Reaction of 1-Pyrroline 1-Oxides with Phosphonates and Phosphoranes. Synthesis of 1-Azabicyclo[3,1,0]hexanes

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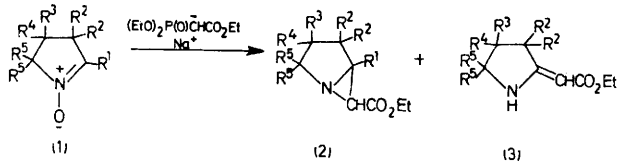
Summary The reaction of 1-pyrroline 1-oxides with triethyl phosphonosodioacetate affords 1-azabicyclo[3,1,0]-hexanes and ethoxycarbonylmethylidenepyrrolidines but is not general for a variety of other phosphonate or phosphinoxy-carbanions.

Breuer and Ronen-Braunstein have recently reported[1] the formation of two isomeric aziridines from the reaction of *N*-methyl-*C*-phenylnitrone with triethyl phosphonosodioacetate. We have been surveying the reactions of a range of phosphonates with 1-pyrroline 1-oxides[2] and have synthesised a number of 1-azabicyclo[3,1,0]hexanes by this method. However, our more extensive results show that aziridine formation is not the only reaction path and also that it is not a general one.

For example, triethyl phosphonosodioacetate reacts with 5,5-dimethyl-1-pyrroline 1-oxide (**1a**) in dimethoxyethane during 36 h to afford the aziridine (**2a**) and the enamine (**3a**) in yields of 62 and 18% respectively. Under the conditions of the reaction these two compounds are not interconvertible and presumably arise from two different decomposition modes of an oxazaphospholidine intermediate. These products, and others following, were characterised by their spectral properties (i.r., u.v., ^{1}H n.m.r., and mass spectra). Also, the aziridine ester (**2a**) (b.p. 56—58° at 0·1 mmHg) was converted by reaction with benzylamine into the related crystalline amide derivative (m.p. 101—103°) which was fully characterised. The enamine (**3a**) was identical with an authentic sample.[3]

The aziridines (**2b** and **c**) and the enamines (**3b** and **c**) were also formed in similar ratios and in combined yields of 50—70% from the same phosphonate and the aldonitrones (**1b** and **c**). The ketonitrone (**1d**) significantly afforded no enamine, but a 50% yield of the aziridine (**2d**). By contrast with these results, the nitrone (**1a**) did not react with methyl, benzyl, or *p*-bromophenacyl diethyl phosphonate or methyldiphenylphosphine oxide in the presence of sodium hydride. Furthermore, no aziridine product could be isolated from the reaction of *C*,*N*-diphenylnitrone with triethyl phosphonosodioacetate.



(1) (2) (3)

a; $R^1 = R^2 = R^3 = R^4 = H, R^5 = Me$
b; $R^1 = R^3 = R^4 = H, R^2 = R^5 = Me$
c; $R^1 = R^2 = R^3 = H, R^4 = Ph, R^5 = Me$
d; $R^1 = R^3 = R^4 = Me, R^2 = R^5 = H$

$Ph_3P{=}CH{-}CO_2Et$

(4)

In view of the earlier results of Huisgen and Wulff[4] on the formation of oxazaphospholidines from nitrones and triphenylphosphoranes, we also investigated the behaviour of the ylide ethoxycarbonylmethylene triphenylphosphorane (**4**) with the cyclic nitrones (**1a**, **b**, and **d**). The aziridine (**2a**) and the enamine (**3a**) were again formed from the nitrone (**1a**), in similar ratio and in a 36% overall yield, which was raised to 75% using benzoic acid catalysis[5] in refluxing benzene for 6 h. The more hindered tetramethyl aldonitrone (**1b**) and the ketonitrone (**1d**) failed to react.

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