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PHOSPHINIC ACIDS AND DERIVATIVES. 5. DISPLACEMENT AT PHOSPHORUS STUDIED THROUGH ALKALINE HYDROLYSIS OF ALKYL DIPHENYLPHOSPHINATES. EFFECT OF ORIENTATION. OF THE PHENYL RINGS ON RATES OF DISPLACEMENT[1, 2]

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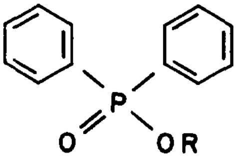
The problems of the mechanism of displacement at phosphorus and the nature of π bonding to phosphorus have continued to be challenging ones.[3] In some recent communications, phosphinates have been reported as substrates in studies of alkaline hydrolysis of esters.[4] We report here a summary of some of our most important results for diarylphosphinates including data on hydrolysis in oxygen-18 water and the effect of changing orientation of aryl rings with respect to the OPO plane.

Hydrolyses of methyl and isopropyl diphenylphosphinate (**1**, R = CH_3 and $CH(CH_3)_2$ respectively) were carried out in alkaline 33/67 (v/v) dioxane/water enriched with approximately 1.76 atoms % ^{18}O. Diphenylphosphinic acid (**1**, R = H) was isolated after about 90% hydrolysis and analyzed for ^{18}O. Two separate experiments at 75° and 43° gave the identical result of 0.97 atoms of oxygen from water incorporated into diphenylphosphinic acid during hydrolysis of the methyl ester. One experiment on **1**(R = $-CH(CH_3)_2$) resulted in 1.00 atoms incorporated. In a separate hydrolysis of **1**(R = $-CH(CH_3)_2$) to 50% completion, 0.98 atoms of oxygen from solvent were incorporated into diphenylphosphinic acid, but the starting ester had the same oxygen-18 content as starting ester isolated from a hydrolysis to 50% completion in unenriched water. These results establish that in alkyl diphenylphosphinates (with the probable exception of t-alkyl esters where elimination is indicated[5]), *alkaline hydrolysis occurs with complete attack of hydroxide at phosphorus, and there is no exchange into the phosphinyl oxygen during hydrolysis. If exchange takes place, the exchange rate is at least 200 times slower than the rate of hydrolysis.*



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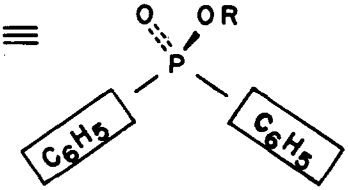

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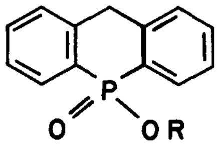

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This result is in contrast to Bender's[6] research which established an intermediate in the alkaline hydrolysis of carboxylic esters. However, the absence of exchange in phosphinates may not indicate absence of an intermediate. An intermediate could be formed, but hydrolysis could still be faster than exchange for a number of reasons.[7] The stability of pentacoordinate phosphorus compounds[8] certainly indicates the probable presence of addition intermediates in displacement at phosphorus.[9]

The relative rates of hydrolysis of some esters are given in Table I. The rate law is $v = k[\text{Ester}][\text{HO}^-]$. The steep dependence of rate on the nature of the alkyl group is striking and is not observed in acetates (Table I). Since acetates are quite free of steric hindrance,[10] the relative rates of acetates may be taken as an approximate measure of the inductive effect of the alkyl groups. The balance of the rate sequence for attack at diphenylphosphinyl phosphorus is probably due to steric effects. Therefore, *displacement at tetrahedral phosphinyl phosphorus appears to be quite sensitive to steric effects.*[4, 11]

Finally, we report some data relative to the question of the nature of π interactions between phenyl rings and phosphinyl phosphorus.[12] An intriguing question concerns the problem of angular relation between the planes of the phenyl rings and the O-P-O plane. Moffitt[13] has considered this question from a theoretical viewpoint for sulfones--probably the closest sulfur analog to phosphinates. Crystal structures[14] show that diphenylphosphinates have the expected "A-frame" conformation (2) of the two phenyl rings. We have synthesized diphenylmethane-2,2-phosphinic acid (3) (R = H).[15] The phenyl rings are turned towards a more coplanar arrangement in this acid although they are not completely coplanar because 3 will have a butterfly conformation as in 9,10-dihydroanthracene. The rate of alkaline hydrolysis of the methyl ester (3, R = CH_3) has been measured at three temperatures over a 30° range. The relative rates and activation parameters are compared to 1(R = CH_3) in Table II. It is clear that the change in orientation of the phenyl rings has had a negligible effect. Although the rate difference exceeds experimental error, it is so small that it could be due to any number of factors. Therefore, *there appears to be no angular dependence on π interaction between a phenyl ring and phosphinyl phosphorus*. This might be expected if π bonding did involve orbitals at phosphorus with considerable d character--d orbitals should be able to accommodate any orientation of the phenyl rings.

Table I

Rates of Alkaline Hydrolysis of Alkyl Diphenylphosphinates in 33% Dioxane-Water[a] at 50°

R	$(C_6H_5)_2PO_2R$ $(10^4k(M^{-1}sec^{-1})$	$HO^- +$ $(C_6H_5)_2PO_2R$ k_{rel}	$HO^- +$ CH_3CO_2R k_{rel}
Methyl	138	320	6
Ethyl	11.4	27	4
n-Propyl	4.94		
Isobutyl	2.26		
Isopropyl	0.429	1	1
Neopentyl	0.397		

[a] Solvent prepared from 33 parts dioxane and 67 parts water by volume at 25.°

[b] E. J. Salmi and R. Leimu, *Suomen Kemistilehti*, **20B**, 43 (1947).

Table II

Data for Alkaline Hydrolysis of **1** ($R = CH_3$) and **3** ($R = CH_3$) in 33% Dioxane-Water at 50°

Compound	$10^2k(M^{-1}sec^{-1})$	$\Delta F^{*a}_{50°}$	$\Delta H^{*a}_{50°}$	$\Delta S^{*b}_{50°}$
1 ($R = CH_3$)	2.24	21.7	12.1	-29.6
3 ($R = CH_3$)	1.72	21.6	13.1	-26.1

[a] Units are kcal/mole [b] Units are cal/deg. mole

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2. C. E. Diebert, Ph.D. Thesis, University of California, Los Angeles, 1966.

3. P. Haake, D. R. McCoy, W. Okamura, S. R. Alpha, S. Wong, D. A. Tyssee, J. P. McNeal, and R. D. Cook, *Tetrahedron Letters*, 5243 (1968), and references cited therein.

4. W. Hawes and S. Trippett, *Chem. Comm.*, 577 (1968) and references cited therein.

5. The t-butyl ester (**1**, R = $-C(CH_3)_3$) undergoes first order decomposition (rate independent of $[HO^-]$)and isobutylene is produced.[2]

6. M. L. Bender, *J. Am. Chem. Soc.*, **73**, 1626 (1951).

7. Important factors might be the preferred conformation of the pentavalent intermediate, pseudorotation, acidity of the intermediate, and the mechanism of decomposition of the intermediate.[8]

8. E. L. Muetterties and R. A. Schunn, *Quart. Rev.*, **20**, 245 (1966); R. J. Gillespie, *J. Chem. Ed.*, **40**, 295 (1963); F. H. Westheimer, *Accounts of Chemical Research*, **1**, 70 (1968).

9. It is consistent with hydrolysis through an intermediate that in aryl esters the transition state does not appear to involve breaking of the P—OAr bond.[3]

10. R. W. Taft in M. S. Newman "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, 1956, p. 593.

11. P. Haake, R. D. Cook, and W. Schwarz, *Tetrahedron Letters*, 5251 (1968); R. D. Cook, Ph.D. Thesis, UCLA, 1967.

12. In other research we have shown that aryl rings give both resonance and inductive interaction with phosphorus in phosphinates; reference 3. This research also indicates that rates of alkaline hydrolysis are fairly sensitive measures of electron density at phosphinyl phosphorus.

13. H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

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15. Previously synthesized in low yields by G. O. Doak, L. D. Freedman, and J. B. Levy, *J. Org. Chem.*, **29**, 2382 (1964). Our route involves ring closure of the carboxylic acid obtained by oxidation of phenyl-o-tolylphosphinic acid and reduction of the resulting keto compound.