Table I. Stable Structures for MX_4 Systems

	High spin	Low spin		High spin	Low spin
d^0	T_d	T_d	d^6	D_{2d}	D_{4h}
d^1	D_{2d}	D_{2d}	d^7	T_d	D_{4h}
d^2	T_d	D_{4h}	d^8	D_{2d}[b]	D_{4h}
d^3	D_{2d}	[a]	d^9	D_{2d}	D_{2d}
d^4	D_{2d}	D_{4h}	d^{10}	T_d	T_d
d^5	T_d	D_{4h}			

[a] Less than D_{2d} symmetry. [b] Spin-orbit forces can remove the first-order Jahn–Teller effect. $NiCl_4^{2-}$ has T_d symmetry: L. Sacconi, *Transition Metal Chem.*, 4, 199 (1968).

tion. This means a low, or zero, activation energy for conversion into either D_{2d} or T_d symmetry. In combination with the conclusions from the first-order Jahn–Teller effects, we can assign a most stable structure for each four-coordinate system according to the number of d electrons and the spin state. Table I summarizes the results for all systems.

The predictions are in accord with experimental facts where known. Note that the conclusions for D_{4h} are based on no interaction with other groups above and below the plane. Such interactions could raise the (a_{2u}) level markedly and stabilize the planar form. Four simple ligands such as halide or cyanide lead to D_{2d} structures in solution for copper(II) complexes,[12] so that axial solvent perturbations are not sufficient in these cases to create planarity.

It is clear that Jahn–Teller effects can be used to predict the stable structures of molecules in general. In practice an MO scheme is required which need be only qualitatively correct. It also follows that an incorrect MO scheme may predict structures wrongly. A test for stability to second-order Jahn–Teller distortions should always be applied to MO calculations.

[12] D. Forster, *Chem. Commun.*, 113 (1967); O. Mønsted and J. Bjerrum, *Acta Chem. Scand.*, 21, 1116 (1967).

Ralph G. Pearson
Chemistry Department, Northwestern University
Evanston, Illinois 60201

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Cyclic Peroxyesters. II.[1] A Novel Ketene Elimination and Decarboxylation Reaction[2]

Sir:

Acyclic peroxides are reduced by phosphines and phosphites into the corresponding deoxy derivatives.[3] The equation below illustrates this general oxygen extrusion reaction for acyclic peresters and triphenylphosphine.[4] However, only few cyclic peroxides have been

$$RCO_3\text{-}t\text{-}Bu + (C_6H_5)_3P \rightarrow RCO_2\text{-}t\text{-}Bu + (C_6H_5)_3PO$$

submitted to this reaction. For example, ozonides are reduced to ketone products,[5] ascaridole is converted to its endooxide,[3a] while phthalic anhydride is formed from phthaloyl peroxide[6] when these cyclic peroxides are treated with triphenylphosphine. In this communication we describe an unusual fragmentation reaction resulting from the reduction of β-peroxylactones by trivalent phosphorus.

The union of equimolar amounts of β-alkyl-β-phenyl-β-peroxypropiolactone (**1**) and triphenylphosphine in *n*-hexane at room temperature leads to quantitative precipitation of triphenylphosphine oxide and the evolution of a gas. Examination of the reaction mixture by vapor phase chromatography indicates the presence of α-alkylstyrene (**2**) and alkyl phenyl ketone (**3**). Infrared analysis shows in addition small quantities of β-alkyl-β-phenyl-β-propiolactone (**4**), as evidenced by its characteristic carbonyl stretching frequency at 1830 cm^{-1}. This thermally labile product does not survive gas chromatographic analysis and decomposes into carbon dioxide and the substituted styrene (**2**).[7] The product composition of this novel fragmentation reaction is illustrated in Scheme I. As indicated in this scheme, the formation of ketone product requires that ketene is present in the gaseous products besides carbon dioxide. Indeed, the ketene was trapped by menthol, benzyl alcohol, and phenol and identified by means of infrared spectra and retention times with the authentic acetates.

In order to elucidate the mechanism of this unprecedented ketene elimination and decarboxylation reaction, the effect of the solvent, the β-alkyl substituent of the peroxylactone, and the nucleophilic character of the triarylphosphine were examined. The quantitative product data are summarized in Table I. In all cases a quantitative balance in terms of styrene (**2**) and ketone (**3**) products was obtained. The product data show that with increasing size of β-alkyl substituent the proportion of ketene elimination is increased over decarboxylation (entries 1–4 in Table I) On the other hand, the proportion of decarboxylation is increased over ketene elimination with increasing polarity of the solvent (entries 4–7 in Table I). Similarly, increasing electron donation by the triarylphosphine substituent (entries 9–11 in Table I) promotes the degree of decarboxylation over ketene elimination.

The kinetics of this reaction was studied by following the rate of disappearance of the characteristic 1810-cm^{-1} carbonyl stretching frequency of the peroxylactone. Most of the triarylphosphines reacted too rapidly with the peroxylactones to provide accurate kinetic data, and for this reason the phosphites were used. Since triphenyl phosphite (entry 8 in Table I) gave the same products as the triarylphosphines, the use of the phosphites to study the kinetics of this reaction is justified.

The kinetic data, summarized in Table II, were obtained by running the reaction directly in a thermally equilibrated infrared cell, using the variable temperature accessory of Barnes Engineering Co. The wavelength drive mechanism of the Perkin-Elmer 237B Infracord was locked at the desired frequency, and the signal output was relayed to a Heath servorecorder using the ordinate scale expansion accessory. The rate constants in Table II were computed from the kinetic runs using an IBM 1130 computer. The reaction follows the second-order rate law, first order in both the peroxide and nucleophile, through

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[1] For paper I in this series, see F. D. Greene, W. Adam, and G. A. Knudsen, *J. Org. Chem.*, 31, 2087 (1966).

[2] Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[3] (a) L. Horner and W. Jürgeleit, *Ann.*, **591**, 138 (1955); (b) J. I. G. Cabogen, *Quart. Rev.* (London), **16**, 208 (1962).

[4] D. B. Denney, W. F. Goodyear, and B. Goldstein, *J. Am. Chem. Soc.*, **82**, 1393 (1960); **83**, 1726 (1961).

[5] A. G. Davies, "Organic Peroxides," Butterworth & Co. (Publishers) Ltd., London, 1961, p 133.

[6] L. Horner and M. Brueggemann, *Ann.*, **635**, 27 (1960).

[7] (a) E. Grovenstein, Jr., and D. E. Lee, *J. Am. Chem. Soc.*, **75**, 2639 (1953); (b) H. J. Hagemeyer, Jr., *Ind. Eng. Chem.*, **41**, 765 (1949).

Table I. Vpc Product Data of the Reaction of β-Peroxylactones with Trivalent Phosphorus Nucleophiles

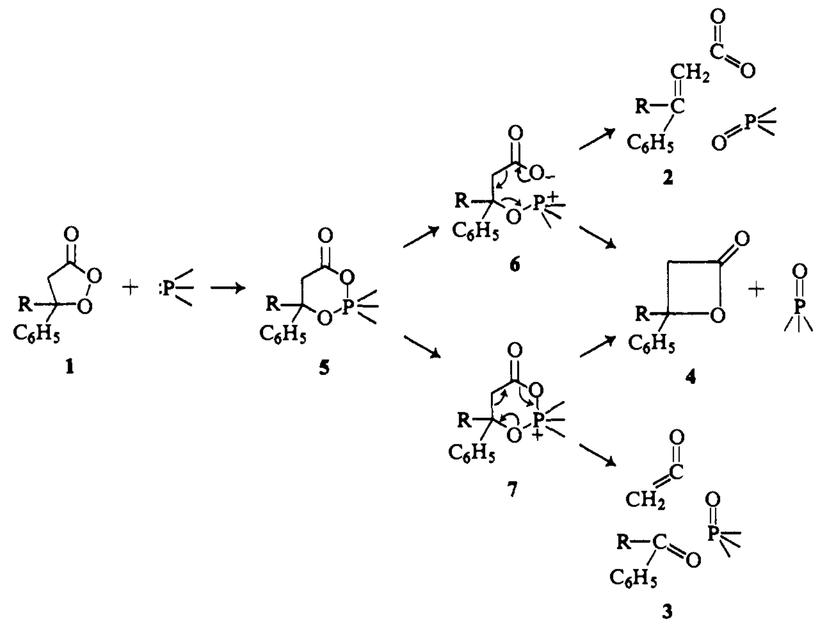
Entry	β-Alkyl substituent	Nucleophile	Solvent	Average yields,[a] %		Ratio
				Styrene	Ketone	
1	Methyl	$(C_6H_5)_3P$	*n*-Hexane	85.3	14.7	5.80
2	Ethyl	$(C_6H_5)_3P$	*n*-Hexane	53.3	46.7	1.14
3	Benzyl	$(C_6H_5)_3P$	*n*-Hexane	46.0	54.0	0.85
4	Isopropyl	$(C_6H_5)_3P$	*n*-Hexane	33.3	66.7	0.50
5	Isopropyl	$(C_6H_5)_3P$	Benzene	36.5	63.5	0.58
6	Isopropyl	$(C_6H_5)_3P$	Acetone	47.0	53.0	0.89
7	Isopropyl	$(C_6H_5)_3P$	Acetonitrile	63.6	36.4	1.75
8	Methyl	$(C_6H_5O)_3P$	Cyclohexane	92.1	6.5	14.2
9	Methyl	$(p\text{-}CH_3C_6H_4)_3P$	Cyclohexane	89.3	9.9	8.98
10	Methyl	$(C_6H_5)_3P$	Cyclohexane	86.7	12.5	6.95
11	Methyl	$(p\text{-}ClC_6H_4)_3P$	Cyclohexane	82.2	17.7	4.65

[a] The error in these numbers is less than 2-3% of the listed values.

Table II. Kinetic Data of the Reaction of β-Peroxylactones with Trivalent Phosphorus Nucleophiles

Entry	β-Alkyl substituent	Nucleophile	Solvent	Temp, °K	*k*, l. mol^{-1} sec^{-1}
1	Methyl	$(C_2H_5O)_3P$	Cyclohexane	303.2	5.94 ± 0.10
2	Methyl	$(C_2H_5O)_3P$	Cyclohexane	310.8	10.1 ± 0.20
3	Methyl	$(C_2H_5O)_3P$	Cyclohexane	318.0	16.1 ± 0.32
4	Ethyl	$(C_2H_5O)_3P$	Cyclohexane	318.0	5.02 ± 0.06
5	Benzyl	$(C_2H_5O)_3P$	Cyclohexane	318.0	3.96 ± 0.07
6	Isopropyl	$(C_2H_5O)_3P$	Cyclohexane	318.0	1.94 ± 0.04
7	Ethyl	$(C_6H_5O)_3P$	Cyclohexane	310.8	0.0688 ± 0.0018
8	Ethyl	$(CH_3O)_3P$	Cyclohexane	310.8	1.77 ± 0.02
9	Ethyl	$(C_2H_5O)_3P$	Cyclohexane	310.8	3.33 ± 0.06
10	Ethyl	$(i\text{-}C_3H_7O)_3P$	Cyclohexane	310.8	4.56 ± 0.04
11	Ethyl	$(C_2H_5O)_3P$	Carbon tetrachloride	310.8	3.57 ± 0.05
12	Ethyl	$(C_2H_5O)_3P$	2-Nitropropane	310.8	3.24 ± 0.05
13	Ethyl	$(C_2H_5O)_3P$	Acetonitrile	310.8	3.33 ± 0.06
14	Benzyl	$(p\text{-}ClC_6H_4)_3P$	Cyclohexane	303.0	57.9 ± 0.73

Scheme I. Mechanism of the Reaction of β-Peroxylactones with Trivalent Phosphorus Nucleophiles



five to six half-lives. The activation parameters lie in the range $\Delta H^{\neq} = 12.3\text{–}15.2$ kcal/mol and $\Delta S^{\neq} = 28.2\text{–}21.7$ cal/°K mol for the various β-substituted peroxylactones. The rate of reaction decreases with increasing size of the β-alkyl group (entries 3-6 in Table II). As expected, the rate of reaction increases with increasing nucleophilicity of the phosphite (entries 7-10 in Table II). An excellent Hammett plot of the relative rates against the σ^* values of the phosphite substituents was obtained with a ρ value of −0.73.[8] The most significant evidence concerning the

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[8] K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1963.

mechanism of this reaction is the virtually complete absence of a kinetic solvent effect (entries 9, 11–13 in Table II).

The absence of a solvent effect on the rate of reaction but the presence of a solvent effect on the product distribution require a mechanism in which the kinetic step and product step are clearly separated in two distinct events.[4] For this reason we propose a mechanism (Scheme I) in which the phosphorus nucleophile is initially inserted into the peroxide bond *via* a slow step leading to the pentacovalent phosphorus intermediate **5**.[9] In a subsequent fast step the unstable pentacovalent intermediate **5** then opens up to produce the two possible dipolar ions **6** and **7**.[10] The dipolar ion **6** fragments into α-alkylstyrene (**2**) and carbon dioxide, while the dipolar ion **7** disproportionates into alkyl phenyl ketone **3** and ketene.[11] The small amount (about 6–9%) of β-alkyl-β-phenyl-β-propiolactone (**4**) is presumably formed by internal nucleophilic displacement of phosphine oxide or phosphate from either dipolar ion. All attempts to trap the pentacovalent phosphorus intermediate **5** have failed so far.[12] In fact, a kinetic experiment has shown that the rate of peroxylactone consumption is identical within experimental error with the rates of formation of styrene, ketone, and β-lactone. Therefore, no appreciable amount of the pentacovalent intermediate **5** accumulates during the course of the reaction.

The experimental details and the elaborate discussion of the mechanism of this novel ketene elimination and decarboxylation reaction will be presented shortly.

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[9] F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

[10] D. B. Denney and S. T. D. Gough, *J. Am. Chem. Soc.*, **87**, 138 (1965).

[11] A. Eschenmoser, D. Felix, and G. Ohloff, *Helv. Chim. Acta*, **50**, 708 (1967).

[12] J. S. Cohen, *J. Am. Chem. Soc.*, **89**, 2543 (1967).

[13] M.S. Thesis, University of Puerto Rico, Sept 1966.

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Waldemar Adam, Robert J. Ramirez,[13] Shih-Chuan Tsai[14]
Department of Chemistry, University of Puerto Rico
Río Piedras, Puerto Rico 00931

Received December 2, 1968

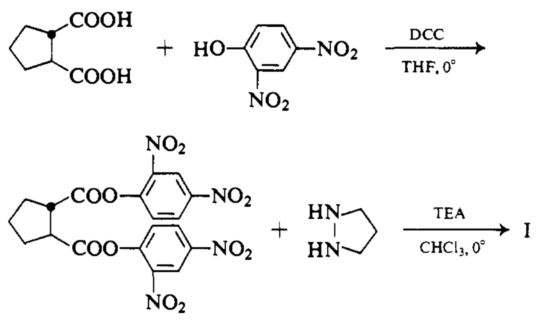
Optical Rotatory Properties of Cyclic Compounds Related to Diketopiperazines

Sir:

We have been interested in the optical rotatory properties of rigid molecules containing at least two identical neighboring chromophores as a way of further exploring the predictions of the exciton theory[1,2] and of providing useful models for macromolecular systems.

We wish to report some preliminary results on the optical properties of four cyclic compounds (Table I) that are related isomerically to diketopiperazine systems. These cyclic compounds were obtained from the appropriate optically active dicarboxylic acids and cyclic hydrazines by a method, chosen to avoid racemization,[3] which is illustrated in Scheme I. Compound I is isomeric with prolylprolyldiketopiperazine.

Scheme I



The optical rotatory properties of amino acid diketopiperazines, which have been investigated recently,[4-6] show a relatively strong $n-\pi^*$ Cotton effect together with a rather weak $\pi-\pi^*$ Cotton effect. Although diketopiperazines show an unusually high rotation, our cyclic compounds display rotation four times higher, a remarkable result obtained by rearranging the disposition of the amide chromophores in the molecule.[7]

Optical rotatory dispersion (ORD), circular dichroism (CD), and ultraviolet (uv) data obtained in trifluoroethanol (TFE) for these cyclic compounds are reported in Table I. Generally, measurements were carried out at concentrations of about $10^{-2}\,M$, but dilutions up to $10^{-6}\,M$ did not appreciably affect the results.

The uv spectrum of compound IV shows a band at 210 mμ and another strong band at about 250 mμ (Figure 1). The presence of the latter band in the spectrum is also evident in the related open-chain compound V, diisobutyrylpyrazolidine (Figure 2). The assignment of the shorter wavelength band in the uv spectrum to a $\pi-\pi^*$ transition of the amide group and of the longer wavelength band to an $n-\pi^*$ transition of the same chromophore seems reasonable enough in compound V. These results would have provided a basis for a similar assignment in the remaining compounds, except for the high intensity of the longer wavelength band which must be taken into account (Figure 1, Table I). Approximately the same situation occurs in the other compounds that were investigated (Table I).

Although there is little doubt that an $n-\pi^*$ transition is present in that region, it seems unlikely that it can be responsible for the high absorption observed. Probably, the bulk of the effect comes from the longer wavelength

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[1] For a review of exciton theory and its applications to organic molecules, see: M. Kasha, *Radiat. Res.*, **20**, 55 (1963).

[2] J. A. Schellman, *Accounts Chem. Res.*, **1**, 144 (1968).

[3] D. F. DeTar, M. Gouge, W. Honsberg, and U. Honsberg, *J. Amer. Chem. Soc.*, **89**, 988 (1967).

[4] (a) D. Balasubramanian and D. B. Wetlaufer, *ibid.*, **88**, 3449 (1966); (b) D. Balasubramanian and D. B. Wetlaufer in "Conformation of Biopolymers," G. N. Ramachandran, Ed., Academic Press, New York, N. Y., 1967, p 147.

[5] J. A. Schellman and E. B. Nielsen, in ref 4b, p 109.

[6] F. A. Bovey, private communication.

[7] Molecular models indicate that the geometry of the central ring differs from a planar diketopiperazine and this may cause the chromophore to be inherently dissymmetric.