Tetrahedron Letters No. 50, pp 4483 - 4486, 1975. Pergamon Press. Printed in Great Britain.

REARRANGEMENTS IN ORGANOPHOSPHOROUS COMPOUNDS· THE REACTION OF DIALKYL ACYL- AND AROYLPHOSPHONATES WITH DIAZOMETHANE.[1]

Daniel Kost

Department of Chemistry, Ben Gurion University of the Negev, Beersheva, Israel

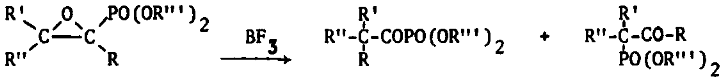
and

M. S. Sprecher

Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel

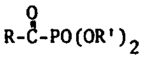
(Received in UK 27 October 1975; accepted for publication 3 November 1975)

Rearrangements of organophosphorous compounds involving a 1,2 shift of a dialkoxyphosphinyl group $\{-PO(OR)_2\}$ to an electron deficient migration terminus have attracted considerable interest in recent years. Migrations from carbon to carbon,[2,3,4] carbon to nitrogen,[5] and carbon to oxygen[6] have been reported An order of decreasing migratory aptitude of substituents migrating from carbon to carbon was established for the acid catalyzed rearrangement of dialkyl α,β-epoxyphosphonates·[2,3] phenyl > dialkoxyphosphinyl > alkyl ∿ H.



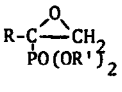
We now report a study of the reaction of dialkyl aroylphosphonates with diazomethane, where the migratory aptitude of the dialkoxyphosphinyl group greatly exceeds that of a phenyl or even a para-anisyl group. We present a rationale for this result, and provide evidence to support the proposed mechanism of the rearrangement.

Arbuzov[7] reported that diazomethane reacts with diethyl acetylphosphonate (1a) to yield mainly diethyl 1,2-epoxy-2-propylphosphonate (2a), along with some diethyl acetonylphosphonate



$R-\overset{O}{\overset{\|}{C}}-PO(OR')_2$

1



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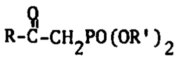
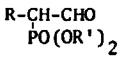


$R-\overset{O}{\overset{\|}{C}}-CH_2PO(OR')_2$

3



$R-\underset{PO(OR')_2}{CH}-CHO$

4

$R-CH_2-COPO(OR')_2$

5

a, R = CH_3, R' = Et

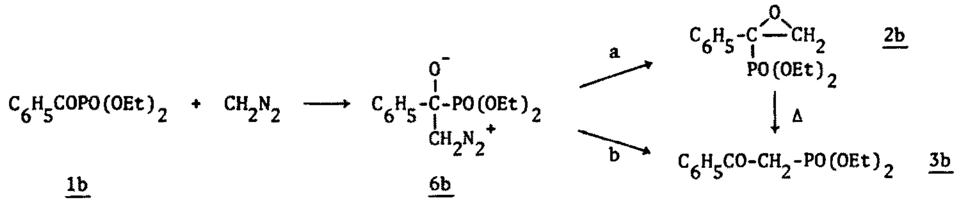
b, R = C_6H_5, R' = Et

c, R = m-Cl-C_6H_4, R' = CH_3

d, R = p-MeO-C_6H_4, R' = CH_3

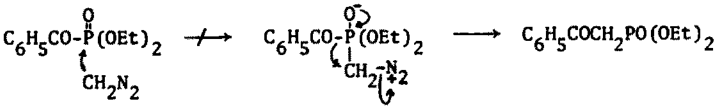
(3a). Diethyl benzoylphosphonate (1b), however, gave only diethyl phenacylphosphonate (3b) under similar conditions. Whether this reaction constitutes a new direct rearrangement of the dialkoxyphosphinyl group, or whether an α,β-epoxyphosphonate is formed initially and then is thermally rearranged, has been a matter of some controversy (Scheme 1).

Scheme 1



Churi and Griffin[2] proposed the mechanism of Route a, in accord with their finding that α,β-epoxyphosphonates underwent thermal rearrangement to β-ketophosphonates. The direct migration of the phosphorous group to the electron deficient methylene carbon atom was proposed by Kirby and Warren[8] In both of these mechanisms the diethoxyphosphinyl group migrates in preference to a competing phenyl group. However, the mechanism of Route a does not agree with the observation that in epoxyphosphonate rearrangements phenyl migrates in preference to dialkoxyphosphinyl.[3] We therefore prepared[9] the postulated intermediate 2b, and subjected it to the reaction conditions (solution in ether at ambient temperature for 24 hr). 2b was recovered unchanged from the reaction mixture. In fact, 2b could be distilled without detectable change at 195-7°(22 torr), and hence it may be excluded as a possible intermediate as shown in Route a Moreover, when further heated up to 250°, 2b decomposed without formation of 3b. The main product that could be detected was the aldehyde 4b, which resulted from ring opening and hydride shift.

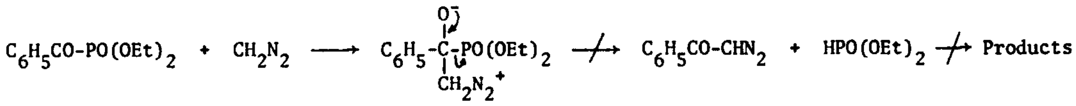
Two control experiments provide further support for the mechanism of Route b. A conceivable nucleophilic attack on phosphorus followed by benzoyl migration was excluded by the



observation that diethyl phenylphosphonate did not react with diazomethane under similar

$$C_6H_5PO(OEt)_2 + CH_2N_2 \longrightarrow NR$$

conditions. The failure of diazoacetophenone to react with diethylphosphite excluded a possible



$$C_6H_5CO\text{-}PO(OEt)_2 + CH_2N_2 \longrightarrow C_6H_5\text{-}\overset{O^-}{\underset{CH_2N_2^+}{C}}\text{-}PO(OEt)_2 \not\longrightarrow C_6H_5CO\text{-}CHN_2 + HPO(OEt)_2 \not\longrightarrow \text{Products}$$

dissociation - recombination mechanism involving these intermediates.

In order to examine the reaction of diazomethane with 1b, 1c and 1d, a 50-100% excess of diazomethane in dry ether solution was allowed to react with the aroylphosphonate at 0°, and after 15 minutes the solvent was removed at room temperature and reduced pressure The residue was practically pure β-ketophosphonate 3b, 3c and 3d, respectively, as shown by its pmr and ir spectra. Distillation afforded over 90% yields of the pure products. It is thus evident that the dialkoxyphosphinyl group migrates preferentially even to the *para*-anisyl group, which is known to rearrange very readily in various 'carbonium ion' type rearrangements.[10] However, it has been shown recently[11] that the dominant factor in similar rearrangements is not the ability of the migrating group, but rather the ability of the group that stays behind to support a positive charge. In the present reaction, though the positive charge developing on the migration origin is stabilised mainly by the oxygen lone pair of electrons, the additional support by the phenyl group is sufficient to promote migration of the diethoxyphosphinyl group. The alternative

Transition States: a, Phosphorus migration, b, Phenyl migration.

migration of the phenyl group would lead to the less favourable transition state where a positive charge is formed next to the electronegative phosphonyl group. One may view this situation, alternatively, as an effect of product stability on the course of the reaction migration of the phosphonyl group leads to formation of the stable dialkyl phenacylphosphonate, 3, whereas the rather reactive and unstable α-ketophosphonate 5 would form if the aryl group were to migrate. The stability of the product is reflected in the transition state stability.

The reaction of two other diazoalkanes with substituted benzoylphosphonates is worthy of note Pudovik reported that diphenyldiazomethane, upon its reaction with 1b, yielded mainly an epoxyphosphonate as a result of ring closure, in analogy to the reaction of 1a to yield 2a.[12] An attempt to prepare an epoxyphosphonate from 1b and phenyldiazomethane in a similar way resulted in the formation of diethyl desylphosphonate, $C_6H_5COCH(C_6H_5)PO(OEt)_2$, as a result of phosphonyl migration, similar to the reaction with diazomethane.

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