

- (8) Cf. ref 4a, p 109, and 4b, p 41.  
 (9) Although  $F_2$  is not appreciably dissociated ( $K$  for  $F_2 \rightleftharpoons 2F \approx 10^{-20}$  at 298 K), the concentration of F atoms is generally assumed to be kinetically significant and thus capable of initiating the chain fluorination of organic substrates at room temperature. However, initiation by *molecular* fluorine seems certain for low-temperature (< -40 °C) fluorination of alkanes; cf. (a) W. T. Miller, Jr., S. D. Kocfi, Jr., and F. W. McLafferty, *J. Am. Chem. Soc.*, **78**, 4992 (1965), and ref 4c, p 13. In view of these considerations, F atoms from the dissociation of  $F_2$  can be hardly assigned any kinetic relevance at the much lower temperatures (down to -154 °C) used in the present study. In addition, and more conclusively, orientation in nitrobenzene fluorination affords a mechanistic probe, already applied to fluorination by other reagents; see (b) M. J. Shaw, H. H. Hyman, and R. Filler, *J. Org. Chem.*, **36**, 2917 (1971), to discriminate between electrophilic and homolytic substitution. The latter (cf. (c) G. H. Williams, *Int. Ser. Monogr. Org. Chem.*, **1**, 68 (1960), and (d) "Advances in Free Radical Chemistry", Vol. II, G. H. Williams Ed., Academic Press, New York, N.Y., 1965) is shown to yield a high para/meta isomeric ratio, in contrast to the experimental results obtained in this study.  
 (10) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *J. Am. Chem. Soc.*, **76**, 2597 (1954).  
 (11) Visiting Chemist at Chemistry Department, Brookhaven National Laboratory, on leave of absence from University of Rome, 00100 Rome, Italy.  
 (12) Research carried out at Brookhaven National Laboratory under contract with the Department of Energy and supported by its Division of Biomedical and Environmental Research.

F. Cacace,<sup>11,12</sup> A. P. Wolf\*<sup>12</sup>

Department of Chemistry  
 Brookhaven National Laboratory  
 Upton, New York 11973

Received November 3, 1977

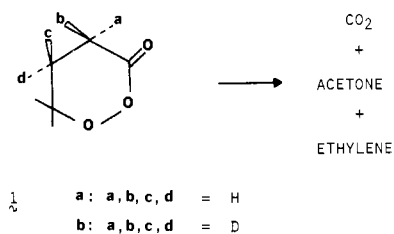
### Thermolysis of $\gamma$ -Peroxy- $\gamma$ -butyrolactones: Alternate Modes for Fragmentation

Sir:

With acyclic peroxy esters or their cyclic analogues, the peroxy lactones, the principal means by which thermal decompositions take place involve O-O bond homolysis followed by or concerted with  $\beta$  scission leading to  $CO_2$  loss.<sup>1</sup> We present evidence here for two alternate fragmentation paths in a series of  $\gamma$ -peroxy- $\gamma$ -butyrolactones functionally substituted at the  $\beta$  position of the ring.

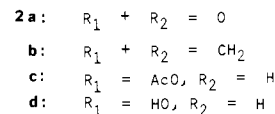
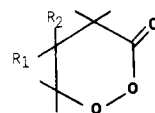
The thermally induced homolytic cleavages of  $\beta$ -peroxy- $\beta$ -propiolactones have been studied intensively by Adam.<sup>2</sup> The results of these studies are consistent with a path having O-O bond breaking as the first step followed by a step in which migration of a  $\beta$  substituent is concerted with  $CO_2$  loss. Activation enthalpies for the compounds studied were 31.0-31.7 kcal/mol and  $\Delta S^\ddagger$  values varied from -1.0 to 0.3 eu.

A few  $\gamma$ -peroxy- $\gamma$ -butyrolactones have been reported<sup>3,4</sup> and Adam and Szendrey<sup>5</sup> have studied the thermolysis of **1a** in detail. The  $\Delta H^\ddagger$  for **1a** is 34.1 kcal/mol and  $\Delta S^\ddagger$  is 6.6 eu.



Thermolysis proceeds as shown. Consistent with the observation of a secondary deuterium isotope effect of  $1.27 \pm 0.2$  for **1b**, they proposed a reaction path in which  $C_{acyl}-C_\alpha$  bond breaking is concerted with O-O scission. The mechanism derives further support from the observation that the cis and trans dideterio derivatives of **1** produce deuterated ethylenes nonstereospecifically, thus ruling out concerted three-bond scission.

We have prepared the  $\gamma$ -peroxy- $\gamma$ -butyrolactones **2a-d** and studied their thermal fragmentations.<sup>6</sup> The reaction products



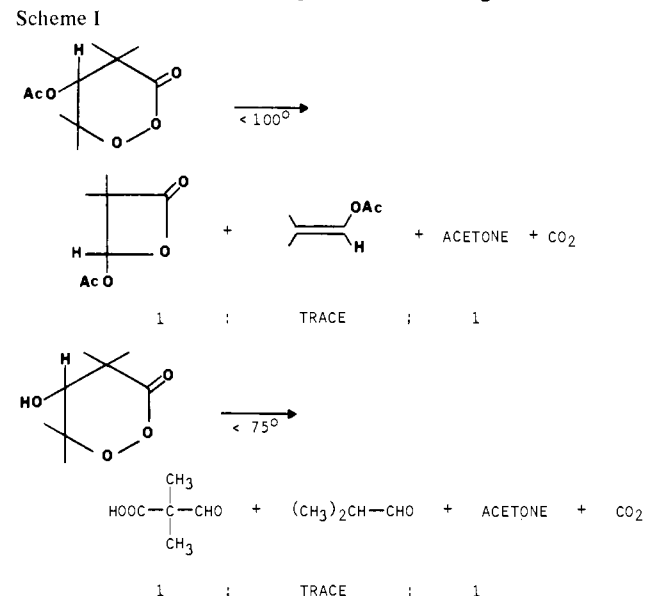
from **2a** were acetone, tetramethyl-1,3-cyclobutanedione (the dimer from dimethyl ketene) and  $CO_2$ . The principal products (>80%) from **2b** are dimethylallene, acetone, and  $CO_2$ .

The fragmentations of **2c** and **2d** take a very different course from those of the first two with deketonation being preferred to decarboxylation (Scheme I).<sup>7</sup> Reactions conducted at temperatures higher than those indicated in the sequences in Scheme I do show larger amounts of the enol acetate or isobutyraldehyde. These compounds are formed as decarboxylation products from the  $\beta$ -propiolactone<sup>8</sup> and the malonic aldehydic acid, respectively; however, it is not yet clear whether small amounts of them can be formed directly from **2c** and **2d** by a minor competing thermolysis path.

The thermolyses of compounds **2a-c** in benzene solution follow first-order kinetics. Rate constants were obtained at three temperatures and activation parameters were found as follows: **2a**,  $\Delta H^\ddagger = 26.96 \pm 0.15$ ,  $\Delta S^\ddagger = 5.27 \pm 0.07$ ; **2b**,  $\Delta H^\ddagger = 34.18 \pm 0.17$ ,  $\Delta S^\ddagger = 8.99 \pm 0.04$ ; **2c**,  $\Delta H^\ddagger = 33.15 \pm 0.12$ ,  $\Delta S^\ddagger = 0.55 \pm 0.06$ . The thermal behavior of **2d** is erratic and we have not been able to obtain satisfactory kinetic data for it. The low temperatures at which complete decomposition<sup>9</sup> of **2d** takes place (1 h at 74 °C in benzene) suggest that this compound may have the lowest  $\Delta H^\ddagger$  of any  $\gamma$ -peroxy lactone yet prepared. Further work on **2d** is in progress.

In a classic work on thermolyses of acyclic peresters Bartlett and Hiatt<sup>10</sup> showed that substituents capable of providing resonance stabilization could effectively lower both  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  in systems substituted at the acyl center. These observations led to a proposed reaction path in which O-O bond breaking was concerted with  $CO_2$  formation in systems with stabilizing substituents. More recently, Pryor and Smith<sup>11</sup> have proposed a scale for peroxy esters using  $\Delta H^\ddagger$  values to differentiate one-bond (O-O) cleavage processes from those involving multibond homolyses in the transition state. One-bond cleavage is proposed to obtain for compounds having  $\Delta H^\ddagger > 33$  kcal/mol and multibond cleavage is suggested when  $\Delta H^\ddagger < 27$  kcal/mol.

Since a limited number of compounds have been studied thus far, such a scale cannot be devised for either the peroxypropiolactones or the peroxybutyrolactones. However, Adam's studies of **1** suggest a lower limit for  $\Delta H^\ddagger$  for one-bond homolyses with the latter compounds. The observation of a secondary deuterium isotope effect here together with the



product studies provides clear evidence for the simultaneous scission of two bonds in the transition state rather than simple O–O bond breaking followed by decarboxylation.

Thus it can be argued for the peroxybutyrolactones that those compounds whose  $\Delta H^\ddagger$  values are  $\leq$  that for **1a** (34.1 kcal/mol) should experience two- or three-bond homolyses in the transition states leading to their fragmentations. The products obtained from **2c** and **2d** are obviously derived from a different type of two-bond scission than the one governing the fragmentation of **1**. Activated complexes for these two types of fragmentations can be represented as A and B. With



**2c** and **2d**, decarboxylation does not successfully compete with deketonation even though a tertiary alkyl radical would be formed as a result of fragmentation from a type B complex. Although the ease of thermolysis of **2a–d** does appear to parallel the expected stability of the radical centers developing at  $C_\beta$ , the correlation may be fortuitous. Ring conformation may also play a significant role in determining the ease and mode of fragmentation; this factor may be particularly important with **2a** and **2b** since the presence of an additional  $sp^2$  carbon would limit the available conformations of the peroxy lactone ring.

The  $\Delta H^\ddagger$  for **2a** is well below that of any other  $\gamma$ -peroxy lactone; the transition state for it may involve concerted three-bond cleavage.<sup>12</sup> Neither of the compounds shown (**3** and **4**), which would be formed from alternate two-bond cleavage mechanisms, are found as reaction products. Compounds of



type **3** require temperatures  $>100$  °C to force their decarboxylation<sup>13</sup> and compound **4** is known<sup>14</sup> to be stable up to 120 °C. Thermolysis of **2a** could be accomplished at temperatures as low as 90 °C; therefore **3** and **4** should have been observable if formed. Although **2b** has the highest  $\Delta H^\ddagger$  of the compounds we studied, the value is approximately the same as the activation enthalpy for **1a**. Neither an oxetane nor a  $\beta$ -propiolactone has been identified as a reaction product here either, although thermolysis of **2b** does yield small amounts of compounds (five by HPLC analysis) not yet characterized and the reactions must be conducted at higher temperatures than for **2a**.

Additional work must be done with the peroxy lactones to establish ground rules, but it is clear that substituents can dictate the course of their fragmentation reactions.

## References and Notes

- (1) L. A. Singer in "Organic Peroxides", Vol. I, D. Swern, Ed., Wiley-Interscience, New York, N.Y., 1970, p 265.
- (2) (a) W. Adam and Y. M. Cheng, *J. Am. Chem. Soc.*, **91**, 2109 (1969); (b) W. Adam, Y. M. Cheng, C. Wilkerson, and W. A. Zaidi, *ibid.*, **91**, 2111 (1969); (c) W. Adam and C. Wilkerson, *Chem. Commun.*, 1569 (1971).
- (3) W. Adam and L. Szendrey, *Chem. Commun.*, 1299 (1971).
- (4) D. H. Gibson and J. T. Joseph, *Tetrahedron Lett.*, 3483 (1972).
- (5) W. Adam and L. Szendrey, *J. Am. Chem. Soc.*, **96**, 7135 (1974).
- (6) Compounds **2b** and **2d** were prepared by oxidations of cyclobutanones as we described<sup>4</sup> for **2a**; **2c** was prepared by acetylation of **2d**. All peroxy lactones had satisfactory elemental analyses and showed the expected spectral properties.
- (7) Thermolysis of a  $\beta$ -acetoxy- $\beta$ -peroxy- $\beta$ -propiolactone proceeds with deketonation (actually loss of acetic anhydride) as a minor competing path

(H. L. Wilson Ph.D. thesis, University of Louisville, 1975); in this case an  $\alpha$ -lactone is formed as the other product (trapped by reaction with an alcohol).

- (8) This compound has been characterized through elemental analysis, spectral properties ( $\nu_{C=O}$  1850, 1775  $cm^{-1}$ ) and thermolysis to the enol acetate (for which satisfactory analysis was also obtained).
- (9) Caution! A neat sample of **2d** detonated when heated to 70 °C.
- (10) P. D. Bartlett and R. R. Hlatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).
- (11) W. A. Pryor and K. Smith, *J. Chem. Kinet.*, **3**, 387 (1971).
- (12) Since **2a** and **2b** are cyclic compounds, concerted three-bond cleavage of either would constitute a  $[2\pi_s + 2\pi_s + 2\pi_s]$  cycloreversion reaction.
- (13) H. Staudinger, Fr. Felix, and H. Harden, *Helv. Chim. Acta*, **8**, 306 (1925).
- (14) B. L. Murr, G. B. Hoey, and C. T. Lester, *J. Am. Chem. Soc.*, **77**, 4430 (1955).

Dorothy H. Gibson,\* Joseph T. Joseph

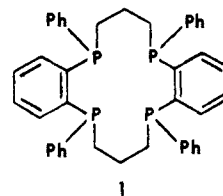
Department of Chemistry, University of Louisville  
Louisville, Kentucky 40208

Received January 23, 1978

## Properties and Structure of a Tetrakis(*tert*-phosphino) Macrocycle

Sir:

We recently reported the isolation of the macrocycle **1**, a potential polydentate ligand for transition metal complexation.<sup>1</sup> This material, mp 229–230 °C, <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$



–28.94 (s),<sup>2</sup> was the one of five possible isomers (three meso and two *dl* pairs) which we designate as isomer A. We wish now to report the isolation, properties, and structure of a second isomer (B),<sup>2</sup> mp  $\sim$ 160–165 °C, <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  –26.10 (s).<sup>3,4</sup>

At slightly above its melting point (165–170 °C) isomer B converts completely into A<sup>5</sup> as evidenced by <sup>31</sup>P NMR spectroscopy and the melting point of the resolidified material. However, heating either pure A or B in the melt at 240 °C (0.25 h) or in refluxing xylene (135 °C, 1 h) gave a mixture of A and B in a ratio of  $1.7 \pm 0.2$ ,<sup>6</sup> by <sup>31</sup>P NMR spectroscopy. Thus the complete conversion of B  $\rightarrow$  A in the melt at  $\sim$ 165 °C is a kinetic process where A is removed from equilibrium by crystallization. Additionally, we did not observe significant amounts of the other three possible isomers (<3%) by <sup>31</sup>P NMR in these thermal equilibration studies.

Both isomers A and B incorporate solvents ( $\sim$ 1 mol of, e.g., benzene, cyclohexane, acetone, tetrahydrofuran) upon recrystallization, but these solvents are not bound strongly enough to allow x-ray diffraction data collection at ambient temperatures. We now report the structure of isomer B, determined at –40 °C to be the *cis-syn-cis* species. A freshly dried single crystal from acetone-THF was transferred to a Syntex P2<sub>1</sub> autodiffractometer where it was bathed in a cold stream of dry N<sub>2</sub>. Crystals are tetragonal, *I*4<sub>1</sub>/*a* (No. 88), *a* = 25.504, *c* = 13.792 Å. Density measurements indicated the presence of no more than eight molecules of B per unit cell. Thus it was known at this stage that the molecule must reside either at a crystallographic inversion center or at a crystallographic twofold axis. Intensity data were gathered for the 4392 unique reflections with  $2\theta < 52^\circ$  (graphite-monochromatized Mo K $\alpha$  radiation). The 2390 reflections with  $I \geq 2\sigma_1$  were used in the structure solution and refinement.<sup>7</sup>

Solution of the structure by direct methods<sup>8</sup> revealed that the molecule was located at the crystallographic twofold