

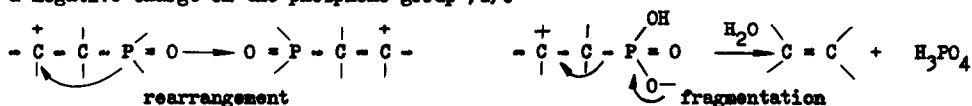
DEAMINATION AND REARRANGEMENT OF 1-PHENYL-1-HYDROXY-2-AMINOETHYLPHOSPHONIC ACID

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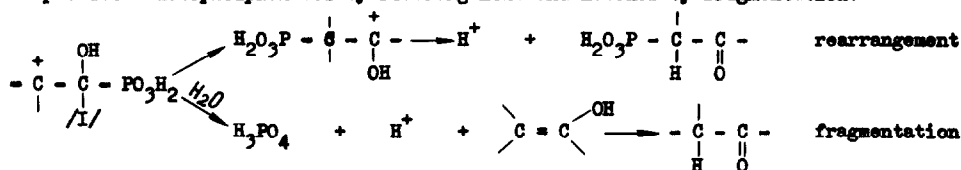
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Phosphorus-containing carbonium ions are known to rearrange by a migration of the phosphono group to electron deficient carbon /1/ or undergo a fragmentation to unsaturated compounds and inorganic phosphate /2/. The latter reaction is restricted to carbonium ions capable of developing a negative charge on the phosphono group /2/.

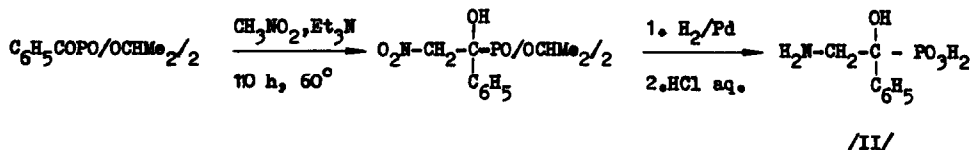


Other transformations of such carbonium ions are more obvious and include vinylphosphonate formation by proton loss and reaction with water to produce hydroxylated compounds /1,2/.

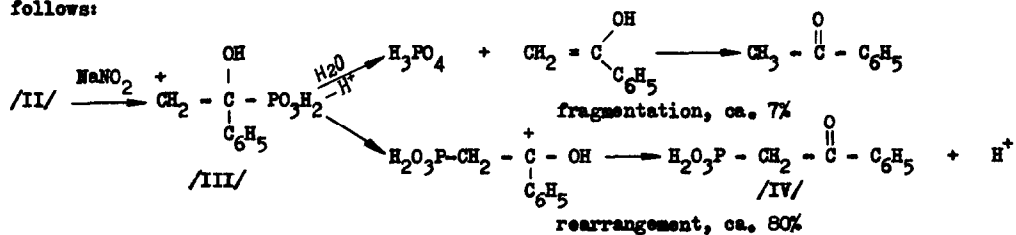
The as yet unknown carbonium ions /I/ bearing a hydroxy and a phosphono group might be expected to produce 2-ketophosphonates by rearrangement and ketones by fragmentation:



The obvious way to investigate the fate of carbonium ions /I/ is via the diazotization of 1-hydroxy-2-aminophosphonic acids. In this communication we report our results with one representative of this virtually unknown class of compounds, viz. with 1-hydroxy-1-phenyl-2-aminoethylphosphonic acid /II/. The synthesis of /II/ was accomplished in 40 percent total yield from diisopropyl benzoyl phosphonate using a reaction sequence including condensation with nitromethane /3/, reduction and hydrolysis /4/:



The diazotization of /II/ was carried out as follows: A solution of 0.01 mole of /II/ in 40 ml of water was treated with 5 ml of 4 N NaNO_2 at room temperature. After 4 hours the evolution of N_2 practically ceased and the solution was acidified with 2 ml of 10 N H_2SO_4 to destroy the excess of NaNO_2 . Colorimetric determinations /2/ indicated that in repeated experiments the amount of unreacted /II/ was ca. 5% and that ca. 7% of inorganic phosphate was formed. The latter is attributed to fragmentation rather than to hydrolysis of reaction products /ketophosphonates/ because prolonged boiling of the reaction mixture did not increase the yield of H_3PO_4 . The other product of fragmentation, acetophenone, was isolated in 7% yield from the reaction mixture by extraction with ether. To identify the main product, the solution after diazotization was treated with excess of dinitrophenylhydrazine and the resulting precipitate was reduced with H_2/Pd to yield ca. 80% of 2-amino-2-phenylethylphosphonic acid /based on /II//. In another experiment the reaction mixture after diazotization was passed through a column of Dowex 50 WX2 yielding 76% of phenacylphosphonic acid /IV/. Thus the rearrangement appears to be preferred reaction of carbonium ion /III/ and the events occurring after diazotization of /II/ can be summarized as follows:



Total yields of inorganic phosphate, unreacted /II/ and isolated rearrangement product was ca. 90%. No other products, in particular no product of phenyl group migration could be detected in the reaction mixture by TLC.

Full details of this study will be reported in a later publication.

NOTES AND REFERENCES

1. P. F. Cann and S. Warren, *Chem. Comm.* **16**, 1026 /1970/.
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3. G. H. Baranov, T. A. Matriukova, W. W. Perekalin, N. W. Ponomarenko and N. I. Kabacznik, *Izvest. Akad. Nauk USSR, ser. chim.* 179 /1969/.
4. The structures of all reported compounds were confirmed by combustion analysis, IR, comparison with authentic samples or independent syntheses.