Behar, *J. Am. Chem. Soc.*, 89, 4549 (1967).

smaller than the equilibrium values (*ca.* 1.05/D) predicted by molecular orbital methods.[9,10] This is reasonable since the over-all processes, from perester to alkyl radical, carbon dioxide, and *t*-butoxy radical, are probably exothermic in these cases. Thus, only fractional radical character should be present at the α-carbon atom in the corresponding transition states. This is contrasted to limiting solvolysis reactions in which the activation energy for the reverse of primary ion-pair formation is very small. The formation of the primary ion pair should therefore be nearly equivalent to an equilibrium as long as the ion pair is restricted to have full charge separation with no residual covalent (dipolar) cation-leaving group bond. Other factors, such as the mechanism of solvation of such an ion pair are the more serious complications in interpreting β effects for ionic processes.

One could attempt to estimate the fractional radical character in the transition states corresponding to decomposition of **2**, **3**, and **4** by dividing the observed β effect by the calculated[10] effect. The values for **2** (34%) and **3** (32%) are reasonable and in the expected order assuming Hammond's postulate. The pivaloyl compound **4** appears to have too little radical character (21%) in isooctane by this criterion. On the other hand, its activation enthalpy is anomalously low compared to the estimated total hyperconjugative resonance energy available to the *t*-butyl radical (12 kcal/mol). The situation is further complicated, in this case, by the difference in the value of the β effect in chlorobenzene and isooctane. There is a significant reduction in both the rate and isotope effect in the less polar (less viscous) hydrocarbon solvent. Thus it appears that the charge separation postulated in the transition states for decomposition of substituted phenylacetyl peresters ($\rho = 1.09$[19]) also plays a role in determining the magnitude of the β-isotope effect. Further work is needed before additional speculation is warranted on the details of the decomposition of this perester. A possible rationalization of the low enthalpy is relief of strain.

We believe several conclusions emerge from the present study. The double-labeling method appears to be a reliable method for estimating fairly small isotope effects. The gross feature of concerted decomposition for all four of the present compounds appears to be reinforced by these results. The magnitudes of β-deuterium isotope effects appear to be completely ascribable to changes in zero-point energy which attend hyperconjugative weakening of the β-C-H stretching vibrations. The most important result, at least in our view, which emerges from these studies takes the form of the question which is raised as to the nature of the bonding of acyloxy radicals in general. Further work in this field is planned with the hope of gaining a better insight into this and related questions.

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. Visible spectral measurements were made on a Cary 15 spectrophotometer. Mass spectra were determined using a modified Consolidated Electrodynamic 26-614 residual gas analyzer. Gas phase chromatography was carried out on a homemade apparatus, through a dibutylphthalate column.

Materials. Chlorobenzene was purified by the method previously described.[9] Isooctane (spectroquality reagent grade) was distilled from sodium, bp 98.5–99.0°, and stored over molecular sieves at room temperature.

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.[20] Purification was by recrystallization in small amounts of absolute ethanol under nitrogen to a constant extinction coefficient of 595 at 776 mμ for one batch and 611 at 776 mμ for another batch, in benzene solution (lit.[21] 607).

Pivalic acid and phenylacetic acid were obtained from Matheson Coleman and Bell. 2-Phenylpropionic acid was obtained from Aldrich Chemical Company. α,α-Dimethylphenylacetic acid was obtained from City Chemical Corp.

Peresters. The peresters were prepared from the corresponding acid chloride by a modified Schotten-Baumann procedure. An ether solution of the acid chloride was stirred at 0° for 5 hr with water solution containing 2 equiv of potassium hydroxide and 3 equiv of *t*-butyl hydroperoxide. The ether solution containing the perester was separated from the aqueous solution, washed three times with 20% potassium hydroxide and once with water, and dried over calcium chloride and the ether removed under reduced pressure.

The peresters were purified by pumping under high vacuum for 1 hr to remove all traces of *t*-butyl hydroperoxide. They were then passed through a column of Woelm activity 1 basic alumina at −10° using ether eluent. Before each kinetic run the compounds were rechromatographed and all traces of ether removed by pumping under high vacuum. A purity of 100% was assumed on the basis of the nmr and infrared spectra and the reproducible kinetic behavior. The deuterated peresters were shown to have less than 1% hydrogen in their relevant positions by nmr peak areas.

The protonated peresters which were enriched by oxygen-18 in the carbonyl oxygens were prepared by adding a twofold excess of oxygen-18-enriched water (5.0% oxygen-18 from BioRad Laboratories, 0.58% D) to the acid chlorides in dry acetonitrile. The solutions were stirred at room temperature or heated gently for 10–20 hr. The labeled acid chlorides were then synthesized from the labeled acids using thionyl chloride.

α,α-Dimethyl-d_6-phenylacetic Acid. To a solution of 0.1085 mol of *n*-butyllithium in 75 ml of freshly purified tetrahydrofuran was added 5.77 g (0.04931 mol) of benzylcyanide in 25 ml of tetrahydrofuran at room temperature.[22] The solution was heated gently for 0.5 hr after the addition was complete, and the amount of *n*-butane evolved was measured by a gas buret. The solution of dilithium benzylcyanide was pushed by a stream of nitrogen to a dropping funnel attached to a three-necked flask containing 15 g (0.103 mol) of methyl-d_3 iodide (Stohler Isotope Chemicals) in 50 ml of tetrahydrofuran. The addition of the dilithium benzylcyanide solution produced an exothermic reaction. Work-up yielded an orange oil which was taken up in ether, washed with water, and dried over calcium chloride. No further purification was done on the oil, and it was used directly in the next step.

The oil was hydrolyzed in 20% potassium hydroxide and tetrahydrofuran solution. The solution was refluxed and 30% hydrogen peroxide was added over a period of 6 hr. The solution was cooled, sodium chloride was added, and the organic phase was extracted three times with ether. An orange residue was left after evaporation of the ether which yielded white crystals after crystallization from carbon tetrachloride. This hydrolysis procedure was repeated three times to yield 2.020 g (0.0120 mol, 24.2% from benzylcyanide) α,α-dimethyl-d_6-phenylacetamide, as white crystals after crystallization, mp 155.0–157.8° (lit.[23] for α-α-dimethylphenylacetamide, 159.5–160.0°). Infrared N-H_2 stretch at 3440 and 3560 cm^{-1}, CD stretch at 2240, carbonyl stretch at 1675.

To 1.936 g (0.0114 mol) of α,α-dimethyl-d_6-phenylacetamide in 40 ml of refluxing carbon tetrachloride was added 11.0 g (0.168 mol) of nitrosyl chloride in 35 ml of carbon tetrachloride. The solution was refluxed for 1 hr after addition. Potassium hydroxide solution (80 ml of 20%) was added and the mixture refluxed for 7 hr. The

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

[22] E. M. Kaiser and C. R. Hauser, *ibid.*, **88**, 2348 (1966).

[23] J. F. Bunnett and T. K. Brotherton, *J. Org. Chem.*, **23**, 904 (1958).

organic acid was isolated in 1.620 g yield (0.00953 mol or 83.3% from amide).

Hydratropic Acid-β-d_3. Acetophenone was reduced by lithium aluminum hydride in ether to yield α-hydroxyethylbenzene in 89.9% yield. The alcohol was converted to α-chloroethylbenzene by reaction with thionyl chloride in 89.8% yield. α-Cyanoethylbenzene was prepared from the chloride by reaction with sodium cyanide in dry dimethyl sulfoxide at 60° for 3 hr. The yield of α-cyanoethylbenzene was 85.4% from the chloride. The nitrile was hydrolyzed by refluxing in 33% aqueous potassium hydroxide for 24 hr to give α-methylphenylacetic acid in 97.8% yield. α-Methyl-d_3-phenylacetic acid was prepared from the analogous cyanide by hydrolysis in 99% D_2O. The cyanide was prepared, in the same manner as the protonated cyanide, from acetophenone-d_3, which was prepared by basic exchange of the acidic α protons of acetophenone in 99% D_2O at 100°. The deuterated α-methylphenylacetic acid contained deuterium at the α position. This was exchanged in basic water to yield α-methyl-d_3-phenylacetic acid, with 100% deuteration in the methyl position and no deuteration at other positions on the molecule, according to nmr analysis. α-Methylphenylacetic acid-α-d_1 was prepared from the protonated acid by exchange in basic 99% D_2O at 100°.

Phenylacetic acid-α,α-d_2 was prepared by basic exchange of the alpha protons in 99% D_2O at 100°.

Pivalic acid-d_9 was prepared by a Grignard sequence from *t*-butyl-d_9 chloride.

Kinetic Methods. The infrared and pseudo-first-order galvinoxyl methods for measuring the perester decomposition rates were previously described.[9]

The double-labeling method required preparation of solutions of the protonated, deuterated, and approximately 50:50 mixture of protonated–deuterated peresters in about 0.04 *M* concentration of perester and 0.12 *M* styrene with isooctane as solvent. A 50 ml solution was prepared out of which 20 ml was pipetted into each of two breakseal flasks for the "short" reaction time, with 5 ml put into each of two breakseal flasks for the "infinity" reaction time. The "short" reaction flasks were heated for 15–25% of total perester decomposition, the per cent of decomposition based on the infrared kinetic rate constants. The "infinity" reaction flasks were heated for ten half-lives to ensure complete decomposition of perester.

The breakseal flasks were opened on a vacuum line, and the volatile gases were allowed to expand into a mass spectrometer tube, with the breakseal cooled to −78°. The breakseal flask was closed off, and the volatile gases were condensed in the mass spectrometer tube at −200°. The only gases detectable from all the peresters except the pivaloyl were carbon dioxide and isooctane. Since isooctane does not give a fragment at mass peaks 44, 45, or 46, the ratios of 46/44 and 45/44 from carbon dioxide could be determined directly, without further purification of the carbon dioxide. The carbon dioxide from *t*-butyl perpivalate was contaminated with isobutane and isobutylene, which gave mass peaks at 45 and 46. The carbon dioxide was separated from all contaminants by chromatography at room temperature through a dibutyl phthalate column connected to a vacuum line, with helium as the carrier gas.

The 46/44 ratios for the protonated, deuterated, and mixed peresters for short and infinity reaction times were used to calculate the isotope effect directly. The denominator of the expression equals the ratio of the moles of protonated to deuterated weighed out initially times the ratio of the number of moles of carbon dioxide produced per mole of protonated perester to the number of moles of CO_2 produced per mole of deuterated perester (*n*H/*n*D). Since the initial weights of the two peresters in the mixture are known, the *n*H/*n*D ratio can be calculated.

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 only contaminant in the carbon dioxide produced from the decomposition of the phenylacetyl hydratropyl and cumyl peresters was isooctane.

Complete Conformational Analysis of 3-Phenylpropanol

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Abstract: The nmr spectrum of the aliphatic protons in $PhCH_2CH_2CH_2OH$ has been completely analyzed with the aid of various stereospecifically dideuterated derivatives. It is shown that the conformer with Ph, CH_2OH *trans* disposed is more stable than the *gauche* rotamer by 0.5 kcal $mole^{-1}$. In contrast, the rotamers with $PhCH_2$, OH *trans* and *gauche*, respectively, are about statistically populated. Two kinds of differential isotope effects on chemical shifts are noted.

We recently suggested an approximate method of conformational analysis of substituted ethanes[1] and demonstrated an unequivocal method of identifying the structure of the most stable conformer of some 1,1,2-trisubstituted ethanes.[2] As previously mentioned, our approach is applicable with greater validity to 1,2-disubstituted ethanes,[3] and in fact comparison of results derived from our simplified model with those from a more exact analysis seems quite favorable.[4] The explicit assumptions in our model as applied to the latter system are (1) that angular dependence of vicinal coupling constants follows a $\cos^2$ function, $J = J_0 \cos^2 \phi$, and (2) all dihedral angles, ϕ, are 60° when substituents are *trans* but the angle is 65° when substituents are *gauche*. We showed[1] the energy differences calculated for 1,2-disubstituted ethanes is not particularly sensitive to the choice of dihedral angle near 60°, and further pointed out that conformational energy *differences* in the same compound as induced by changes in solvent should be reproduced quite well by this model. We report here on the application and results of our method to conformational analysis of 3-phenylpropanol (**1**), where the rotamer distribution about *both* bonds a and b, $PhCH_2\underset{a}{--}CH_2\underset{b}{--}CH_2OH$, has been determined and the most stable conformer has been identified. A later publication will deal with the conformational analysis of several 2-phenylethyl derivatives, of which this can be considered a member.

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(1) E. I. Snyder, *J. Am. Chem. Soc.*, **88**, 1165 (1966).

(2) M. Buza and E. I. Snyder, *ibid.*, **88**, 1161 (1966).

(3) See N. L. Allinger and coworkers, *ibid.*, **90**, 1199 (1968), for indication that one of the assumptions necessary for trisubstituted ethanes, but absent in the extension to 1,2-disubstituted ethanes, may not be generally applicable.

(4) G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *ibid.*, **89**, 1125 (1967).