

THE REARRANGEMENT OF DIALKYL α,β -EPOXYPHOSPHONATES

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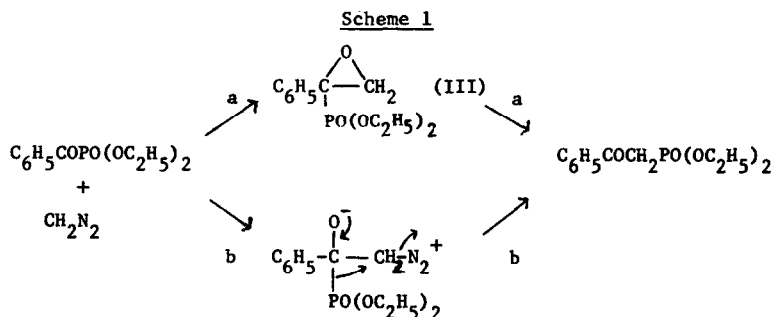
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The migration of a dialkoxyposphono group to an electron deficient terminus appears to have been substantiated to date for only two classes of rearrangements.^{2,3} A number of α,β -epoxyvinylphosphonates of type I have been converted by Churi and Griffin to α -formylalkylphos-



phonates (II), some by heating, others (Ia, Ib) by treatment with boron trifluoride etherate. The latter reactions are undoubtedly "carbonium-ion" type rearrangements involving cleavage of the tertiary C-O bond and 1,2 migration of the diethoxyphosphono substituent in preference to hydrogen. A prior report by Arbuzov⁴ that the reaction of diethyl benzoylphosphonate with diazomethane yielded diethyl phenacylphosphonate was interpreted by Griffin² as proceeding by thermal rearrangement of an intermediate epoxide (III; path a of Scheme 1) and involving cleavage of the H₂C-O bond with migration of the diethoxyphosphono group in preference to the phenyl group. The direction of the postulated cleavage of the oxirane ring of III is inconsistent with findings



in this laboratory.⁵ The interpretation of Kirby and Warren⁶ that the reaction proceeds via path b of Scheme 1 is more attractive. It views the rearrangement as being of the "carbonium ion" type and concludes that in such rearrangements "the (CH₂CH₂O)₂PO group migrates better than the phenyl group".⁶

In a previous communication³ we reported the Baeyer-Villiger rearrangement of diethyl

aryolphosphonates and showed that in that rearrangement the rate of C → O migration of the diethoxyphosphono group far exceeded even that of a *p*-methoxyphenyl group. However, in presence of the results recorded below, this exceptional migratory aptitude of the phosphono residue was interpreted as the consequence of a transition state stabilized by $d\pi - p\pi$ bonding of a type not available in C → C migrations.

We now present evidence that in the C → C migrations occurring on Lewis acid catalyzed rearrangement of epoxides, the migratory aptitude of a dialkylphosphono group, while exceeding that of hydrogen or an alkyl group, is smaller than that of a phenyl group.

The α,β -epoxyphosphonates IV,VI,VII and VIII were prepared by the methods indicated in Table 1. These methods do not permit a firm conclusion as to the configuration (E or Z⁷) of the products. The spectral properties of the latter were also of no avail in this connection. We therefore developed a method for the preparation of α,β -epoxyphosphonates from the corresponding α,β -unsaturated phosphonate esters, by the action of *m*-chloroperbenzoic acid in refluxing methylene chloride (48 hrs.).⁸ The configuration of α,β -unsaturated phosphonic acids and esters may be assigned on the basis of their NMR spectra,⁹ and the well-established stereospecificity of the epoxidation reaction permits deduction of the configuration of the epoxides. Compounds IV and V (Table 1) of known configuration were prepared in this manner. Determination of the products of rearrangement of stereoisomeric epoxides of known configuration was of significance in the present investigation since it had been found previously that such an isomeric pair may yield different products.¹⁰ A similar observation is reported herein.

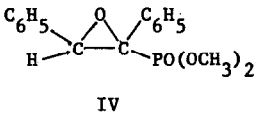
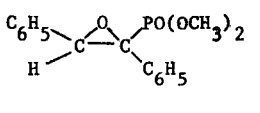
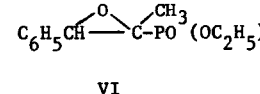
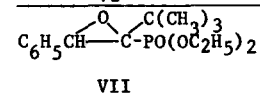
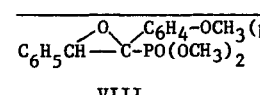
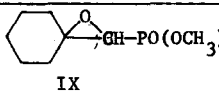
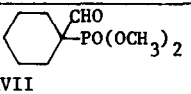
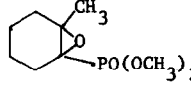
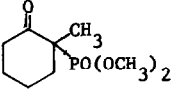
Treatment of methylene chloride solutions (5 ml) of 50 mg each of the epoxides listed in Table 1, with boron trifluoride-etherate (0.25 ml) for 24 hrs. at ambient temperatures, resulted in the formation of the products shown.

The quantitative conversion of IX to XVII confirms the report of Griffin on the diethoxy homolog of IX that the phosphono substituent migrates in preference to hydrogen. Similarly, the products XIV,XV and XVIII obtained from VI,VII and X respectively, show that $(RO)_2PO$ migrates faster than alkyl. Though it may be argued that XVIII results from methyl migration following (P-)C-O cleavage in X,¹¹ this appears unlikely, since in that case one would also expect the product of ring contraction¹²; furthermore, the "carbonium ion" formed by $(CH_3^-)C-O$ cleavage in X is presumably the stabler one.

The rearrangement of (E)- α -dimethoxyphosphonostilbene oxide (IV) led to dimethyl diphenylacetylphosphonate (XII) in 66% yield, while that of the Z isomer (V) produced XII in 34% yield as the only product of (H+)C-O cleavage. These results establish the preferential migration of the phenyl over the dimethoxyphosphono group.

The formation of the aldehyde XIII proceeds by cleavage of the (P-)C-O bond. While this is a noteworthy phenomenon (cf. also formation of XVI from VIII) it is not pertinent to the present discussion. There remains an ambiguity regarding the mechanism of formation of XI. It, and the apparent contradiction between the findings presented here and the report of Arbuzov⁴ as interpreted by Kirby and Warren⁶, remain to be clarified.

Table 1

Starting Epoxide ^a	Method of Synthesis ^b	Rearrangement Product(s) ^a	Yield %	n.m.r. -ppm. downfield from TMS(δ) ^e i.r.- ν (C=O) in cm^{-1}
 IV	A, C	$\text{C}_6\text{H}_5\text{C}(\text{O})\text{CH}(\text{C}_6\text{H}_5)\text{PO}(\text{OCH}_3)_2$ XI + $(\text{C}_6\text{H}_5)_2\text{CHC}(\text{O})\text{PO}(\text{OCH}_3)_2$ XII	11 ^c 66 ^c	5.37($\equiv\text{CH}$, d, J_{PH}^{22} Hz) 1680 in KBr 5.81($\equiv\text{CH}$, d, $J_{\text{PH}}^{1.3}$ Hz) 1690 in KBr; 1700 in CHCl_3
 V	C	$(\text{C}_6\text{H}_5)_2\text{CHC}(\text{O})\text{PO}(\text{OCH}_3)_2$ XII + $\text{H}-\text{C}(\text{O})-\text{C}(\text{C}_6\text{H}_5)_2\text{PO}(\text{OCH}_3)_2$ XIII	34 66	as above 9.90(CHO , d, J_{PH}^4 Hz) 1720 in CHCl_3
 VI	A	$\text{CH}_3-\text{C}(\text{O})\text{CH}(\text{C}_6\text{H}_5)\text{PO}(\text{OC}_2\text{H}_5)_2$ XIV	100	4.44($\equiv\text{CH}$, d, J_{PH}^{24} Hz) 1715 neat
 VII	A	$(\text{CH}_3)_3\text{CC}(\text{O})\text{CH}(\text{C}_6\text{H}_5)\text{PO}(\text{OC}_2\text{H}_5)_2$ XV	33 ^d	4.87($\equiv\text{CH}$, d, J_{PH}^{20} Hz) 1700 in CHCl_3
 VIII	A	$\text{H}-\text{C}(\text{O})-\text{C}(\text{C}_6\text{H}_5)\text{PO}(\text{OCH}_3)_2$ XVI	100	9.77(CHO , d, J_{PH}^4 Hz) 1725 in CHCl_3
 IX	B	 XVII	100	9.53 (CHO , s) 1720 in CHCl_3
 X	C	 XVIII	100	1.36(CH_3 , d, J_{PH}^{15} Hz) 1700 in CHCl_3

(a) The n.m.r., i.r., u.v. and mass spectra of starting epoxides and rearrangement products were in complete agreement with assigned structures. (b) A - Reaction of α -haloketone with dialkyl phosphite¹³; B - Darzen type condensation of dimethyl chloromethylphosphonate with cyclohexanone in presence of sodamide in benzene (cf. Ref. 2); C - epoxidation of α, β -unsaturated phosphonate ester with *m*-chloroperbenzoic acid. (c) 12% of IV was recovered unchanged. (d) Other products obtained resulting from (P)C-O cleavage. (e) n.m.r. spectra determined in CDCl_3 solution on a Varian HA-100 spectrometer.

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