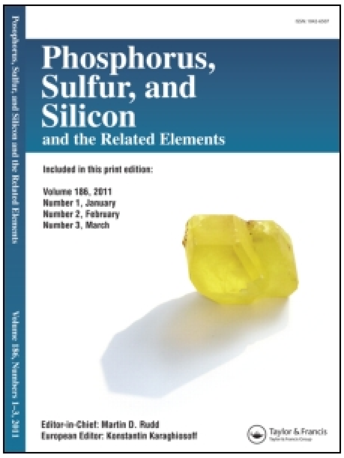

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REACTIONS OF PHOSPHINES WITH ACETYLENES. PART 19.[1] CONFIGURATIONAL AND CONFORMATIONAL ANALYSIS OF 1,2-DIMETHOXYCARBONYL-2-TRIS(CYANOETHYL)PHOSPHONIUM-ETHANE SULPHONATES

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REACTIONS OF PHOSPHINES WITH ACETYLENES. PART 19.[1] CONFIGURATIONAL AND CONFORMATIONAL ANALYSIS OF 1,2-DIMETHOXYCARBONYL-2-TRIS(CYANOETHYL)PHOSPHONIUM-ETHANE SULPHONATES

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1,2-Dimethoxycarbonyl-2-tris(cyanoethyl)phosphonium-ethane sulphonates are present in both *threo* and *erythro* forms in TFA (trifluoroacetic acid) and DMSO (dimethylsulphoxide). The relative proportions change from a 5 : 1 ratio for a solution in DMSO to a 1 : 1 ratio for a solution in TFA. The predominant conformation in the *threo* betaine also depends on the nature of the medium–the conformer with the vicinal protons *trans* predominates in DMSO while that with the ester groups *trans* predominates in TFA. In contrast the *erythro* form adopts essentially the same conformation in both solvents.

INTRODUCTION

The reaction of triphenylphosphine with electrophilic acetylenes in the presence of sulphur dioxide and water has been shown to give 2-phosphonium-ethane sulphonates (1; R = Ph).[2] The n.m.r. spectra and chemical properties of these systems indicate that rotation about the $\alpha\beta$ carbon–carbon bond is restricted by a strong attraction between the phosphonium atom and the sulphonate group and that, as a result, the molecules adopt mainly one conformation in solution. Nevertheless, this can be controlled to some extent by altering the solvent and the character of the alpha and beta substituents. We considered that if an additional means of controlling these conformational changes could be found the betaine system might become a suitable vehicle for a study of the angular dependence of the PCCH and HCCH n.m.r. vicinal coupling constants. Although there have been several systematic studies of

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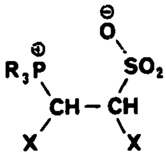
the vicinal coupling effects in phosphoryl compounds there have been few corresponding studies of phosphonium salts.

RESULTS AND DISCUSSION

We have been investigating the conformational effects of changing the substituent on the phosphorus atom in a number of 2-phosphonium-ethane sulphonates (**1**). During these studies we have observed some interesting effects for the 2-cyanoethyl substituted betaine (**1**; R = $NCCH_2CH_2$, X = CO_2Me). Thus, for example, it was immediately apparent from the n.m.r. spectra that both the *threo* and *erythro* forms of the 2-cyanoethyl substituted betaine (**1**; R = $NCCH_2CH_2$, X = CO_2Me) were able to coexist in solution, something not observed in the systems we have previously studied. Furthermore, while one diastereoisomer adopted the same major conformation in both TFA and DMSO the other did not. In addition, the large values of $^3J_{PH}$ observed in this system suggests that the *trans* $^3J_{PH}$ value may be much larger than we had previously assumed which has implications for our interpretation of the spectral data for the 1,2-dicyano-2-phosphonium-ethanesulphonate betaines (**1**; X = CN) previously reported.[3]

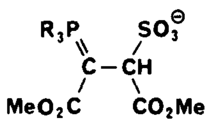


(**1**)

The n.m.r. spectra of a solution of the betaine (**1**; R = $NCCH_2CH_2$, X = CO_2Me) in TFA contains two sets of signals which were interpreted as corresponding to approximately equal amounts of the *threo* and *erythro* diastereoisomers, whereas a solution in DMSO gave spectra in which the two sets of signals were in an approximately 5 : 1 ratio. This was most clearly observed in the ^{31}P proton-decoupled n.m.r. spectra which showed signals at δ 40.50 and 41.38 p.p.m.[4] in TFA and signals at δ 38.42 and 39.95 p.p.m. in DMSO. Furthermore, successive additions of TFA to the DMSO solution caused a gradual change in the chemical shifts, the intensities and the couplings of the signals towards those observed in the TFA solution, and vice versa. The changes, which were most marked in the range 50–80% TFA, showed that the major diastereoisomer (δ_P 38.42) in DMSO was responsible for the signal at δ_P 40.50 in TFA.

The ^1H and ^{13}C n.m.r. spectra of the betaines (**1**; R = $NCCH_2CH_2$, X = CO_2Me) in deuterated TFA or in DMSO containing a trace of deuterium oxide, show that there is rapid exchange of the α-proton in both media. These observations together with the changes in the relative signal intensities and coupling constants in mixed solvents show that both configurational (*threo/erythro*) and conformational equilibration are occurring under these conditions. Considering the relative rates of these equilibria it is concluded that the two sets of signals observed in the n.m.r. spectra arise from the *threo* and *erythro* configurations exchanging at a rate below that of the n.m.r. time scale whilst the changes in coupling constants reflect changes in the conformational equilibria at rates above that of the n.m.r. time scale.

It should be noted that the rates of exchange of the α-methine proton in the betaines (**1**; R = $NCCH_2CH_2$, X = CO_2Me) in deuterated TFA and moist DMSO are much faster than in the triphenylphosphonium betaines (**1**; R = Ph, X = CO_2Me).[2] Although this reflects the relative stabilising effects of the tris (cyanoethyl)-phosphonium and triphenylphosphonium groups the mechanisms of exchange may differ in the two solvent systems. Thus, whilst the intermediacy of the phosphonium ylide (**2**) probably accounts for the exchange in DMSO, an acid catalysed mechanism involving the enol (**3**) is more likely in acidic media. If this is so, the faster rate of exchange for the cyanoethyl betaines indicates a greater stability for the ylide (**2**; R = CH_2CH_2CN) and enol (**3**; R = CH_2CH_2CN) compared with the corresponding triphenylphosphonium compounds (**2**; R = Ph) and (**3**; R = Ph). This difference parallels the much weaker basicity of the tris(cyanoethyl)phosphine compared to triphenylphosphine[5] and suggests that similar electronic factors may control the basicities of the phosphines and ylides.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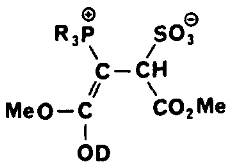

(3)

The major diastereoisomer of the betaine (**1**; R = $NCCH_2CH_2$, X = CO_2Me) in DMSO has a large HCCH coupling constant (9.8 Hz) and is therefore assigned as the *threo* configuration (**4**; R = $NCCH_2CH_2$, X = CO_2Me) with the predominant conformation being that with the two vicinal protons approaching a *trans* orientation (**4a**; R = $NCCH_2CH_2$, X = CO_2Me). This conformation is consistent with the observed PCCH coupling constant (12.8 Hz). Although this value of $^3J_{PH}$ is much larger than that previously observed (2 Hz) for the triphenylphosphonium betaine (**1**; R = Ph, X = CO_2Me)[2] it is less than half that observed in the minor diastereoisomer of the betaine (**1**; R = $NCCH_2CH_2$, X = CO_2Me) in DMSO. The assignment of the predominant conformation is further supported by the ^{13}C n.m.r spectrum of the major component in DMSO (see Table I) which contains the largest value for J_{PCCC}(13 Hz) observed in this system, suggesting a *trans* arrangement between the phosphonium and β-ester groups.

In contrast, the minor diastereoisomer of the betaine (**1**; R = $NCCH_2CH_2$, X = CO_2Me) in DMSO has vicinal coupling constants $^3J_{HH}$ 3.3Hz and $^3J_{PH}$ 27.4 Hz which indicate that the conformation of the *erythro* diastereoisomer is dominated by structure (**5a**; R = $NCCH_2CH_2$, X = CO_2Me).

The identities of the two diastereoisomers in TFA could not be established directly from the ^1H n.m.r. spectra but they were determined by following the chemical shift changes of the two ^{31}P n.m.r. signals in mixed DMSO-TFA solutions. The ^{31}P signals in TFA were first related to those in DMSO and then to the corresponding ^1H n.m.r. signals in TFA by selective ^{31}P irradiation. The component

TABLE I

^{13}C n.m.r. parameters[a] for (1; R = CH_2CH_2CN, X = CO_2Me)

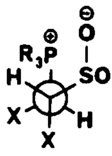
Solvent:	Dimethyl sulphoxide		Trifluoroacetic acid
Diastereoisomer:	erythro	threo	erythro/threo
αC	[b]	40.44(45)	44.96(55), 43.91(54)
βC	63.95	62.20	66.66, 64.66
αCO	—	165.64	168.31, 167.49
βCO	—	166.73(13)	170.31(5), 168.68(4)
α and β OMe	53.11, 54.13	52.57, 54.13	56.97, 56.77, 56.33, 56.14
$αCH_2$	17.24[c](43)	15.44(47.5)	20.81(49), 18.96(44)
$βCH_2$	10.75	10.50	13.06, 12.91
CN	118.32(22)	118.32(22)	118.32(14.5)

[a] Resonance positions are p.p.m. relative to TMS, and are accurate to ±0.7 Hz. Values in parenthesis are those for coupling to phosphorus.

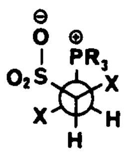
[b] Signal obscured by DMSO resonance.

[c] Only one half of doublet clearly visible.

in TFA which was assigned to the *erythro* configuration (5) in this way gave $^3J_{HH}$ and $^3J_{PH}$ coupling constants of 2.2 Hz and 27.6 Hz respectively (cf 3.3 Hz and 27.4 Hz in DMSO) showing that the conformational populations of this diastereoisomer are little altered by the nature of the medium. On the other hand, the couplings for the *threo* diastereoisomer changed markedly as the concentration of TFA increased, the final values of $^3J_{HH}$ 3.7 Hz and $^3J_{PH}$ 22Hz indicating a predominance of the gauche conformer (**4b**; R = $NCCH_2CH_2$, X = CO_2Me). The ^{13}C n.m.r. spectra of the diastereoisomers in TFA (Table I) were difficult to assign unambiguously and attempts to use ^{31}P selective decoupling techniques to determine those signals which arose from particular diastereoisomers proved inconclusive. Fortunately, however, the coupling between the β-carbonyl carbon and the phosphorus atoms for the betaines in TFA were similar for both diastereoisomers (5 Hz and 4 Hz) and are consistent with the proposed conformations.

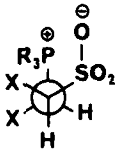


(**4a**)

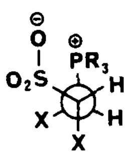


(**4b**)

It is interesting to note that while the conformations adopted by the *erythro* form in DMSO and TFA given similar values for $^3J_{PH}$ (27.4 and 27.6 Hz respectively) a significant difference in the values of $^3J_{HH}$ (3.3 and 2.2 Hz respectively) is observed. This difference cannot be explained by assuming a contribution from the rotamer (**5b**; R = $NCCH_2CH_2$, X = CO_2Me) since this would produce variations in $^3J_{PH}$ rather than $^3J_{HH}$. Indeed the constant value for $^3J_{PH}$ suggests no change in the rotamer population on change of solvent which is most satisfactorily interpreted as indicating an extreme conformational preference for the rotamer (**5a**; R = $NCCH_2CH_2$, X = CO_2Me) in both solvents. It must therefore be concluded that variations in $^3J_{HH}$ arise from subtle changes in the dihedral angle in the system. If



(5a)



(5b)

one postulates dihedral angles between the vicinal protons of 60 $-$ Ψ in DMSO and 60 $+$ Ψ in TFA then the $^3J_{PH}$ values would remain constant in the two solvents while permitting a change in $^3J_{HH}$. Calculations based on a consideration of the likely variation of $^3J_{HH}$ with Ψ suggest that a value for Ψ of only about 3° would be sufficient to explain the observed change in $^3J_{HH}$.

In contrast, a consideration of the n.m.r. data for the *threo* conformation suggests that here the data is best interpreted as indicating that both rotamers (**4a** and **4b**; R = $NCCH_2CH_2$, X = CO_2Me) are populated to some extent. In TFA the value of $^3J_{PH}$ of 22 Hz is much smaller than observed for the corresponding *trans* coupling in the *erythro* system and similarly the value of $^3J_{HH}$ (9.8 Hz) in DMSO is slightly smaller than that expected for the rotamer (**4a**; R = $NCCH_2CH_2$, X = CO_2Me). These differences are not readily explained by simply proposing changes in the dihedral angles in these systems. However, attempts to explain the observed values of $^3J_{PH}$ and $^3J_{HH}$ on the basis of simply assuming an equilibrium between the two rotamers (**4a** and **4b**; R = $NCCH_2CH_2$, X = CO_2Me) are equally unsatisfactory. Calculations based on a consideration of the estimated values of the gauche and *trans* values of both $^3J_{PH}$ and $^3J_{HH}$ indicate that, in order to explain the observed values of $^3J_{PH}$ and $^3J_{HH}$ it is necessary to propose not only an equilibrium between the conformers (**4a** and **4b**; R = $NCCH_2CH_2$, X = CO_2Me) but also that these conformers are distorted slightly from the fully staggered arrangement. The observation that the conformer (**4b**; R = $NCCH_2CH_2$, X = CO_2Me) is significantly populated in the *threo* system may indicate that there is a favourable interaction between the β carbonyl oxygen and the phosphonium centre leading to an enhanced stability for this conformer. Such an interaction is also possible in the favoured *erythro* conformer (**5a**; R = $NCCH_2CH_2$, X = CO_2Me).

Whilst these results are still in accordance with a strong association between the phosphonium and sulphonate groups they clearly show that there is sufficient mobility for the conformers (**4a** and **4b**; R = $NCCH_2CH_2$, X = CO_2Me) to be in rapid equilibration. The nature of the interconversion is a matter of speculation but it may be such that the system is able to oscillate between its major conformers whilst still maintaining the association between the phosphonium and sulphonate groups. The large solvent effects on the n.m.r. parameters would suggest that solvation is of considerable importance and probably makes a major contribution towards the stabilisation of certain conformers leading to the dramatic changes observed for the *threo* diastereoisomer.

Finally, in view of the large *trans* $^3J_{PH}$ vicinal coupling observed in the diesterbetaine (**1**; R = $NCCH_2CH_2$, X = CO_2Me) it is necessary to reconsider the interpretation previously reported for the 1,2-dicyano-2-phosphonium-ethane sulphonate betaines (**1**; X = CN).[3] In these latter systems only one diastereoisomer was

TABLE II

^{1}H n.m.r. parameters for (**1**; R = CH_2CH_2CN, X = CO_2Me)[†]

Solvent: Diastereoisomer:	Dimethyl sulphoxide erythro	 threo	Trifluoroacetic acid erythro	 threo
δH_α	4.85	4.62	5.07	5.14
δH_β	4.61	4.68	5.40	5.32
$J_{H_\alpha H_\beta}$	3.3	9.8	2.2	3.7
J_{PH_α}	−16.0	−15.0	−16.0	−16.0
J_{PH_β}	27.4	12.8	27.6	22.0
δOMe	3.76, 3.65		4.01, 4.02, 4.03, 4.04	

[†] Spectra were analysed with the aid of ^{31}P decoupling techniques and the interpretation confirmed by spectrum simulation.[6]

observed. The triphenyl-substituted system (**1**; R = Ph, X = CN) in TFA gave $^3J_{PH}$ 11Hz and $^3J_{HH}$ 0.97 Hz, with similar values in DMSO. The conclusion that 11 Hz represented a *trans* $^3J_{PH}$ coupling in these systems must now be in doubt in view of the large value (27.6 Hz) observed for this coupling in the *erythro* configuration of the diester-betaine (**1**; R = $NCCH_2CH_2$, X = CO_2Me) in TFA. If one assumes that the values of $^3J_{PH}$ are similar in the two systems then the data for the dicyano-betaine (**1**; R = Ph, X = CN) is now more consistent with the *erythro* conformation (**5b**; R = Ph, X = CN), distorted so that the vicinal protons have a dihedral angle approaching 70°, rather than the *threo* conformer (**4b**; R = Ph, X = CN) previously suggested.

If this is the case it serves to highlight the dramatic effects of changing the substituents on the conformational preferences in these sulphonate betaines. While the conformation (**5b**) would be the major conformer observed for the dicyano-betaine (**1**; R = Ph, X = CN) it is the only conformer not significantly populated in the diester-betaine (**1**; R = $NCCH_2CH_2$, X = CO_2Me). Further work is clearly necessary before the conformational importance of the various structural features can be assessed for these systems.

EXPERIMENTAL

^{1}H, ^{13}C and ^{31}P n.m.r spectra were obtained on JEOL MH 100 and FX 100 spectrometers.

1,2-Dimethoxycarbonyl-2-tris(cyanoethyl)phosphonium-ethane Sulphonate. The adduct was prepared by the method previously described[2] using tris(cyanoethyl)phosphine in place of triphenylphosphine and gave the white sulphonate (**1**; R = $NCCH_2CH_2$, X = CO_2Me) m.p. 151.5–152°C (decomp.). (Found: C, 43.5; H, 4.81; N, 10.0; $C_{10}H_{20}O_7N_3PS$ requires C, 43.2; H, 4.79; N, 10.1%); λ_{max} 2260(CN), 1725(CO), 1300–1215 cm^{-1} (SO_3 overlapping bands); n.m.r. data in Tables I and II.

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