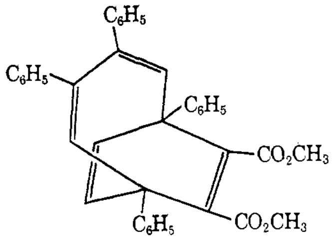
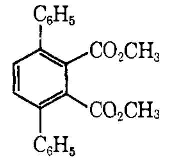
tion[10,11] to give II. The formation of adduct IV is accounted for similarly by 1,4 bonding with the exposed C-4,5,6,7 diene system or by interception of species V.

The adduct of VII with dimethyl acetylenedicarboxylate did not contain a 1,2-diphenylcyclobutene chromophore ($\lambda_{max}^{CH_3OH}$ 272 nm (log ϵ 3.96); $\lambda_{max}^{C_6H_{14}}$(fluorescence) 385 nm) and on irradiation it yielded dimethyl 3,6-diphenylphthalate (X). These and other data lead to structure IX for this adduct and confirm the position of attack of the dienophile at carbons 4 and 7 of photoisomer VII.


IX


X

Acknowledgment. We thank the Petroleum Research Fund of the American Chemical Society (PRF 328-A) for its support of this work.

[10] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

[11] Cyclization of a *cis,trans*-1,3-cyclooctadiene has been reported (K. M. Schumate, P. N. Neuman, and G. J. Fonken, *J. Am. Chem. Soc.*, **87**, 3996 (1965); R. S. H. Liu, *ibid.*, **89**, 112 (1967)).

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The Mechanism of Hydrolysis of Diethyl 2-Carboxyphenylphosphonate[1]

Sir:

The hydrolysis of diethyl 2-carboxyphenylphosphonate, I, has been estimated[2] to proceed some 8 × 10^7 times faster than that of the *para* isomer. A mechanism involving general acid catalysis was suggested[2] similar to that advocated by Bender and Lawlor[3] for salicyl phosphate. We have investigated the reaction in detail with the following results and conclusions.

The rate of hydrolysis of the first ester function[4] of I, followed by pH-stat titration, is expressed by eq 1, giving the pH profile shown in Figure 1. The rate of hydrolysis of diethyl 2-carboxymethylphenylphosphonate,[5] VII, $pK_a = 4.2$, was found to be 5.4×10^{-5} min^{-1} at pH 3.0 and 79.5° which is some *10^5 times slower* than that of the diester I. The final hydrolysis product of I is the acid III.

Partial hydrolyses of I in D_2O at pD 3.5 were halted by the addition of alkali to pD 10 and shown to contain an intermediate not present in the products of complete hydrolysis and having the same nmr spectrum as the monoester II, which is best obtained by controlled alkaline hydrolysis of the ester anhydride V. The pH profile for the hydrolysis of the monoester II, which can be followed by change in optical density[6] at 252 nm, is well expressed by eq 2 (Figure 1).

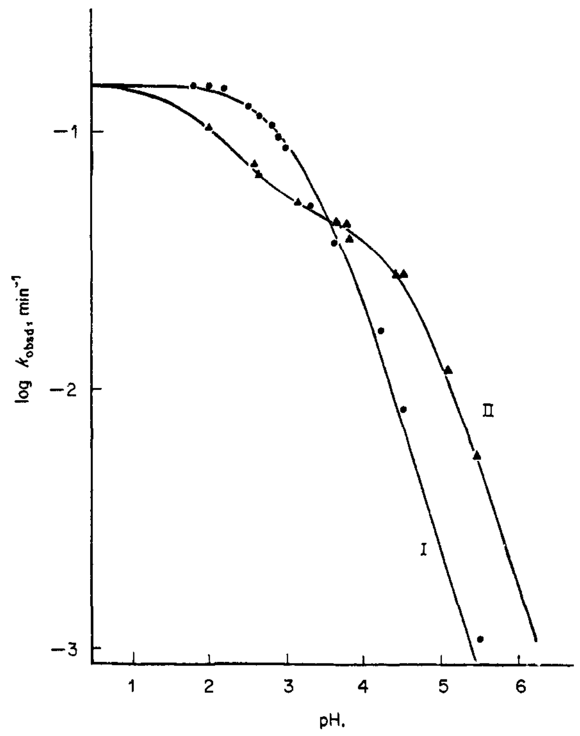
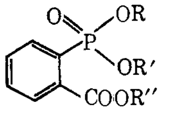
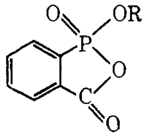
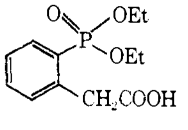
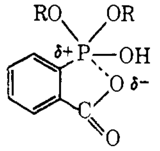


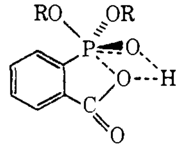
Figure 1. Dependence of k_{hydr} on pH. Solid lines calculated from rate constants given in text. Experimental values: diester I, ●; monoester II, ▲.


I, R = R′ = Et; R″ = H
II, R = Et ; R′ = R″ = H
III, R = R′ = R″ = H
IV, R = Et; R′ = Me; R″ = H


V, R = Et
VI, R = H


VII


A


B

$$k_I^{obsd} = 0.156a_H/(a_H + K_1) \text{ min}^{-1} \tag{1}$$

$$k_{II}^{obsd} = \frac{0.15a_H^2 + 0.0637K_2a_H}{K_2K_3 + K_2a_H + a_H^2} \text{ min}^{-1} \tag{2}$$

$K_1 = 7.08 \times 10^{-4}$, $K_2 = 7.94 \times 10^{-3}$, and $K_3 = 3.98 \times 10^{-5}$ *M*.

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[1] This research was supported in part by a scholarship (to M. J. B.) from the United Coke and Chemical Co.

[2] M. Gordon, V. A. Notaro, and C. E. Griffin, *J. Am. Chem. Soc.*, **86**, 1898 (1964).

[3] M. L. Bender and J. M. Lawlor, *ibid.*, **85**, 3010 (1963).

[4] All kinetic experiments were performed in aqueous solution, ionic strength 0.1 at 25 ± 0.1°, except where otherwise indicated.

[5] All new compounds described have been adequately characterized by analytical and spectroscopic data.

[6] Although hydrolysis of II produces a second phosphorus acid function, $pK_a = 9.17$, II is fully protonated in the pH range studied for the hydrolysis of I and does not interfere with the first-order kinetic form of k^{obsd}.

The anhydride V, produced on gentle thermolysis of I, is hydrolyzed rapidly to II in acid or alkaline solution and thence to the parent acid III. The rate of the first hydrolysis step is 26 times faster than that of I at pH 2.0 and at higher pH's becomes too fast to measure by titration. Similarly the acid anhydride VI, obtained by pyrolysis of III, also hydrolyzes to III at a rate too fast to measure by titration or spectroscopy in the range pH 1 to 10. Thus both V and VI satisfy the kinetic requirement for their being intermediates in the hydrolysis of I to III.

The introduction of MeOD into a solution of V in $CDCl_3$ results in the immediate addition of methanol to phosphorus to give IV, shown by the appearance of a characteristic doublet at τ 6.13 in the nmr spectrum. In the presence of deuterated *p*-toluenesulfonic acid the same addition of methanol to phosphorus is followed by a slower replacement of the POEt signal by increased POMe resonance. In contrast, hydroxylamine at pH 5 or 7 rapidly converts V into a hydroxamic acid revealed by ferric chloride assay.[7] This reaction, characteristic of acyl phosphates,[3,8] is not given by the diesters I and VII or by the acid III under similar conditions. Nevertheless, hydroxamic acid is produced (with first-order kinetic rate) when I is slowly hydrolyzed in 4 *M* hydroxylamine buffer at pH 4.7. This is substantive evidence that V is an intermediate in the hydrolysis of I to II and, by analogy, that VI is formed in the hydrolysis of II to III.

Finally, the hydrolysis of carbonyl ^{18}O-enriched ester I provides the acid III with no significant loss of isotope. Also, the acid III after brief equilibration with ^{18}O-enriched water shows incorporation of isotope into all three phosphorus oxygens but not into the carboxyl group. These experiments establish that hydrolysis of I does not involve C–O cleavage at any stage in the formation of III.

We interpret these results to mean that the hydrolysis of I proceeds through successive intermediates V, II, and VI to the acid III, with alternate ring-closure and ring-opening processes. It may be significant that this route avoids any process which would violate the rules of pseudorotation.[9] Two possible transition states with apical orientation of the attacking oxygen are A and B. The specific acid nucleophilic catalysis mechanism A does not account for the observation (Figure 1) that the monoanion of ester II exhibits pH-independent hydrolysis in the range 3.5 to 5.5 and also that on protonation of the anion the hydrolysis rate increases only twofold. We prefer the concerted, four-center transition state B which is in accord with all the data presented here and has important stereochemical implications which will be discussed elsewhere in detail.

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(7) F. Lipmann and L. C. Tuttle, *J. Biol. Chem.*, **159,** 21 (1945).

(8) G. Di Sabato and W. P. Jencks, *J. Am. Chem. Soc.*, **83,** 4393 (1961).

(9) F. H. Westheimerk *Accounts Chem. Res.*, **1,** 70 (1968).

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Stereochemical Nonrigidity in Phosphorus Trifluoride Substituents of Trifluoromethylcobalt Tetracarbonyl

Sir:

The study of stereochemically nonrigid compounds has become an important area of investigation in recent years. In the field of coordination chemistry, these studies have been directed particularly toward organometallic compounds containing cyclic polyolefins. In these compounds, hydrogen atoms, which on simple inspection appear to be unquestionably nonequivalent, frequently appear equivalent at room temperature on the nmr time scale. Low-temperature studies have allowed the investigation of the processes that allow this equivalence to occur.[1]

Some five-coordinate species are also thought to be stereochemically nonrigid. Both of the compounds PF_5[2] and $Fe(CO)_5$[3] have been shown to have a trigonal-bipyramid structure, yet F^{19} and C^{13} nmr studies[4,5] fail to show the expected nonequivalence between the axial and equatorial atoms. It has been postulated that a rapid internal inversion creates an average environment of the nuclei resulting in the apparent equivalence. However, variable-temperature studies have not given any confirmation of the mechanism for these compounds. Indeed, only rarely have studies given support for such a mechanism in five-coordinate systems[6] and never with five-coordinate transition metal carbonyl complexes.

We present here some clear-cut cases of stereochemical nonrigidity in the five-coordinate system of compounds $CF_3Co(PF_3)_x(CO)_{4-x}$. For the compound where $x = 1$, $CF_3Co(CO)_3(PF_3)$, fluorine nmr studies at room temperature produce spectra that can be accounted for on the basis of only one species. In the 30° spectrum of Figure 1, resonance centered 634 Hz downfield from the reference, $CFCl_3$, belongs to the methyl fluorines. This resonance is split into a doublet by the phosphorus with a J_{FCP} of 58 Hz, and this

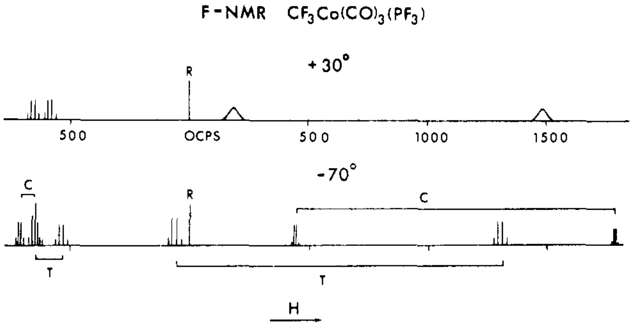

Figure 1. Fluorine nmr spectra of $CF_3Co(CO)_3(PF_3)$ at 30 and −70°—diagrammatic representation (reference, $CFCl_3$).

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(1) For a review of some of these studies, see F. A. Cotton, *Accounts Chem. Res.*, **1,** 257 (1968).

(2) K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, **4,** 1775 (1965).

(3) A. W. Hanson, *Acta Cryst.*, **17,** 930 (1962); J. Donohue and A. Caron, *ibid.*, **17,** 663 (1964).

(4) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21,** 279 (1953).

(5) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *ibid.*, **29,** 1427 (1958); R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58,** 1893 (1962).

(6) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2,** 613 (1963).