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SYNTHESIS OF α-PHOSPHORYLATED CYCLOPENTANONES BY INTRAMOLECULAR CARBENOID CYCLIZATIONS OF α-DIAZO β-KETO ALKYLPHOSPHONATES AND PHOSPHINE OXIDES

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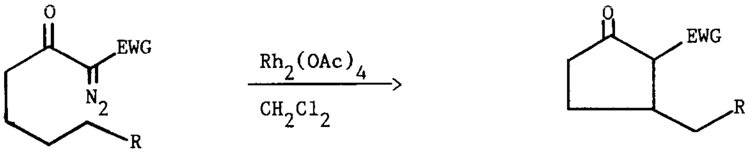
Summary : α-diazo β-ketoalkylphosphonates and phosphine oxides undergo intramolecular carbenoïd cyclizations under rhodium (II) catalysis to afford substituted diethoxyphosphono-2 and diphenylphosphono-2 cyclopentanones which, under Wittig-Horner conditions, lead to α-methylene cyclopentanones.

The intramolecular carbenoid cyclization of α-diazocarbonyl compounds has proved to be of great value, to organic chemists, for the carbocyclic ring formation (1). Except for the cyclopropanation, the five membered ring cyclization under rhodium (II) catalysis (scheme 1) is by far the most documented reaction (2)(3).

scheme 1



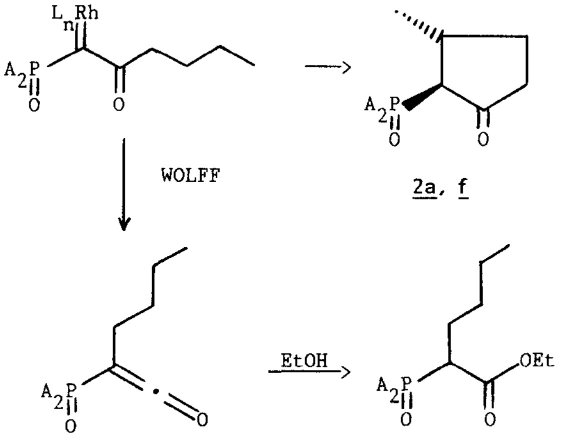
1   2

Using this methodology, Taber and coworkers (2a - h) have prepared α-carboalkoxy cyclopentanones 2 from the corresponding acyclic α-diazo β-ketoesters 1 (EWG = CO_2R'). Very recently the carbenoid intramolecular cyclization of α-diazo β-ketosulfones 1 (EWG = $PhSO_2$) have been published (4). This prompts us to report our results on the behaviour of α-diazo β-ketophosphonates and phosphine oxides 1 [EWG = $(R'O)_2P(O)$, $Ph_2P(O)$] which under similar conditions could give the α-phosphorylated cyclopentanones 2. Under Wittig-Horner conditions these cyclic compounds 2 will eventually lead to α-alkylidene cyclopentanones.

Following essentially the procedure of Taber (2a) a methylene chloride solution of α-diazo β-ketophosphonates or phosphine oxide 1, prepared by a diazo transfer reaction (4)(5), is added *slowly* to a *refluxing* suspension of rhodium (II) acetate (2 mole %) in the same solvent. After one to three hours of heating the diazo compound has disapeared as shown by TLC and ^{31}P NMR spectroscopy leading in fair to good yields, after work up and purification, to the title compounds 2 [EWG = $(R'O)_2P(O)$, $Ph_2P(O)$] (see table). Stereochemical assigments are based on ^1H and ^{13}C NMR spectroscopy and by comparison with reported data for the esters analogs (2a-g).

The deviations of the yields from the quantitative are due to a side reaction, the Wolff rearrangement of the carbene or carbenoid intermediate. This rearrangement, which has not been reported in the cyclization of α-diazo β-keto esters, competes here with the intramolecular C-H insertion (scheme 2) :

Scheme 2



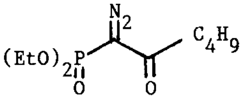
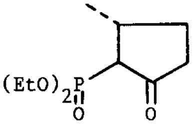
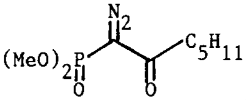
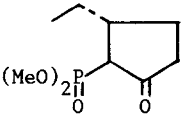
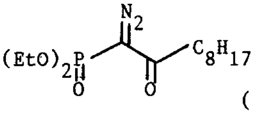
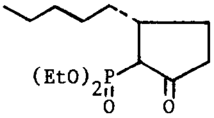
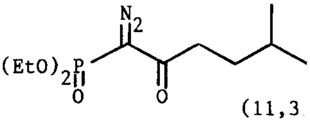
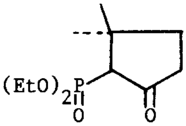
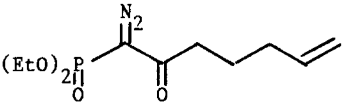
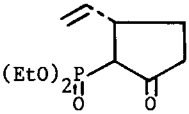
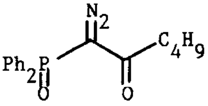
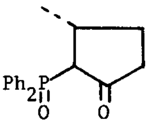
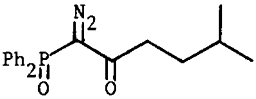
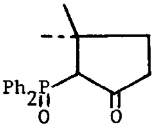
	A = C_2H_5O	Ph
2a, f	67 %	50 %
3a, f	30 %	45 %

The ketene pathway has been demonstrated, in two cases (2a,f) by adding ethanol just before the usual work up. The substituted phosphonoacetate and phosphine oxide (3a, f) were obtained in 30 % and 45 % yields respectively beside the required phosphorylated cyclopentanones (2a, f). The diethyl butylphosphonoacetate 3a has been synthetized independantly, following the procedure of Vandewalle (6), by a photoinduced wolff rearrangement of the diethyl α-diazo β-ketohexylphosphonate 1a.

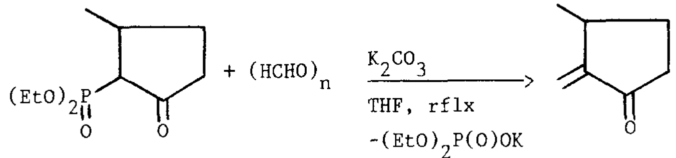
The differences between the phosphorylated compounds and their carbonylated analogs (lower yields, reflux vs room temperature, wolff rearrangement) can be rationalized in terms of electronic, steric and kinetic effects. The bulky phosphoryl group, which is less electron withdrawing than its carbonyl counterpart renders the carbenoid intermediate less electrophile, allowing the competition between the Wolff rearrangement and the cyclization to take place.

In order to illustrate this interesting extension of the intramolecular cyclisation of α-diazoketones to the phosphorus compounds, diethoxyphosphono-2 cyclopentanone 2a, thus obtained, was submitted to the Wittig-Horner olefination (scheme 3) :

TABLE

Entry	α-Diazo β-ketophosphonates and phosphine oxides **1** (δ ^{31}P NMR)	α-phosphoryl cyclopentanones **2** (isolated yield, δ ^{31}P NMR)
a	 (11,2 ppm)	 (67%, 22,4 ppm)
b	 (14,3 ppm)	 (40%, 25,1 ppm)
c	 (11,3 ppm)	 (66%, 22,4 ppm)
d	 (11,3 ppm)	 (70%, 20,9 ppm)
e	 (11,1 ppm)	 (48%, 21,6 ppm)
f	 (22,6 ppm)	 (50%, 30,0 ppm)
g	 (22,3 ppm)	 (33%, 27,3 ppm)

Scheme 3



2a

53 %

Under Villieras' conditions (7) the α-methylene β-methylcyclopentanone was prepared in 53 % yield showing conclusively that α-diazo β-ketoalkylphosphonates and phosphine oxides should be useful in the construction of α-alkylidene β-substituted cyclopentanones, versatile intermediates for elaboration to complex natural products.

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