substitutents on conductance and other physical properties of **1** as well as **2**.

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Received September 27, 1971

Steric Driving Forces in Perester Decomposition. *tert*-Butylperoxy Di-*tert*-butylacetate[1]

Sir:

The question of concerted cleavage of both O–O and C–CO_2 bonds during the thermal reactions of *tert*-butyl peresters has been of considerable interest. This problem has been examined recently by the study of the effect of solvent viscosity,[2] secondary isotope effects,[3] bridgehead strain,[4] and pressure[5] on the rates and products of perester decomposition.[6]

This report presents a new approach for investigating transition-state structure in perester decompositions, the steric driving force for the reaction. This method has been utilized to great advantage for the study of ionization processes;[7] for example, the relative rates of solvolysis (eq 1) of di-*tert*-butylcarbinyl tosylate (**1a**) and

$$\underset{\substack{\textbf{1a},\ R\ =\ t\text{-Bu}\\ \textbf{b},\ R\ =\ Me}}{R_2CHOTs} \longrightarrow [R_2CH\cdots OTs]^* \xrightarrow{-OTs} R_2C^+H \qquad (1)$$

isopropyl tosylate (**1b**) have been measured to be 630 in 97% trifluoroethanol, and calculated to be 120,000 in trifluoroacetic acid.[7b] This rate acceleration was ascribed largely to relief of steric strain for **1a** on ionization, with a possible additional contribution from methyl participation.

To examine the occurrence of steric acceleration in perester reactions we prepared *tert*-butylperoxy di-*tert*-butylacetate (**2a**). Reaction of di-*tert*-butylacetyl chloride[8] with *t*-BuOOH–pyridine gave **2a** as a pale yellow oil: ir (cumene) 1764 cm^{-1} (C═O); nmr (CCl_4) δ 1.10 (s, 18, CH-*t*-*Bu*$_2$), 1.28 (s, 9, O-*t*-Bu), and 1.97 (s, 1, *CH*-*t*-Bu).[9] The kinetics of thermal decomposition of **2a** were examined in cumene solution and the measured rate constants are given in Table I along with suitable data for comparison.[10] The products of the reaction at 70° are given in Table II.

Table I. Rates of Decomposition of *tert*-Butylperoxy Di-*tert*-butylacetate (**2a**) in Cumene[a]

Per-ester	Temp, °C	k_1(sec^{-1}) × 10^6	k_{rel}	ΔH^*, kcal/mol	ΔS^*, eu
2a	85.4	24.4		29.9	7.9
	70.2	3.56			
	54.7	0.438			
	90.6[b]	44.6	6.7		
	60.0[b]	0.915			
2b[c]	90.6	6.67	1.0	31.8	9.4
	60.0[b]	0.106			

[a] Rates were measured by the infrared method using 0.09 *M* solutions, and the reported values are the averages of two runs at each temperature. Excellent first-order rate plots were obtained for at least two half-lives, and duplicate runs agreed within less than ±2% in all cases. [b] Calculated from data at other temperatures. [c] Reference 10.

Table II. Products of Decomposition of *tert*-Butylperoxy Di-*tert*-butylacetate (**2a**) at 70° in Cumene[a]

Product	Mol/mol of perester	Product	Mol/mol of perester
CO_2	0.89	*t*-BuOH	0.84
CH_4	0.01	*t*-Bu$_2$CH$_2$	0.74[b]
		Acetone	0.17

[a] Determined using 0.4 *M* solutions. [b] Products derived from combination of *t*-Bu$_2$CH groups with solvent were also detected.

The similarity in reactivity of **2a** and **2b** indicates that both of these peresters are reacting by the same mechanism, and a concerted two-bond cleavage (eq 2) is most

$$\underset{\substack{\textbf{2a},\ R\ =\ t\text{-Bu}\\ \textbf{b},\ R\ =\ Me}}{R_2CHCO_3\text{-}t\text{-Bu}} \longrightarrow [R_2CH\cdots CO_2\cdots O\text{-}t\text{-Bu}]^* \xrightarrow[-CO_2]{-t\text{-Bu}\dot{O}} R_2\dot{C}H \qquad (2)$$

consistent with the observed results.[6,11] The most telling piece of evidence for the concerted cleavage is the 50-fold greater rate of reaction of *tert*-butylperoxy isobutyrate (**2b**) over *tert*-butylperoxy acetate.[10,11a]

The remarkable feature of the reactivity of the di-*tert*-butylperacetate **2a** is the small rate enhancement (a factor of 6.7 at 90.6°) relative to the dimethylperacetate **2b**. The corresponding factor for trifluoroacetolysis of the structurally related tosylates was 120,000. This latter comparison was made under conditions where backside solvent participation, which accelerates the reactivity of the less highly substituted derivatives, is minimized, but backside solvent displacement could not be involved in the perester reactions. Steric repulsion of the leaving group may also be a factor in cleavage reactions of highly substituted substrates, and while the relative magnitudes of this interaction are difficult to assess, it appears the potential relief of strain from this cause is at least as great in the perester system. Furthermore inductive acceleration of the rate of **2a** could account for a major fraction of the **2a**/**2b** rate ratio.[4a] Thus the rate acceleration due to relief of steric strain in the dialkylperacetates is remarkably small. This result strongly suggests that rather little rehybridization of the carbon bonded to the carboxy group occurs in the transition state of perester decompositions leading to secondary radicals, and is in accord with the description of the

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(1) Supported by the U. S. Army Research Office—Durham. Part V in the series "Steric Crowding in Organic Chemistry"; part IV: G. J. Abruscato, R. G. Binder, and T. T. Tidwell, *J. Org. Chem.*, submitted for publication.

(2) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970).

(3) T. Koenig, J. Huntington, and R. Cruthoff, *ibid.*, **92**, 5413 (1970).

(4) (a) R. C. Fort, Jr., and R. E. Franklin, *ibid.*, **90**, 5267 (1968); (b) J. P. Lorand, S. D. Chodroff, and R. W. Wallace, *ibid.*, **90**, 5266 (1968); (c) L. B. Humphrey, B. Hodgson, and R. E. Pincock, *Can. J. Chem.*, **46**, 3099 (1968); (d) G. A. Razuvajev, L. S. Boguslavskaya, V. S. Etlis, and G. V. Brovkina, *Tetrahedron*, **25**, 4925 (1969); (e) S. F. Nelsen and E. F. Travecedo, *J. Org. Chem.*, **34**, 3651 (1969).

(5) R. C. Neuman, Jr., and J. V. Behar, *ibid.*, **36**, 54, 57 (1971).

(6) For a general review of the relation between perester structure and reactivity, see C. Rüchardt, *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).

(7) (a) P. D. Bartlett and T. T. Tidwell, *J. Amer. Chem. Soc.*, **90**, 4421 (1968); (b) S. H. Liggero, J. J. Harper, P. v. R. Schleyer, A. P. Krapcho, and D. E. Horn, *ibid.*, **92**, 3789 (1970).

(8) M. S. Newman, A. Arkell, and T. Fukunaga, *ibid.*, **82**, 2498 (1960).

(9) Satisfactory carbon and hydrogen analyses were obtained for **2a**.

(10) P. D. Bartlett and L. B. Gortler, *J. Amer. Chem. Soc.*, **85**, 1864 (1963).

(11) (a) P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958); (b) L. A. Singer in "Organic Peroxides," Vol. 1, D. Swern, Ed., Wiley, New York, N. Y., 1970.

transition state which has been developed on the basis of the other investigations mentioned above.[3-6] The proposal[6,12] that relief of steric crowding is an important factor in perester decompositions evidently is not applicable in these cases.[13]

[12] C. Rüchardt and I. Mayer-Ruthardt, *Chem. Ber.*, **104**, 593 (1971).

[13] Professor Ch. Rüchardt has also observed only minimal steric acceleration in decomposition of certain peresters and azo compounds leading to radicals (unpublished results privately communicated).

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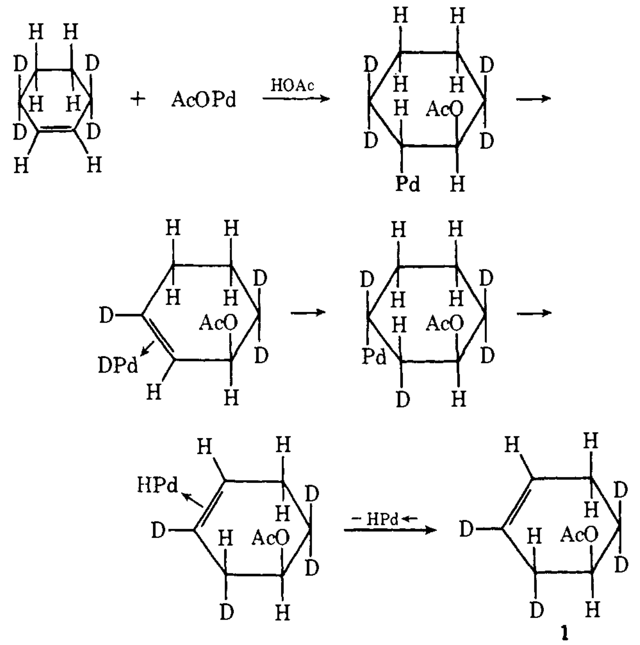
Received October 22, 1971

Stereochemistry of Phenylpalladation of Cyclohexene[1]

Sir:

The oxidation of cyclohexene-*3,3,6,6-d*$_4$ by a mixture of $PdCl_2$ and $CuCl_2$ in acetic acid was previously reported[2] to give products which were consistent with trans acetoxypalladation followed by cis palladium(II) hydride (or deuteride) eliminations and readditions. Thus the structure of the homoallylic acetate formed can be explained by Scheme I. **1** was also formed by the oxidation of cyclohexene-*3,3,6,6-d*$_4$ with $Pd(OAc)_2$ in acetic acid.[3]

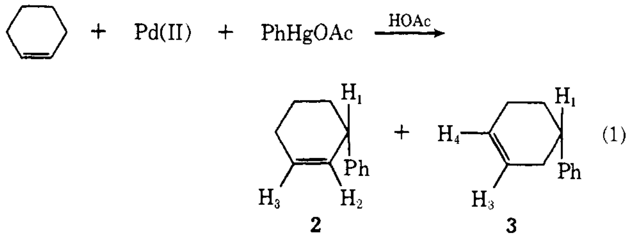
Scheme I



Although Scheme I is believed to be most consistent with known palladium(II) chemistry, there are other mechanistic paths which will give **1** as product. Cis acetoxypalladation and trans palladium(II) hydride (or deuteride) elimination and readdition is one possibility. This route is considered very unlikely because it would require free hydride to exist in a protonic solvent such as acetic acid. Another possibility is cis acetoxypalladation followed by 1,2 shifts of hydrogen (or deuterium) and Pd(II) by concerted diaxial ⇄ diequatorial type shifts.[3]

One way to test Scheme I is to use a reagent that will add cis to cyclohexene. If homoallylic product arises from cis palladium hydride (or deuteride) eliminations and readditions as shown in Scheme I, the arrangement of protons in the homoallylic product will be different from that found in **1**. Such a reagent is apparently phenylpalladium. Reaction of olefins with this reagent, formed *in situ* by the exchange of arylmercury(II) compounds with palladium(II) salts, has been studied extensively,[4] and stereochemical results indicate that phenylpalladation and palladium(II) hydride elimination have the same stereochemistry.[5] Since the phenyl is covalently bonded to palladium(II), phenylpalladation would be expected to be a cis process. For that reason the oxidation of cyclohexene and its deuterated analog by mixtures of phenylmercuric acetate and Pd(II) salts was studied.

The oxidation with PhHgOAc and either $Pd(OAc)_2$ or catalytic amounts of $PdCl_2$ plus $CuCl_2$ gave two main products by vapor phase chromatography (vpc).[6] Each peak was collected by preparative vpc and identified by nmr. The spectra indicated both were phenyl-substituted cyclohexenes,[7] one the allylic isomer and the other the homoallylic isomer. The reaction thus proceeds as shown by eq 1. The first peak to elute, which was about one-half the area of the second peak, was assigned the structure **2** on the basis of the chemical shifts of the H_1 protons. Thus in **3**, δ_1 is at 2.78 ppm, while in **2** it is shifted to 3.41 ppm. Such a shift is expected when the double bond is moved closer to H_1. Furthermore in **3** the olefinic protons are unresolved at approximately δ 5.76 ppm, using a 60-MHz spectrometer. When the double bond is moved closer to the phenyl, they are resolved with δ_2 ~5.7 ppm and δ_3 ~5.9 ppm. Aromatic protons appear as a sharp singlet at δ 7.25 ppm in both isomers.



The $Pd(OAc)_2$ run was repeated using cyclohexene-*3,3,6,6-d*$_4$, and the products were again collected by preparative vpc and their nmr spectra taken. On the basis of the chemical shifts and area measurements the products were assigned structures **4** and **5**. In **4**, H_1

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[1] Hercules Research Center Contribution No. 1578.

[2] P. M. Henry and G. A. Ward, *J. Amer. Chem. Soc.*, **93**, 1494 (1971).

[3] S. Wolfe and P. G. C. Campell, *ibid.*, **93**, 1497 (1971).

[4] R. F. Heck, *ibid.*, **90**, 5518 (1968), and following papers.

[5] R. F. Heck, *ibid.*, **91**, 6707 (1969).

[6] All runs were made at 25°. $Pd(OAc)_2$ reaction mixtures contained 0.2 mol of $Pd(OAc)_2$, PhHgOAc, and cyclohexene per liter of acetic acid. The $PdCl_2$ runs contained 0.01 mol of $PdCl_2$, 0.2 mol of PhHgOAc and cyclohexene, and 0.4 mol of $CuCl_2$ per liter of acetic acid. All reactants except the Pd(II) salts were mixed and stirring begun. The reaction was then started by adding the Pd(II) salts. Since the salts were sparingly soluble in acetic acid all runs were heterogeneous. Reaction time was 2 hr. Conversion of cyclohexene was about 50%. Reaction mixtures were worked up by diluting with CH_2Cl_2 and washing with water to remove inorganic salts and acetic acid. After drying, the organic phase was concentrated to a known volume and analyzed by vpc. A 20-ft 20% Lac 446 on 60–80 mesh Chromosorb W column was used. Temperature was 200° and helium flow rate was 100 ml/min.

[7] The $PdCl_2$ plus $CuCl_2$ reaction mixtures produced little, if any, saturated products. Contrast this with the results in the acetate reaction mixtures.[2]