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THE SCHMIDT REACTION OF DIALKYL AROYLPHOSPHONATES

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In previous communications (2,3) we have reported on the migration of a dialkoxyphosphono group to an electron deficient carbon atom in the acid catalyzed rearrangement of α,β-epoxyphosphonates (2) and to electron deficient oxygen in the Baeyer-Villiger oxidation of dialkyl aroylphosphonates (3). We now report some novel results in the Schmidt rearrangement of dialkyl aroylphosphonates, in which the migration terminus is an electron deficient nitrogen.

From the reaction of a chloroform solution of diethyl p-chlorobenzoylphosphonate(I) with hydrazoic and sulfuric acid we isolated six products:- i) p-chloroformanilide (II; 65% yield); ii) diethyl N-(p-chlorophenyl)carbamoylphosphonate (III; 19%) (4); iii) p-chloraniline (IV; 4%); iv) diethyl N-(p-chlorobenzoyl)phosphoramidate (V; 1.8%), identified by comparison with an authentic sample prepared by the reaction of p-chlorobenzamide with PCl_5 followed by treatment with sodium ethoxide-ethanol (5), mp 112°-113.5°; v) p-chlorobenzoic acid (VI; 4%); vi) diethyl α-(diethoxyphosphonyloxy)-p-chlorobenzylphosphonate (VII; 1.8%) identified by comparison with an authentic sample prepared by the reaction of diethyl phosphorochloridate with diethyl α-hydroxy-p-chlorobenzylphosphonate in pyridine solution.

The formation of II, III and IV, which together constitute 88% of the reaction products, involves the migration of the p-chlorophenyl group to the electrophilic nitrogen. Only about 2% of the products (i.e.V) can be attributed to migration of the diethoxyphosphono group.

The formation of II from I is mechanistically interesting. We believe it occurs by way of the p-chlorophenylisonitrile as shown in the Scheme, since control experiments showed that I is stable under the reaction conditions if either hydrazoic acid or sulfuric acid is omitted, and that III is not the precursor of II.

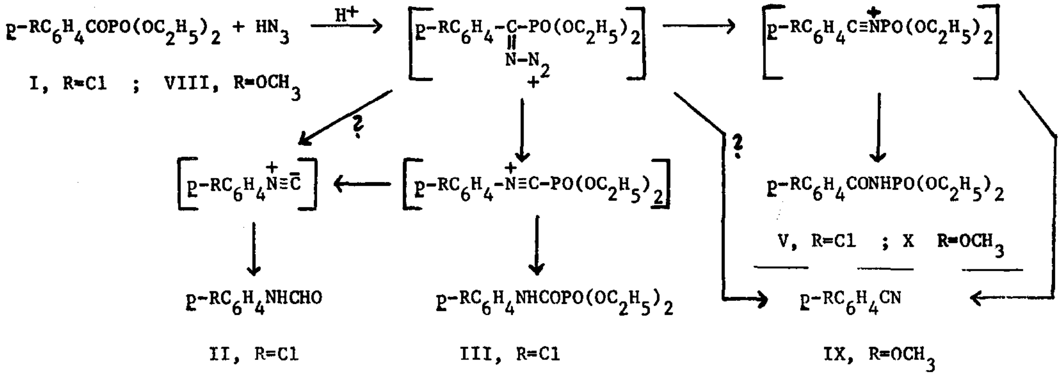
Hydrolytic processes are undoubtedly responsible for the production of IV and VI, though part of the former may be formed via p-chlorobenzoylazide. The action of diethyl phosphite, released hydrolytically, on unreacted I may yield VII (6).

In surprising contrast, the Schmidt reaction of diethyl p-anisoylphosphonate (VIII) under the same conditions yielded only three products:- p-anisonitrile (IX, ~65% yield); diethyl N-(p-anisoyl)phosphoramidate (X; 30%), mp 118.5°-119°; and 2% of an as yet unidentified product. The structure of X was confirmed by comparison with an authentic sample prepared in a manner similar to V (5).

The formation of X, and possibly also of IX, involves the migration of the diethoxyphosphono group. Control experiments established that X is not the precursor of IX. The contention that the reaction proceeds by nucleophilic attack of azide on the carbonyl carbon, rather than the phosphorus, is supported by our finding that diethyl benzylphosphonate is recovered quantitatively after subjection to the Schmidt reaction conditions. The fact that X is the product of an intramolecular rearrangement, rather than of a conceivable series of reactions involving cleavage and recombination, was demonstrated by carrying out the reaction of VIII in the presence of dimethyl phosphite, as well as the reaction of dimethyl p-anisoylphosphonate in the presence of diethyl phosphite. The N-(p-anisoyl)phosphoramidate isolated in both cases showed no exchange of the dialkoxyphosphono group.

We direct attention to two of the noteworthy aspects of these results. The formation of V and X are the first substantiated examples of the migration of a dialkoxyphosphono group to a formally electron deficient nitrogen terminus. Secondly, the preferential migration of the p-chlorophenyl group in I contrasted to the absence of p-methoxyphenyl migration in VIII constitutes an inversion of the usual order of the migratory aptitudes of these two groups as found in the Schmidt reaction of substituted benzophenones (7), as well as in various other types of molecular rearrangements induced by adjacent electron deficient centers.

The products we have obtained in the Schmidt reaction of a number of other dialkyl aroylphosphonates are in consonance with the above results. Thus diethyl benzoylphosphonate yielded formanilide (53%), diethyl N-phenylcarbamoylphosphonate (9%), aniline (14%), diethyl benzoylphosphoramidate (3%). Unlike the above, but like VIII, diethyl 3,4-methylenedioxybenzoylphosphonate yielded only diethyl N-(3,4-methylenedioxybenzoyl)phosphoramidate (28%) and 3,4-methylenedioxybenzonitrile (57%). Details of these and further experiments as well as their implications as regards the mechanism of the Schmidt reaction will be discussed in the full paper.



Footnotes and References

1. a) Author to whom inquiries should be addressed; b) on leave from Bar-Ilan University, Israel.
2. M. Sprecher and D. Kost, Tetrahedron Letters, 703 (1969).
3. M. Sprecher and E. Nativ, Tetrahedron Letters, 4405 (1968).
4. All compounds reported herein have ir, pmr and mass spectra fully in accord with assigned structures, and new compounds gave satisfactory elemental analyses.
5. cf. A.V. Kirsanov, R.G. Makitra, Zhur. Obshchei Khim. **28**, 35 (1958); Chem. Abstr., **52**, 12787b (1958).
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