Tetrahedron Letters No.42, pp. 4405-4408, 1968. Pergamon Press. Printed in Great Britain.

THE BAEYER - VILLIGER OXIDATION OF DIALKYL AROYLPHOSPHONATES (1,2)

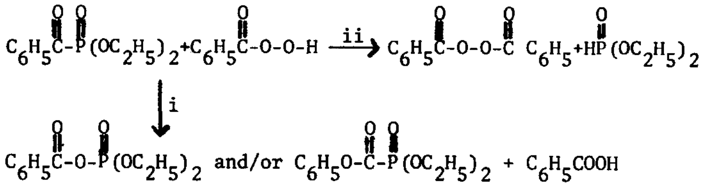
Milon Sprecher (3) and Ephraim Nativ

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

(Received in UK 8 July 1968; accepted for publication 23 July 1968)

We wish to report on the products and mechanism of the reaction of dialkyl aroylphosphonates with perbenzoic acid. The conversion of such $\underline{\alpha}$ - ketophosphonates to dinitrophenylhydrazones (4) on the one hand, and their facile hydrolysis to carboxylic acids and dialkyl phosphite (4) on the other, evidence their dual character as ketones and as acylating (rather than phosphorylating) agents. Consequently, the reaction of perbenzoic acid with diethyl benzoylphosphonate might, a priori, be expected to proceed either by path i) to yield diethyl benzoyl phosphate and/or diethyl phenoxycarbonylphosphonate, the products of a Baeyer-Villiger type rearrangement; or by path ii) to yield benzoyl peroxide and diethyl phosphite. (See Scheme 1).

SCHEME 1



$$C_6H_5\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{P}}(OC_2H_5)_2+C_6H_5\overset{O}{\overset{\|}{C}}-O-O-H \xrightarrow{ii} C_6H_5\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}\ C_6H_5+H\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$$

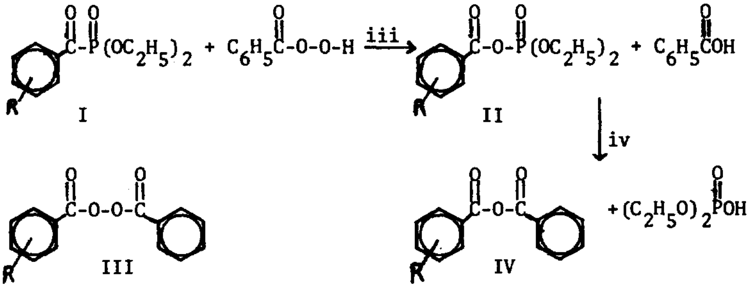
$$\downarrow i$$

$$C_6H_5\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{P}}(OC_2H_5)_2 \text{ and/or } C_6H_5O-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{P}}(OC_2H_5)_2 + C_6H_5COOH$$

In fact, diethyl aroylphosphonates were found to react with perbenzoic acid exclusively, or almost exclusively, by path i) with migration of the diethoxyphosphonyl group, yielding diethyl aroyl phosphates.

Diethyl benzoylphosphonate (Ia) (5), diethyl p-fluorobenzoylphosphonate (6) (Ib, bp 130°/1mm, n_D^{22} 1.4992, 2,4-dinitrophenylhydrazone mp 192°), diethyl m-chlorobenzoylphosphonate (6) (Ic, bp 127°/0.4mm, n_D^{22} 1.5346, 2,4-dinitrophenylhydrazone mp 156°) and diethyl p-methoxybenzoylphosphonate (Id) (4) were prepared by the reaction of triethyl phosphite with the aroyl chloride (4). Solutions of Ia-d, both in ethyl acetate and in benzene were reacted with 1.05 molar amount of perbenzoic acid in the dark for 13-16 days at ambient temperatures, or for 3-5 days at 32°, till at least 85% of the α- ketophosphonate was consumed. Chromatographic separation of the products on silica gel permitted the isolation of 70-85% yields of diethyl aroyl phosphates (7) IIa-d, respectively; 2-4% aroyl benzoyl peroxides (10) IIIa-d, respectively; 2-6% ethyl benzoate; 10-20% aroyl benzoyl anhydrides (11) IVa-d, respectively; and diethyl phosphate (Scheme 2).

SCHEME 2



a, R = H -

b, R = p-F -

c, R = m-Cl-

d, R = p-CH_3O-

No evidence for the formation of diethyl phenoxycarbonylphosphonate could be found in any of the experiments, nor were phenols detectable in the acid or base hydrolysis products of the total reaction mixtures. Following the progress of the reaction by infra-red spectroscopy and thin layer chromatography, it was established that the primary products are IIa-d and that the anhydrides IVa-d (and diethyl phosphate) are formed subsequently, presumably by reaction iv. Upon prolonged standing of the reaction mixtures, compounds of type II are completely converted to anhydrides of type IV. The diaroyl peroxides III are the products of the reaction of perbenzoic acid either with II or with I (reaction type ii) Scheme 1).

The following control experiments bear on the mechanism of reaction iii). The reaction of Ia with *m*-chloroperbenzoic acid gave IIa and no IIc. Benzoyl peroxide did not react with diethyl phosphite, either in the presence or absence of benzoic acid, under the conditions of reaction iii). No IIa was formed when a mixture of Ia and diethyl phosphate was kept under the conditions of reaction iii) either in the presence or absence of benzoic acid. Reaction of carbonyl-O^{18} labeled Ia (2,48 atom % excess O^{18}) with normal perbenzoic acid yielded labeled IIa which, upon treatment with aniline gave O^{18} labeled benzanilide (2.00 atom % excess O^{18}) and diethyl phosphate. The latter, isolated as its benzylthiouronium salt (9), was essentially devoid of label (0.04 atom % excess O^{18} calc. for all of the excess isotope in one position) (12). Diethyl benzylphosphonate did not react with perbenzoic acid under the conditions of reaction iii).

These results indicate that reaction iii) is, in fact, a Baeyer-Villiger rearrangement (13). If we assume the cationic mechanism (13) of the normal Baeyer-Villiger to be valid for reaction iii), then the latter constitutes the first reported migration of a phosphonate function to an electron deficient oxygen (14). It is noteworthy that in this case the migration aptitude of the diethoxyphosphonyl group has been shown to *greatly exceed even that of the p-methoxyphenyl group*, and we suggest that the pertinent transition state is stabilized by *d*π - *p*π bonding involving overlap of the *occupied* "non-bonding" *p*-orbital of the oxygen, which is the migration terminus, with a *d* orbital of the phosphorous.

Footnotes and References

1. A grant from the Research Committee of Bar Ilan University in support of this research is gratefully acknowledged.
2. Abstracted from the M.Sc thesis of E.N.
3. On sabbatical leave at the Department of Chemistry, Tel-Aviv University.
4. K.D. Berlin and H.A. Taylor, *J.Am.Chem.Soc.*, **86**, 3862 (1964).
5. M.I. Kabachnik and P.A. Rosüskaya, *Bull.Acad.Sci.U.S.S.R.*, *Classe Sci. Chim.*, 364 (1945); *Chem.Abstr.*, **40**, 4688 (1946).
6. The infrared, pmr and mass spectra and elemental analyses of lb and lc, as well as the elemental analyses of their 2,4-dinitrophenylhydrazones were in complete accord with assigned structures.

Footnotes and References con'd.

7. The structures of IIa-d were confirmed by their infrared and pmr spectra, their elemental analyses, and their conversion, by reaction with aniline (8) to their respective benzanilides which were identified by comparison with authentic compounds, and to diethyl phosphate which was identified as its benzylthiouranium salt (9). IIa, n_D^{22} 1.6138; IIb, n_D^{22} 1.4767; IIc, n_D^{22} 1.5102; IId, n_D^{22} 1.5112.

8. F. Cramer & K. Günter Gärtner, *Chem.Ber.*, **91**, 704 (1958).

9. R.G. Harvey & E.V. Jensen, *J.Org.Chem.*, **28**, 470 (1963).

10. The infrared spectra of IIIa-d and their molecular weights, determined by iodometric titration, are in accord with assigned structures. IIIa, mp 105°; IIIb, mp 132°; IIIc, mp 94°; IIId, mp 114°.

11. The mixed anhydrides IV b-d were identified by their infrared spectra and by comparison with authentic samples prepared from benzoic acid and the appropriate substituted benzoyl chloride.

12. We thank Prof. O. Samuel and Mrs. I. Wassermann of the Isotope Department of the Weizmann Institute of Science for the O^{18} analysis.

13. For a review of the Baeyer-villiger oxidation and its mechanism, see a) C.H. Hassall, *Org. Reactions* **9**, 73 (1957) and references quoted there; b) K. Mislow and J. Brenner, *J.Am.Chem.Soc.*, **75**, 2318 (1953); c) C.A. Burton, T.A. Lewis and D.R. Llewellyn, *J.Chem.Soc.*, 1226 (1956).

14. Churi and Griffin (15) recently reported the boron trifluoride catalyzed rearrangement of expoxides involving the migration of a dialkoxyphosphonyl group to a presumably electron deficient carbon. Ignoring possible steric factors, their results showed that in the rearrangement studied by them, the migration aptitude of the phosphono substituent greatly exceeded that of hydrogen.

15. R.H. Churi and C.E. Griffin, *J.Am.Chem.Soc.*, **88**, 1824 (1966).