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Chemoselectivity in the Rhodium(II) Acetate Catalysed Decomposition of α-Diazo-β-keto-γ,δ-alkenyl-δ-aryl Compounds: Aromatic C-H Insertion Reaction or Wolff Rearrangement-Electrocyclization

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Abstract: The rhodium(II) acetate catalysed decomposition of α-diazo-β-keto-γ,δ-alkenyl phosphonates **1** substituted in the δ-position by an aryl group gave rise to mixtures of isomeric hydroxynaphthalenephosphonates, **3** resulting from a Wolff rearrangement-electrocyclization process and **5** resulting from an aromatic C-H insertion reaction. The **3**:**5** ratio was found to depend on the substitution pattern of the γ,δ-double bond. The diazoesters **9** which are the analogs of diazophosphonates **1** showed similar behaviour. In particular the rhodium(II) acetate catalysed decomposition of ethyl 2-diazo-5,5-diphenyl-3-oxopent-4-enoate **9c** led to ethyl 1-hydroxy-4-phenyl-2-naphthalenecarboxylate **11c** and not to ethyl 2-hydroxy-4-phenyl-1-naphthalenecarboxylate **10c** as previously reported. The structure of **11c** was confirmed by X-ray crystallography.

INTRODUCTION

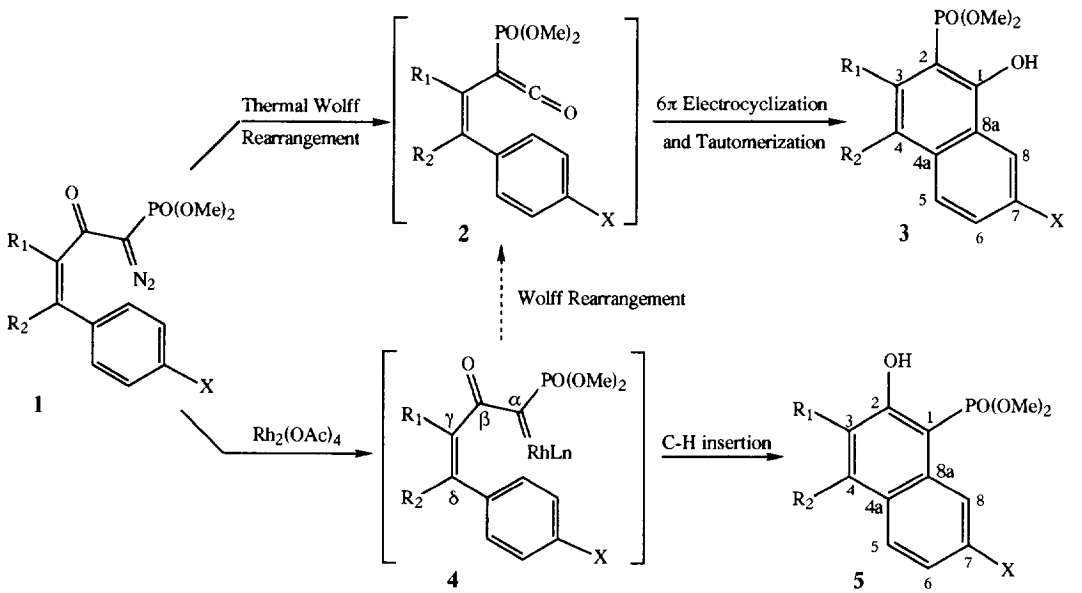
The rhodium(II) catalysed decomposition of α-diazo-β-carbonyl compounds is a well documented process leading to the formation of intermediate rhodium carbenoids which can undergo a variety of reactions like cyclopropanation, C-H or heteroatom-H insertion and ylide formation.[1] Many examples of aromatic C-H insertion reactions resulting from rhodium mediated decomposition of α-diazo-β-keto esters,[2] α-diazoketones,[3] aryl 2-diazobutyrates,[4] *N*-aryl 2-diazoamides[5] and α-diazo-β-phenylmethanesulfonyl esters[6] are known.

We have recently reported that the thermolysis, in refluxing toluene, of some α-diazo-β-keto-γ,δ-alkenyl phosphonates substituted in the δ-position by an aryl group allowed the synthesis of various phenolic compounds, these products being formed by the 6π electrocyclization of an intermediate aryl vinyl ketene resulting from a thermal Wolff rearrangement.[7]

These results suggested that the decomposition of the α-diazo-β-keto-γ,δ-alkenyl-δ-arylphosphonates **1** could be specifically directed either to ketenes **2** through a thermal Wolff rearrangement or to rhodium carbenoids **4** if catalysed by rhodium(II) acetate, allowing respectively the synthesis of dimethyl 1-hydroxy-2-naphthalenephosphonates **3** or isomeric dimethyl 2-hydroxy-1-naphthalenephosphonates **5** (Scheme 1).

However during the course of our previous work,[7c] we have carried out the rhodium(II) mediated decomposition of the diazoalkenylphosphonate **1a** with the aim of synthesizing the naphthol **5a**[8] and we have observed the formation of the naphthol **3a** (yield: 28 %) along with its isomer **5a** (yield: 48 %). Various competitive rhodium carbenoid mediated reactions directed towards two differents groups within the same molecule have been reported; they include C-H, N-H or O-H insertion reactions, cyclopropanation and carbonyl

ylide formation.[2c,5c,9-19] However, only one report, concerning the metal catalysed decomposition of α-alkoxy-α'-diazoketones, in which the Wolff rearrangement is a competing process with aromatic and aliphatic C-H insertion reactions has been studied.[20] The Wolff rearrangement as a side-reaction has been considered in intramolecular cyclizations of rhodium carbenoids resulting from the decomposition of α-diazo-β-ketoalkylphosphonates to explain "deviations of the yields from the quantitative".[21] Diazophosphonates of type 1 can give rise to Wolff rearrangement products which are easy to detect and isolate from the reaction medium, together with aromatic C-H insertion products, and therefore they were well designed for competition experiments. We report here the results of the rhodium(II) acetate catalysed decomposition of α-diazo-β-ketophosphonates **1** and its extension to some ester analogues.



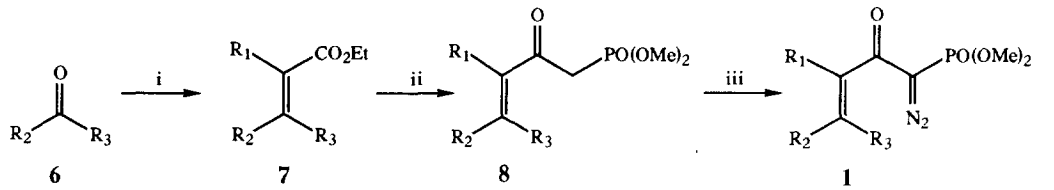
	a	b	c	d	e	f	g	h
R_1	OCH_3	H	H	H	H	H	H	F
R_2	H	H	C_6H_5	4-CH_3O-C_6H_4	4-Cl-C_6H_4	CH_3	CF_3	H
X	H	H	H	CH_3O	Cl	H	H	H

Scheme 1

RESULTS AND DISCUSSION

The α-diazo-β-ketophosphonates **1b-i** required for this study were synthesized according to the sequence outlined in scheme 2. Starting from ketones **6**, the ethyl alkenoates **7c-e**, **7f**,[22] **7h**[23] and **7i**[24] were prepared by a Wadsworth-Horner-Emmons reaction whereas compound **7g**[25] was obtained by a Wittig reaction. The ethyl propenoate **7b** was prepared by semihydrogenation of the corresponding alkyne.[26] Subjected to the action of dimethyl lithiomethylphosphonate (2 eq) compounds **7** were then transformed into β-ketophosphonates **8**. The diazo-transfer reaction was conducted using tosyl azide and potassium carbonate in acetonitrile according to the

conditions reported by Koskinen and Munoz for the preparation of α-diazo-β-ketoesters.[27] The α-diazo-β-ketophosphonates **1** were thus obtained from compounds **7** in overall yields ranging from 38% to 83% .



i) $(EtO)_2OP\text{-}CH_2\text{-}CO_2Et$, NaH (**c-e,i**); $(CF_3CH_2O)_2OP\text{-}CH_2\text{-}CO_2Et$, Et_3N (**f**); $Ph_3P{=}CHCO_2Et$ (**g**); $(EtO)_2OP\text{-}CHF\text{-}CO_2Et$, BuLi (**h**). ii) $CH_3\text{-}PO(OMe)_2$ (2 eq), BuLi, THF. iii) TsN_3, K_2CO_3, CH_3CN.

	b	**c**	**d**	**e**	**f**	**g**	**h**	**i**
R_1	H	H	H	H	H	H	F	H
R_2	H	C_6H_5	4-MeO-C_6H_4	4-Cl-C_6H_4	CH_3	CF_3	H	2,2'-biphenyle
R_3	C_6H_5	C_6H_5	4-MeO-C_6H_4	4-Cl-C_6H_4	C_6H_5	C_6H_5	C_6H_5	

Scheme 2

When the diazophosphonate **1b** was treated with a catalytic amount of rhodium(II) acetate (3 % mol) in boiling benzene, the 2-hydroxy-1-naphthalenephosphonate **5b** resulting from the insertion reaction of the rhodium carbenoid **4b** was formed together with a small amount of isomeric 1-hydroxy-2-naphthalene-phosphonate **3b** (Table 1).

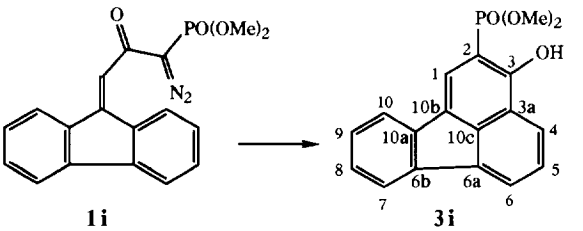
Table (1): **(3:5)** Ratios observed in the rhodium(II) acetate catalysed decomposition of **1** in refluxing benzene

1	**a**[7c]	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**
(3:5) ratios* (yield)	37:63 (76%)	12:88 (86%)	85:15 (78%)	100:0 (90%)	92:8 (77%)	47:53 (90%)	0:100 (75%)	5:95 (81%)	100:0 (86%)

*determined by ^{1}H-NMR.

Surprisingly the introduction of a phenyl group as the R_2 substituent resulted in a dramatic change in the orientation of the decomposition towards the Wolff rearrangement product since the decomposition of **1c** yielded **3c** as the major isomer. The same **3c**:**5c** ratio was obtained when the rhodium mediated decomposition of **1c** was conducted in refluxing dichloromethane (3 h) in place of refluxing benzene (1 h), showing that the reaction temperature did not influence the products distribution. The thermal decomposition of **1c** in refluxing benzene was completed after 30 h; if the reaction was stopped after 1h, only a small amount of **3c** was detected (~ 5% as shown by ^{1}H-NMR). Thus the formation of **3c** should not be the result of a competing thermal Wolff rearrangement but, almost completely, the result of the Wolff rearrangement of a rhodium carbenoid species such as **4c**. The rhodium mediated decomposition of the diazophosphonates **1d,e** in refluxing benzene gave similar results, the naphthalenephosphonates **3** being obtained as exclusive (**d**) or major (**e**) isomer. These results could be explained by a steric interaction between the two R_2 and R_3 aryl groups, preventing the *cis*-R_3 group and the carbenoid centre from achieveing a proximal orientation and thus retarding the aromatic C-H insertion process. However this interpretation was not consistent with the decomposition of the diazophosphonate **1i**, possessing

two bonded R_2 and R_3 aryl groups in a planar arrangement, which gave the fluoranthenephosphonate **3i** as the sole product (Scheme 3).



1i **3i**

Scheme 3

Evidence for electronic effects of the R_2 substituent was given by the decomposition of the diazophosphonates **1f** or **1g** which gave rise to a 47:53-mixture of **3f** and **5f** or exclusively to the insertion product **5g**. Thus the (**3**:**5**) ratios obtained in the rhodium mediated decomposition of diazophosphonates **1b-g, i** could be related to the electron density of the C_γ-C_β bond in the intermediate rhodium carbenoids **4**: δ-substituents acting as mesomerically electron releasing groups (**c-e,i**, R_2 = aryl) increase the electron density of the C_γ-C_β bond, making it more susceptible to attack the electrophilic rhodium carbenoid and favour the Wolff rearrangement pathway whereas δ-substituents which are weak electron releasing (**f**, $R_2 = CH_3$), neutral (**b**, R_2 = H) or electron withdrawing (**g**, $R_2 = CF_3$) have an opposite effect and allow the C-H insertion to compete with the Wolff rearrangement.

As compared with compound **1b**, the introduction of a fluorine atom in γ-position slightly affected the orientation of the decomposition towards the insertion product **5h** (Table 1) whereas the methoxy group had resulted in an increase in the amount of Wolff rearrangement product **3a**.[7c] These results are globally consistent with an electron withdrawing effect of the fluorine atom and an electron releasing effect of the methoxy group on the electron density of C_γ-C_β bond.

To establish unambiguously the structures of isomeric naphthols **3** and **5**, all diazophosphonates **1** were submitted to thermolysis in refluxing toluene to afford almost exclusively the thermal Wolff rearrangement products **3**; minute amounts of isomers **5** (yields ~ 2 %) were also detected in the thermal decomposition of **1b,f,g**. The structures of compounds **3b-i** and **5b,c,e-h** were supported by their IR and NMR spectra. Chemical shifts and coupling constants relative to the benzannulated ring are gathered in Tables 2 and 3.[28] The observed H-P and C-P coupling constants were particularly useful to establish the relative positions of hydroxy and dimethylphosphono groups. Thus compounds **3** possess a $^3J_{HP}$ relative to H-3 (or H-1 for **3i**) in the range 11.9-13.0 Hz whereas compounds **5** show a $^4J_{HP}$ relative to H-3 in the range 5.8-5.9 Hz. A similar and conclusive comparison can be made between **3** and **5** concerning the $^nJ_{CP}$ coupling constants.[29]

Table (2): Pertinent ^{1}H-NMR data of phosphonates **3** and **5** [δ (ppm) and J (Hz)]

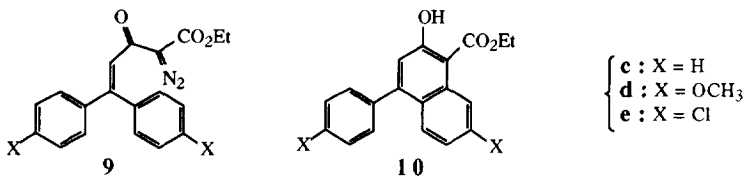
	b (H-3)	b (H-4)	c (H-3)	d (H-3)	e (H-3)	f(H-3)	g (H-3)	h (H-4)	i (H-1)
3	7.30 $^3J_{HP}$ = 12.1	7.39 $^4J_{HP}$ = 3.4	7.22 $^3J_{HP}$ = 12.9	7.07 $^3J_{HP}$ = 13.0	7.18 $^3J_{HP}$ = 11.9	7.10 $^3J_{HP}$ = 12.7	7.78-7.54 $^3J_{HP}$ ~ 13	6.96 $^4J_{HP}$ = 5.4 $^2J_{HF}$ = 10.8	7.73 $^3J_{HP}$ = 12.5
5	7.12 $^4J_{HP}$ = 5.8	7.92 (s)	7.14 $^4J_{HP}$ = 5.9	-	7.06 $^4J_{HP}$ = 5.8	6.95 $^4J_{HP}$ = 5.9	buried in a multiplet	buried in a multiplet	-

Table (3): Pertinent ^{13}C-NMR data of phosphonates **3** and **5** and esters **10** and **11** [δ (ppm) and J (Hz)]

3b	C-1 161.8 $^{2}J_{CP}$ = 7.5	C-2 99.5 $^{1}J_{CP}$ = 181.4	C-3 125.7 $^{2}J_{CP}$ = 6.3	C-4 119.7 $^{3}J_{CP}$ = 13.4	C-4a 137.5 $^{4}J_{CP}$ = 2.0	C-8a 125.1 $^{3}J_{CP}$ = 13.8
3c	C-1 160.9 $^{2}J_{CP}$ = 7.3	C-2 98.7 $^{1}J_{CP}$ = 183.0	C-3 125.8 $^{2}J_{CP}$ = 7.8	C-4 132.1 $^{3}J_{CP}$ = 13.5	C-4a 135.3 $^{4}J_{CP}$ = 2.4	C-8a 125.0 $^{3}J_{CP}$ = 13.8
3d	C-1 159.5 $^{2}J_{CP}$ = 7.4	C-2 99.2 $^{1}J_{CP}$ = 181.8	C-3 123.3 $^{2}J_{CP}$ = 6.4	C-4 131.8 $^{3}J_{CP}$ = 13.8	C-4a 130.8 $^{4}J_{CP}$ = 2.0	C-8a 126.1 $^{3}J_{CP}$ = 14.2
3e	C-1 160.1 $^{2}J_{CP}$ = 7.4	C-2 100.2 $^{1}J_{CP}$ = 183.4	C-3 126.2 $^{2}J_{CP}$ = 6.5	C-4 130.7 $^{3}J_{CP}$ = 13.5	C-4a 133.4 $^{4}J_{CP}$ = 2.4	C-8a 125.8 $^{3}J_{CP}$ = 14.3
3f	C-1 160.2 $^{2}J_{CP}$ = 7.0	C-2 98.1 $^{1}J_{CP}$ = 182.4	C-3 124.6 $^{2}J_{CP}$ = 6.4	C-4 124.9 $^{3}J_{CP}$ = 14.9	C-4a 136.3 $^{4}J_{CP}$ = 2.3	C-8a 125.4 $^{3}J_{CP}$ = 13.4
3g	C-1 164.6 $^{2}J_{CP}$ = 7.7	C-2 97.9 $^{1}J_{CP}$ = 186.9	C-3 125.4 (m)	C-4 118.0 (qd) $^{2}J_{CF}$ = 30.7 $^{3}J_{CP}$ = 13.8	C-4a 132.5	C-8a 125.4 $^{3}J_{CP}$ = 13.2
3h	C-1 163.4 (dd) $^{2}J_{CP}$ = 4.2 $^{3}J_{CF}$ = 8.4	C-2 91.4 (dd) $^{1}J_{CP}$ = 181.1 $^{2}J_{CF}$ = 26.6	C-3 158.9 (dd) $^{2}J_{CP}$ = 1.8 $^{1}J_{CF}$ = 246.7	C-4 101.9 (dd) $^{3}J_{CP}$ = 6.9 $^{2}J_{CF}$ = 21.9	C-4a 136.7(dd) $^{4}J_{CP}$ = 1.0 $^{3}J_{CF}$ = 11.9	C-8a 122.2 (d) $^{3}J_{CP}$ = 12.6
3i	C-3 163.2 $^{2}J_{CP}$ = 8.7	C-2 100.8 $^{1}J_{CP}$ = 179.8	C-1 120.6 $^{2}J_{CP}$ = 7.0	C-10b 128.7 $^{3}J_{CP}$ = 14.8	C-10c 138.5 $^{4}J_{CP}$ = 1.6	C-3a 122.3 $^{3}J_{CP}$ = 15.1
5b[a]	C-1 97.5 $^{1}J_{CP}$ = 176.6	C-2 165.3 $^{2}J_{CP}$ = 6.8	C-3 119.9 $^{3}J_{CP}$ =13.6	C-4 136.9 $^{4}J_{CP}$ = 2.7	C-4a 128.7 $^{3}J_{CP}$ = 11.8	C-8a 133.7 $^{2}J_{CP}$ = 7.8
5c[b]	C-1 98.9 $^{1}J_{CP}$ = 177.8	C-2 164.2 $^{2}J_{CP}$ = 6.8	C-3 120.4 $^{3}J_{CP}$ = 13.7	C-4 148.8 $^{4}J_{CP}$ = 2.8	C-4a 127.9 $^{3}J_{CP}$ = 10.6	C-8a 134.0 $^{2}J_{CP}$ = 8.1
5f[c]	C-1 95.0 $^{1}J_{CP}$ = 178.8	C-2 164.7 $^{2}J_{CP}$ = 6.7	C-3 120.3 $^{3}J_{CP}$ = 13.6	C-4 144.1 $^{4}J_{CP}$ = 2.7	C-4a 128.1 $^{3}J_{CP}$ = 11.8	C-8a 133.5 $^{2}J_{CP}$ = 8.2
5g[d]	C-1 101.6 $^{1}J_{CP}$ = 175.9	C-2 163.20 $^{2}J_{CP}$ = 6.9	C-3 119.4 (dq) $^{3}J_{CP}$ = 14.0 $^{3}J_{CF}$ = 6.1	C-4 133.6 (qd) $^{4}J_{CP}$ = 3.0 $^{2}J_{CF}$ = 30.6	C-4a 123.5 $^{3}J_{CP}$ = 11.8	C-8a 134.4 $^{2}J_{CP}$= 8.0
5h[e]	C-1 100.2 (dd) $^{1}J_{CP}$ = 176.4 $^{3}J_{CF}$ = 1.8	C-2 155.6 (dd) $^{2}J_{CP}$ = 7.7 $^{2}J_{CF}$ = 14.9	C-3 151.5 (dd) $^{3}J_{CP}$ = 21.6 $^{1}J_{CF}$ = 252.2	C-4 118.7 (dd) $^{4}J_{CP}$ = 2.7 $^{2}J_{CF}$ = 17.2	C-4a 127.7(dd) $^{3}J_{CP}$ = 14.3 $^{3}J_{CF}$ = 7.5	C-8a 130.0 (d) $^{2}J_{CP}$ = 6.9
10g	C-1 108.4	C-2 161.8	C-3 119.1(q) $^{3}J_{CF}$ = 6.2	C-4 133.1 (q) $^{2}J_{CF}$ = 30.5	C-4a 125.0 $^{3}J_{CF}$ = 2.8	C-8a 132.8
11c	C-1 160.4	C-2 105.4	C-3 124.9	C-4 131.1	C-4a 135.5	C-8a 124.9
11g	C-1 163.7	C-2 103.9	C-3 124.3 (q) $^{3}J_{CF}$ = 6.4	C-4 117.0 (q) $^{2}J_{CF}$ = 30.9	C-4a 132.4 $^{3}J_{CF}$ = 0	C-8a 125.3

[a]C-8: 124.8 ($^{3}J_{CP}$ = 4.6); [b]C-8: 124.6 ($^{3}J_{CP}$ = 4.8); [c]C-8: 124.9 ($^{3}J_{CP}$ = 5.2); [d]C-8: 125.2 ($^{3}J_{CP}$ = 4.5); [e]C-8: 124.5 ($^{3}J_{CP}$ = 4.5, $^{5}J_{CF}$ = 1.9).

Comparison of the rhodium(II) mediated decomposition of diazophosphonates **1** with literature results concerning analogous diazoesters revealed a different behaviour. A few years ago, Taylor and Davies[2a] reported that the rhodium(II) acetate catalysed decomposition of ethyl 2-diazo-3-oxopent-4-enoates **9c-e** resulted in the exclusive formation of ethyl 4-aryl-2-hydroxy-1-naphthalenecarboxylates **10c-e** through rhodium carbenoid insertion into an aromatic C-H bond (scheme 4). As compared with the diazophosphonates **1c-e**, these results seemed to point out a strong influence of the ester group on the decomposition pathways. However Taylor and Davies gave no spectral data in their communication and we found no subsequent publication on this subject. Hence we considered that the relative positions of the hydroxy and ester groups in compounds **10** were not established and we decided to reinvestigate the decomposition of the diazoester **9c**.



Scheme 4

We prepared the diazoester **9c** by transformation of ethyl propenoate **8c** into the corresponding acid chloride and subsequent reaction with ethyl diazoacetate (Scheme 5). The decomposition of **9c**, in the presence of rhodium(II) acetate according to the conditions of Taylor and Davies (refluxing fluorobenzene, 1 h), gave rise to an ethyl hydroxynaphthalenecarboxylate, described as **10c** by these authors. Surprisingly the thermolysis of **9c** in refluxing toluene furnished the same compound; the identity between both products was evidenced by the equivalence of their melting points, IR and NMR spectra. The comparison of C-4a and C-8a chemical shifts of this compound [δ(C-4a) 135.4 or 124.9; δ (C-8a) 124.9 or 135.4], 1-hydroxy-2-naphthoic acid [δ(C-4a) 136.7; δ(C-8a) 124.2] and 2-hydroxy-1-naphthoic acid [δ(C-4a) 128.0; δ(C-8a) 131.8][30] was revealing. Supposing that the influence of the 4-phenyl substituent on C-4a and C-8a chemical shifts could be considered as negligible, these data showed that this compound seemed more likely to be formulated as ethyl 1-hydroxy-2-naphthalene-carboxylate **11c** rather than its isomer **10c**; furthermore the C-4a and C-8a chemical shifts were very close to those observed for the dimethyl 1-hydroxy-2-naphthalenephosphonate **3c** [δ(C-4a) 135.3; δ (C-8a) 125.0]. Thus the structure **10c** proposed by Taylor and Davies appeared questionable and therefore crystals of hypothetical **11c** were submitted to an X-ray analysis. The X-ray spectrum (Figure)[31] confirmed its structure as **11c** and proved that the product formed in the rhodium(II) acetate catalysed decomposition of the diazo ester **9c** resulted from a Wolff rearrangement-electrocyclisation process and not from an aromatic C-H insertion reaction.

Traces of a second compound, with a smaller R_f than **11c**, were detected by TLC of the crude mixtures obtained by thermal as well as rhodium mediated decomposition of diazo ester **9c**. From the rhodium catalysed decomposition of **9c** in dichloromethane at room temperature (15 h) we were able to isolate about 2 mg of a sample containing 95 % of this compound. Its ^{1}H-NMR spectrum was in agreement with its formulation as ethyl 2-hydroxy-1-naphthalenecarboxylate **10c**.[32] The structures of compounds **10c** and **11c** were consistent with the predictable effects of hydroxy and ethoxycarbonyl groups on H-3 and H-8 chemical shifts as shown in Table (4).

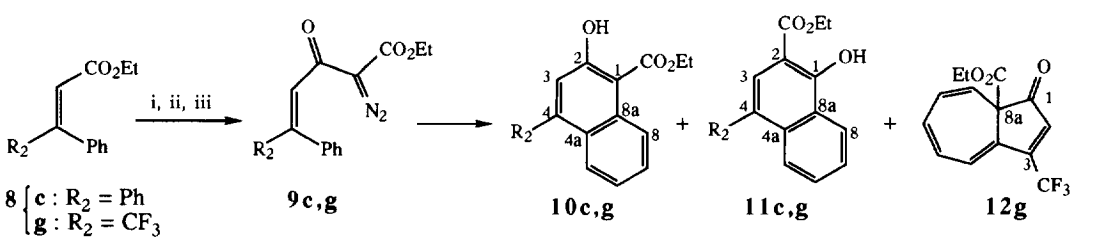
Since the rhodium mediated decomposition of diazo phosphonate **1c** and diazo ester **9c** followed a similar course we finally decided to investigate the decomposition of diazo ester **9g** possessing a trifluoromethyl group

as the R_2 substituent. This compound was prepared in the same way as **9c** (Scheme 5). The rhodium(II) catalysed decomposition of **9g** gave rise to a 74:26-mixture of the insertion product **10g** and azulenone **12g** whereas its thermolysis afforded a 13:78:9-mixture of **10g**, the Wolff rearrangement product **11g** and **12g**. The structures of naphthols **10g** and **11g** were in agreement with their IR and NMR spectra. Comparison of the H-3/H-8 and C-4a/C-8a pairs of chemical shifts between **10g** and **11g** was consistent with the relative positions of the hydroxy and ester groups (Tables 3 and 4). The formulation of the azulenone **12g** was clearly supported by its IR and NMR spectra, the ^{13}C-NMR spectrum showing a ketonic carbonyl (C-1) at δ 198.2 and a quaternary sp^3 carbon (C-8a) at δ 63.6. The formation of the azulenone **12g** results presumably from a cyclopropanation of the aromatic ring by the initially formed carbenoid species producing an intermediate norcaradiene which undergoes a pericyclic rearrangement.[33] Hence, in a similar manner as observed with the diazophosphonate **1g**, no product resulting from the Wolff rearrangement was formed in the rhodium mediated decomposition of the diazoester **9g**.

Thus, the rhodium(II) acetate catalysed decompositions of α-diazo-β-ketoalkenylphosphonates **1** and α-diazo-β-ketoalkenylesters **9** were found to follow similar pathways, exhibiting the same dependence on the nature of the R_2 substituent. Some years ago Corbel et al.[21] had reported that the rhodium(II) catalysed decomposition of α-diazo-β-ketoalkylphosphonates gave side-products resulting from the Wolff rearrangement together with the expected intramolecular aliphatic C-H insertion products whereas the rhodium(II) catalysed decomposition of related α-diazo-β-ketoalkylesters was known to give exclusively aliphatic C-H insertion products; they interpreted the difference by the fact that the dimethylphosphono group, "which is less electron-withdrawing than its carbonyl counterpart, renders the carbenoid intermediate less electrophilic, allowing the competition between the Wolff rearrangement and the cyclization to take place". The behaviour of α-diazo-β-ketoalkenyl compounds appears different since the chemoselectivity does not depend on the presence of the ester or phosphonate group, but only on the substitution pattern of the double bond.

Table (4): Pertinent ^{1}H-NMR chemical shifts (ppm) of esters **10** and **11**

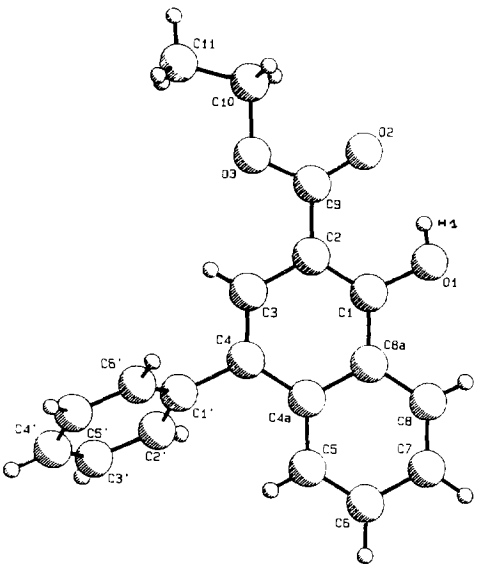
	10c	**11c**	**10 g**	**11g**
H-3	7.06	7.74	7.58	8.20
H-8	8.81	8.50	8.84	8.50



8 { **c** : R_2 = Ph ; **g** : R_2 = CF_3 **9c,g** **10c,g** **11c,g** **12g**

i) KOH, MeOH ; ii)$(COCl)_2$, Et_2O ; iii) N_2CH-CO_2Et

Scheme 5



Dihedral angles Plane (C1,C2,C3,C4,C4a,C5,C6,C7,C8,C8a) and plane (C1',C2'C3',C4,C5,C6'): **65.0°**

Plane (C1,C2,C3,C4,C4a,C5,C6,C7,C8,C8a) and plane (O2,C9,O3,C10,C11): **2.8°**

Intramolecular hydrogen bond distance H1...O2: **2.597 Å**

angle O1-H1...O2: **147.9°**.

Figure: PLUTO[34] drawing of **11c** showing the numbering scheme

CONCLUSION

The (1-naphthol:2-naphthol) ratios observed in the rhodium(II) acetate catalysed decomposition of α-diazo-β-keto-γ,δ-alkenyl compounds **1** or **9** appear to depend mainly on the substitution pattern of the γ,δ-double bond. The chemoselectivity of the decomposition of β-keto-γ,δ-alkenyl rhodium carbenoids towards aromatic C-H insertion *versus* Wolff rearrangement can be related to the electron density of the C_γ-C_β bond, a lower electron density favouring the aromatic C-H insertion.

EXPERIMENTAL

General: Diethyl ether was distilled from potassium hydroxide, pentane from phosphorus pentoxide, tetrahydrofuran from sodium benzophenone ketyl. Benzene and toluene were dried over sodium. Organic solutions were dried over anhydrous sodium sulfate. Column chromatographies were performed using Merck Silica gel 60 (70-230 mesh) and TLC were carried out using Merck Kieselgel 60 F254 plates. Melting points were determined on a Kofler block apparatus. IR spectra were recorded on a Perkin Elmer 1310 infrared spectrophotometer. Nuclear magnetic resonance spectra were recorded in $CDCl_3$ on a Brucker AC200 (200/50 MHz) spectrometer and for specified cases on a Brucker AM300 (300/75 MHz). All NMR recordings were referenced to $CHCl_3$ resonances (7.26 and 77.0 ppm). Splitting patterns abbreviations are: s, singulet; d, doublet; t, triplet; m, multiplet; br, broad; p, pseudo. Multiplicity (^{13}C NMR) was determined by DEPT sequencies. Elemental Analysis and Mass Spectra were performed by Service Central d'Analyse, Centre National de la Recherche Scientifique, 69300 Vernaison, France.

SYNTHESIS OF ETHYL ALKENOATES (7c-e,i)

To a stirred suspension of sodium hydride (60% in oil, 0.6 g, 15 mmol) in anhydrous DME (100 ml) under nitrogen, cooled in a water-ice bath, was added dropwise a solution of triethyl phosphonoacetate (3.36 g, 15 mmol) in anhydrous DME (20 ml). After 15 mn at room temperature the solution was transfered to a separatory funnel and added to a refluxing solution of ketone **6** (18 mmol) in anhydrous DME (80 ml). The reaction mixture was then heated for 24 h (**d**), 8 h (**c,e**) or 5 h (**i**) and was then hydrolyzed with a saturated sodium chloride solution (40 ml). The aqueous phase was extracted with diethyl ether (100 ml) and the combined organic extracts were dried, filtered and concentrated to afford a residue which was purified by chromatography eluting with pentane/diethyl ether 90:10 (**7c,e**), pentane/diethyl ether 85:15 (**7i**) or pentane/diethyl ether 50:50 (**7d**).

Ethyl 3,3-diphenylprop-2-enoate (7c)[35]

Yield 64 %. Oil.

Ethyl 3,3-di(4-methoxyphenyl)prop-2-enoate (7d)[36]

Yield 82 %. Oil.

Ethyl 3,3-di(4-chlorophenyl)prop-2-enoate (7e)

Yield 65 %. Mp 63°C. IR ($CHCl_3$): 1710, 1620, 1590. ^{1}H-NMR: δ 7.38-7.09 (m, 8H); 6.34 (s, 1H); 4.07 (q, 2H, J = 7.1); 1.15 (t, 3H, J = 7.1). ^{13}C-NMR: δ 165.7; 154.1; 138.9; 136.9; 135.8; 134.5; 130.6; 129.6; 128.8; 128.4; 118.2; 60.4; 14.1. Anal. Calcd. for $C_{17}H_{14}O_2Cl_2$: C, 63.57; H, 4.39; Cl, 22.08. Found: C, 63.39; H, 4.39; Cl, 22.20.

Ethyl (9H-fluorenylidene)ethanoate (7i)[23]

Yield 80 %. Mp 78°C.

SYNTHESIS OF β-KETO-γ,δ-ALKENYLPHOSPHONATES (8)

To a stirred solution of dimethyl methylphosphonate (1.24 g, 10 mmol) in anhydrous THF (30 ml) cooled at -80°C, was added dropwise, under nitrogen, 6.25 ml (10 mmol) of *n*-butyllithium 1.6 M in hexanes. The mixture was kept for 45 mn at -60 °C and then a solution of ester **7** (5 mmol) in anhydrous THF (30 ml) was added slowly. The reaction mixture was allowed to react at room temperature for 3 h, and was then quenched with a 1 M aqueous hydrogen chloride solution saturated with sodium chloride (10 ml). The aqueous phase was extracted with diethyl ether (3 x 20 ml), the organic layers were washed with brine, dried, filtered and concentrated to afford a residue which was purified by chromatography eluting with ethyl acetate (**8b,f,h**), diethyl ether/methanol 95:5 (**8c,e,g,i**) or diethyl ether/methanol 93:7 (**8d**).

Dimethyl (Z)-2-oxo-4-phenylbut-3-enylphosphonate (8b)

Yield 97%. Oil. IR (neat): 1685, 1600, 1565,1255, 1030. ^{1}H-NMR: δ 7.61-7.56 (m, 2H); 7.38-7.20 (m, 3H); 6.94 (d, 1H, J = 12.6); 6,33 (d, 1H, J = 12.6); 3.77 (d, 6H, $^3J_{HP}$ = 11.2); 3.36 (d, 2H, $^2J_{HP}$ = 22.4). ^{13}C-NMR: δ 192.4 (d, $^2J_{CP}$ = 6.4); 142.4; 134.6; 129.9; 129.8; 128.3; 127.4; 53.0 (d, $^2J_{CP}$ = 6.4); 42.1 (d, $^1J_{CP}$ = 127.7). Anal. Calcd. for $C_{12}H_{15}O_4P$: C, 56.70; H, 5.95; P, 12.18. Found: C, 56.22; H, 6.09; P, 12.12.

Dimethyl 4,4-diphenyl-2-oxobut-3-enylphosphonate (8c)

Yield 87%. Mp 68°C. IR ($CHCl_3$): 1685, 1650, 1585, 1570, 1245, 1050, 1035. ^{1}H-NMR: δ 7.44-7.19 (m, 10 H); 6.71 (s, 1H); 3.74 (d, 6H, $^3J_{HP}$ = 11.2); 2.96 (d, 2H , $^2J_{HP}$ = 22.2). ^{13}C-NMR: δ 191.7 (d, $^2J_{CP}$ = 6.4); 155.5; 140.6; 138.4; 129.8; 129.7; 129.0; 128.7; 128.5; 128.4; 125.7 (d, $^3J_{CP}$ = 1.8); 52.9 (d, $^2J_{CP}$ = 6.4);

41.5 (d, $^{1}J_{CP}$ = 128.0). Anal. Calcd. for $C_{18}H_{19}O_4P$: C, 65.45; H, 5.80; P, 9.38. Found: C, 65.85; H, 5.93; P, 9.21.

Dimethyl 4,4-di(4-methoxyphenyl)-2-oxobut-3-enylphosphonate (8d)

Yield 97%. Mp 76°C. IR ($CHCl_3$): 1675, 1645, 1605, 1580, 1560, 1250, 1030. ^{1}H-NMR: δ 7.29-7.14 (m, 4H); 6.94-6.83 (m, 4H); 6.57 (s, 1H); 3.86 (s, 3H); 3.83 (s, 3H); 3.75 (d, 6H, $^{3}J_{HP}$ = 11.2); 2.96 (d, 2H, $^{2}J_{HP}$ = 22.2). ^{13}C-NMR: δ 191.6 (d, $^{2}J_{CP}$ = 6.4); 161.2; 160.5; 155.8; 133.5; 131.6; 130.7; 130.6; 123.6; 113.8; 113.7; 55.4; 55.3; 52.9 (d, $^{2}J_{CP}$ = 6.4); 41.3 (d, $^{1}J_{CP}$ = 128.0). Anal. Calcd. for $C_{20}H_{23}O_6P$: C, 61.54; H, 5.94; P, 7.93. Found: C, 61.48; H, 6.02; P, 7.94.

Dimethyl 2-oxo-4,4-di(4-chlorophenyl)but-3-enylphosphonate (8e)

Yield 74%. Mp 90°C. IR ($CHCl_3$): 1685, 1585, 1260, 1040. ^{1}H-NMR: δ 7.38-7.10 (m, 8H); 6.72 (s, 1H); 3.75 (d, 6H, $^{3}J_{HP}$ = 11.2); 3.05 (d, 2H, $^{2}J_{HP}$ = 22.5). ^{13}C-NMR: δ 190.7 (d, $^{2}J_{CP}$ = 6.2); 153.4; 138.8; 136.4; 136.3; 135.2; 131.0; 130.0; 128.8; 128.7; 125.3 (d, $^{3}J_{CP}$ = 1.4); 53.1 (d, $^{2}J_{CP}$ = 6.5); 42.2 (d, $^{1}J_{CP}$ = 127.4). Anal. Calcd. for $C_{18}H_{17}Cl_2O_4P$: C, 54.16; H, 4.29; Cl, 17.76; P, 7.76. Found: C, 54.11; H, 4.29; Cl, 17.76; P, 7.70.

Dimethyl (Z)-2-oxo-4-phenylpent-3-enylphosphonate (8f)

Yield 58%. Oil. IR (neat): 1690, 1615, 1260, 1030. ^{1}H-NMR: δ 7.36-7.27 (m, 3H); 7.22-7.15 (m, 2H); 6.25 (q, 1H, J = 1.4); 3.68 (d, 6H, $^{3}J_{HP}$ = 11.2); 2.85 (d, 2H, $^{2}J_{HP}$ = 22.3); 2.17 (d, 3H, J = 1.4). ^{13}C-NMR: δ 191.8 (d, $^{2}J_{CP}$ = 6.5); 154.9; 140.3; 128.6; 128.4; 127.2; 126.6 (d, $^{3}J_{CP}$ = 1.9); 52.9 (d, $^{2}J_{CP}$ = 6.4); 41.2 (d, $^{1}J_{CP}$ = 128.3); 27.2. Anal. Calcd. for $C_{13}H_{17}O_4P$: C, 58.21; H, 6.39; P, 11.55. Found: C*, 57.65; H, 6.59; P, 11.33. *No better analysis could be obtained.

Dimethyl (E)-2-oxo-4-phenyl-5,5,5-trifluoropent-3-enylphosphonate (8g)

Yield 85%. Oil IR (neat): 1710, 1640, 1285, 1180, 1130, 1030, 980. ^{1}H-NMR: δ 7.45-7.29 (m, 5H); 6.87 (s, 1H); 3.72 (d, 6H, $^{3}J_{HP}$ = 11.3); 2.93 (d, 2H, $^{2}J_{HP}$ = 22.4). ^{13}C-NMR: δ 192.0 (d, $^{2}J_{CP}$ = 6.8); 140.1 (q, $^{2}J_{CF}$ = 31.0); 131.2 (q, $^{3}J_{CF}$ = 4.3); 130.4; 130.1; 129.1; 128.8; 122.7 (q, $^{1}J_{CF}$ = 275.2); 53.1 (d, $^{3}J_{CP}$ = 6.4); 41.7 (d, $^{1}J_{CP}$ = 128.2). Anal. Calcd. for $C_{13}H_{14}F_3O_4P$: C, 48.46; H, 4.38; F, 17.69; P, 9.61. Found: C, 48.18; H, 4.43; F, 17.27; P, 9.74.

Dimethyl (E)-3-fluoro-2-oxo-4-phenylbut-3-enylphosphonate (8h)

Yield 80%. Oil. IR (neat): 1700, 1610, 1270, 1125, 1060, 1030. ^{1}H-NMR: δ 7.53-7.47 (m, 2H); 7.26-7.19 (m, 3H); 6.68 (d, 1H, $^{3}J_{HF}$ = 24.5); 3.68 (d, 6H, $^{3}J_{HP}$ = 11.3); 3.26 (dd, 2H, $^{2}J_{HP}$ = 22.4, $^{4}J_{HF}$ = 4.1). ^{13}C-NMR: δ 185.9 (dd, $^{2}J_{CF}$ = 40.4, $^{2}J_{CP}$ = 7.3); 151.6 (dd, $^{1}J_{CF}$ = 256.0, $^{3}J_{CP}$ = 2.5); 130.2 (d, $^{3}J_{CF}$ = 10.5); 130.1 (d, $^{4}J_{CF}$ = 2.7); 129.6; 128.1; 121.8 (d, $^{2}J_{CF}$ = 27.7); 53.0 (d, $^{2}J_{CP}$ = 6.3); 38.1 (dd, $^{1}J_{CP}$ = 130.4, $^{3}J_{CF}$ = 1.6). Anal. Calcd. for $C_{12}H_{14}FO_4P$: C, 52.95; H, 5.18; F, 6.98; P, 11.38. Found: C, 52.80; H, 5.01; F, 6.56; P, 10.77.

Dimethyl 3-(9-(9H-fluorenylidene)-2-oxopropylphosphonate (8i)

Yield 54%. Oil. IR (neat): 1685, 1625, 1590, 1260, 1050, 1040. ^{1}H-NMR: δ 8.83 (d, 1H, J = 7.7); 7.70 (d, 1H, J = 7.5); 7.61-7.55 (m, 2H); 7.44-7.23 (m, 4H); 7.20 (s, 1H); 3.82 (d, 6H, $^{3}J_{HP}$ = 11.2); 3.41 (d, 2H, $^{2}J_{HP}$ = 22.5). ^{13}C-NMR : δ 190.7 (d, $^{2}J_{CP}$ = 6.1); 148.4; 142.8; 141.5; 138.8; 135.1; 131.8; 131.2; 128.8; 128.3; 127.6; 121.6; 119.9; 119.7 (d, $^{3}J_{CP}$ = 1.5); 119.7; 53.2 (d, $^{2}J_{CP}$ = 6.5); 43.5 (d, $^{1}J_{CP}$ = 127.7). Anal. Calcd. for $C_{18}H_{17}O_4P$: C, 65.85; H, 5.22; P, 9.43. Found: C*, 65.01; H, 5.18; P, 9.88. *No better analysis could be obtained.

SYNTHESIS of α-DIAZO-β-KETO-γ,δ-ALKENYLPHOSPHONATES (1)

To a mixture of β-ketophosphonate **8** (6 mmol) and potassium carbonate (1 g, 7.2 mmol) in acetonitrile (20 ml) cooled in a water-ice bath, under nitrogen, was added dropwise with stirring a solution of tosyl azide[37] (1.42 g, 7.2 mmol) in acetonitrile (5 ml). The cooling bath was removed and the mixture was stirred at room temperature. The disappearance of compound **8** was monitored by tlc. After ~ 1 h potassium carbonate was filtered off and acetonitrile was evaporated *in vacuo* to afford a residue which was purified by chromatography eluting with ethyl acetate:pentane 90:10 (**1b**), diethyl ether/methanol 95:5 (**1c,d**), diethyl ether (**1e,g,i**) or ethyl acetate (**1f**), ethyl acetate:pentane 75:25 (**1h**).

Dimethyl (Z)-1-diazo-2-oxo-4-phenylbut-3-enylphosphonate (1b)

Yield 90 %. Oil. IR (neat): 2115, 1635, 1265, 1050, 1025. ^{1}H-NMR: δ 7.58-7.55 (m, 2H); 7.38-7.27 (m, 3H); 6.89 (d, 1H, J = 12.6); 6.28 (d, 1H, J = 12.6); 3.81 (d, 6H, $^3J_{HP}$ = 12.0). ^{13}C-NMR: δ 184.7 (d, $^2J_{CP}$ = 8.5); 140.8; 134.7; 129.6; 129.5; 128.4; 123.9; 64.6 (d, $^1J_{CP}$ = 216.5); 53.7 (d, $^2J_{CP}$ = 5.6). Anal. Calcd. for $C_{12}H_{13}N_2O_4P$: C, 51.44; H, 4.68; N, 10.00; P, 11.05. Found: C, 51.23; H, 4.80; N, 10.25; P, 10.81.

Dimethyl 1-diazo-4,4-diphenyl-2-oxobut-3-enylphosphonate (1c)

Yield 87%. Oil IR (neat): 2120, 1630, 1585, 1565, 1270, 1050, 1025. ^{1}H-NMR: δ 7.43-7.22 (m, 10 H); 6.80 (s, 1H); 3.82 (d, 6H, $^3J_{HP}$ = 12.0). ^{13}C-NMR: δ (Only 12 resonances were observed) 183.0; 154.7; 140.7; 138.5; 129.7; 129.5; 128.7; 128.5; 128.1; 121.1; 64.6 (d, $^1J_{CP}$ = 215.1); 53.6 ($^2J_{CP}$ = 5.5). Anal. Calcd. for $C_{18}H_{17}N_2O_4P$: C, 60.68; H, 4.81; N, 7.86; P, 8.69. Found: C, 60.75; H, 4.57; N, 8.06; P, 8.33.

Dimethyl 1-diazo-4,4-di(4-methoxyphenyl)-2-oxobut-3-enylphosphonate (1d)

Yield 87%. Mp 112°C. IR ($CHCl_3$): 2115, 1625, 1600, 1580, 1560, 1250, 1050, 1030. ^{1}H-NMR: δ 7.28-7.16 (m, 4H); 6.93-6.83 (m, 4H); 6.65 (s, 1H); 3.84 (s, 3H); 3.84 (d, 6H, $^3J_{HP}$ = 12.0); 3.82 (s, 3H). ^{13}C-NMR: δ 182.7 (d, $^2J_{CP}$ = 11.8); 161.1; 160.2; 155.0; 133.6; 131.3; 130.7; 130.4; 118.6; 113.9; 113.4; 64.2 (d, $^1J_{CP}$ = 216.4); 55.3; 55.2; 53.6 (d, $^2J_{CP}$ = 5.5). Anal. Calcd. for $C_{20}H_{21}N_2O_6P$: C, 57.69; H, 5.08; N, 6.73; P, 7.44. Found: C, 57.40; H, 5.11; N, 6.98; P, 7.46.

Dimethyl 4,4-di(4-chlorophenyl)-1-diazo-2-oxobut-3-enylphosphonate (1e)

Yield 77%. Mp 118°C. IR ($CHCl_3$): 2115, 1635, 1585, 1270, 1055, 1030. ^{1}H-NMR: δ 7.39-7.14 (m, 8H); 6.87 (s, 1H); 3.88 (d, 6H, $^3J_{HP}$ = 11.9). ^{13}C-NMR: δ 182.1 (d, $^2J_{CP}$ = 11.4); 152.7; 138.9; 136.5; 136.2; 134.9; 130.8; 129.8; 128.9; 128.4; 121.3; 65.1 (d, $^1J_{CP}$ = 216.2); 53.7 (d, $^2J_{CP}$ = 5.6). Anal. Calcd. for $C_{18}H_{15}Cl_2N_2O_4P$: C, 50.85; H, 3.56; Cl, 16.68; N, 6.59; P, 7.28. Found: C, 51.14; H, 3.63; Cl, 16.38; N, 6.74; P, 7.42.

Dimethyl (Z)-1-diazo-2-oxo-4-phenylpent-3-enylphosphonate (1f)

Yield 86%. Mp 62-64°C. IR (neat): 2120, 1650, 1620, 1270, 1050, 1030. ^{1}H-NMR: δ 7.37-7.28 (m, 3H); 7.27-7.21 (m, 2H); 6.27 (q, 1H, J = 1.4); 3.77 (d, 6H, $^3J_{HP}$ = 12.0); 2.19 (d, 3H, J = 1.4). ^{13}C-NMR: δ 183.7 (d, $^2J_{CP}$ = 11.8); 153.0; 140.1; 128.3; 128.1; 126.9; 121.7; 64.1 (d, $^1J_{CP}$ = 215.6); 53.5 (d, $^2J_{CP}$ = 5.5); 26.6. Anal. Calcd. for $C_{13}H_{15}N_2O_4P$: C, 53.07; H, 5.14; N, 9.52; P, 10.53. Found: C, 53.18; H, 5.27; N, 9.29; P, 10.21.

Dimethyl (E)-1-diazo-2-oxo-4-phenyl-5,5,5-trifluoropent-3-enylphosphonate (1g)

Yield 79 %. Oil. IR ($CHCl_3$): 2110, 1640, 1620, 1590, 1270, 1055, 1030. ^{1}H-NMR: δ 7.48-7.28 (m, 5H); 6.95 (s, 1H); 3.76 (d, 6H, $^3J_{HP}$ = 12.0). ^{13}C-NMR: δ 182.5 (d, $^2J_{CP}$ = 10.5); 139.6 (d, $^2J_{CF}$ = 31.2); 130.5; 129.9; 128.9; 128.6; 128.1 (d, $^3J_{CF}$ = 5.1); 122.6 (d, $^1J_{CF}$ = 275.0); 65.8 (d, $^1J_{CP}$ = 216.7); 53.9 (d, $^2J_{CP}$ =

5.7). Anal. Calcd. for $C_{13}H_{12}F_3N_2O_4P$: C, 44.84; H, 3.47; F, 16.37; N, 8.04; P, 8.89. Found: C, 44.90; H, 3.72; F, 16.21; N, 7.89; P, 8.53.

Dimethyl (E)-1-diazo-3-fluoro-2-oxo-4-phenylbut-3-enylphosphonate (1h)

Yield 90%. Oil. IR (neat): 2110, 1625, 15270, 1265, 1060, 1030. ^{1}H-NMR: δ 7.55-7.49 (m, 2H); 7.38-7.34 (m, 3H); 6.75 (d, 1H, $^3J_{HF}$ = 24.9); 3.84 (d, 6H, $^3J_{HP}$ = 12.0). ^{13}C-NMR: δ 178.1 (dd, $^2J_{CF}$ = 44.4, $^2J_{CP}$ = 9.1); 151.0 (dd, $^1J_{CF}$ = 263.5, $^3J_{CP}$ = 5.0); 129.9 (d, $^3J_{CF}$ = 10.0); 129.5 (d, $^4J_{CF}$ = 2.8); 129.4 (d, $^5J_{CF}$ = 1.2); 128.4; 119.1 (d, $^2J_{CF}$ =24.9); 63.8 (dd, $^1J_{CP}$ = 218.2, $^3J_{CF}$ = 4.2); 54.0 (d, $^2J_{CP}$ = 5.9). Anal. Calcd. for $C_{12}H_{12}FN_2O_4P$: C, 48.33; H, 4.06; N, 9.39; F, 6.37; P, 10.39. Found: C, 48.18; H, 4.07; N, 9.29; F, 5.99; P, 9.64.

Dimethyl 1-diazo-3-(9'-(9H-fluorenylidene))-2-oxopropylphosphonate(1i)

Yield 71%. Mp 108°C. IR (neat): 2110, 1640, 1620, 1590, 1270,1050, 1025. ^{1}H-NMR: δ 8.84 (d, 1H, J = 7.6Hz); 7.66-7.57 (m, 3H); 7.45-7.21 (m, 5H); 3.94 (d, 6H, $^3J_{HP}$ = 12.0). ^{13}C-NMR: δ 182.1 (d, $^2J_{CP}$ = 12.5); 147.8; 142.7; 141.2; 138.9; 135.0; 131.6; 131.0; 128.8; 128.2; 127.6; 121.4; 119.9; 119.7; 116.6; 66.1(d, $^1J_{CP}$ = 214.2); 53.7 (d, $^2J_{CP}$ = 5.5). Anal. Calcd. for $C_{18}H_{15}N_2O_4P$: C, 61.02; H, 4.27; N, 7.91; P, 8.74. Found: C, 60.94; H, 4.28; N, 8.02; P, 8.60.

THERMOLYSIS OF α-DIAZO-β-KETO-γ,δ-ALKENYLPHOSPHONATES (1)

A solution of diazo compound **1** (1.5 mmol) in anhydrous toluene (50 ml) was refluxed with stirring under nitrogen for 4 h (**1b-f,h,i**) or 7 h (**1g**), until the disppearance of compound **1** was completed as judged by TLC. The solvent was then evaporated in vacuo and the residue was purified by chromatography eluting with diethyl ether/pentane 80:20 (**3b**), diethyl ether/pentane 67:33 (**3d,h,i**), diethyl ether/pentane 60:40 (**3f**) and diethyl ether/pentane 50:50 (**3c,e,g**). Minute amounts of compounds **5b,f,g** (yields ~ 2 %) were detected during the purification.

Dimethyl 1-hydroxy-2-naphthalenephosphonate (3b)

Yield 75%. Mp 38-39°C. IR ($CHCl_3$): 3600-2500, 1625, 1565, 1050, 1030. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 11.36 (d, 1H, J = 1.1); 8.41 (brd, 1H, J = 8.2); 7.81 (brd, 1H, J = 8.3); 7.63 (m, 1H); 7.56 (m, 1H); 7.39 (dd, 1H, J = 8.5, $^4J_{HP}$ = 3.4); 7.30 (dd, 1H, J = 8.5, $^3J_{HP}$ = 12.1); 3.77 (d, 6H, $^3J_{HP}$ = 11.5). ^{13}C-NMR (75 MHz, CD_2Cl_2): δ 161.8 (d, $^2J_{CP}$ = 7.5); 137.5 (d, $^4J_{CP}$ = 2.0); 129.6; 127.9; 126.4 (d, $^5J_{CP}$ = 1.2); 125.7 (d, $^2J_{CP}$ = 6.3); 125.1 (d, $^3J_{CP}$ = 13.8); 123.7 (d, $^4J_{CP}$ = 1.6); 119.7 (d, $^3J_{CP}$ = 13.5); 99.5 (d, $^1J_{CP}$ = 181.8); 53.3 (d, $^2J_{CP}$ = 4.7). Anal. Calcd. for $C_{12}H_{13}O_4P$: C, 57.15; H, 5.20; P, 12.28. Found: C, 57.50; H, 5.48; P, 12.18.

Dimethyl 1-hydroxy-4-phenyl-2-naphthalenephosphonate (3c)

Yield 86 %. Mp 100°C. IR ($CHCl_3$): 3500-2500, 1615, 1565, 1050, 1030. ^{1}H-NMR : δ 11.17 (d, 1H, J = 0.8); 8.50-8.43 (m, 1H); 7.89-7.80 (m, 1H); 7.79-7.50 (m, 2H); 7.50-7.34 (m, 5H); 7.22 (d, 1H, $^3J_{HP}$ = 12.9); 3.78 (d, 6H, $^3J_{HP}$ = 11.5). ^{13}C-NMR : δ 160.9 (d, $^2J_{CP}$ = 7.3); 138.9; 135.3 (d, $^4J_{CP}$ = 2.4); 132.1 (d, $^3J_{CP}$ = 13.5); 130.1; 129.3; 128.4; 127.3; 125.9 (d, $^5J_{CP}$ = 1.1); 125.8; 125.8 (d, $^2J_{CP}$ = 7.8); 125.0 (d, $^3J_{CP}$ = 13.8); 123.9 (d, $^4J_{CP}$ = 1.8); 98.7 (d, $^1J_{CP}$ = 183.0); 53.0 (d, $^2J_{CP}$ = 4.8). Anal. Calcd. for $C_{18}H_{17}O_4P$: C, 65.85; H, 5.22; P, 9.43. Found: C, 65.62; H, 5.28; P, 9.44.

Dimethyl 1-hydroxy-7-methoxy-4-(4-methoxyphenyl)-2-naphthalenephosphonate (3d)

Yield 88 %. Mp 122°C. IR ($CHCl_3$): 3500-2700, 1610, 1575, 1055, 1030. ^{1}H-NMR: δ 11.10 (s, 1H); 7.79-7.74 (m, 2H); 7.35 (d, 2H, J = 8.4); 7.23-7.16 (m, 1H); 7.07 (d, 1H, $^3J_{HP}$ = 13.0); 6.99 (d, 2H, J = 8.5); 3.95 (s, 3H); 3.86 (s, 3H); 3.79 (d, 6H, $^3J_{HP}$ = 11.0). ^{13}C-NMR: δ 159.5 (d, $^2J_{CP}$ = 7.4); 158.9; 157.8; 132.2;

131.8 (d, $^3J_{CP}$ = 13.8); 131.1; 130.8; 127.6; 126.1 (d, $^3J_{CP}$ = 14.2); 123.3 (d, $^2J_{CP}$ = 6.4); 121.4; 113.8; 102.0; 99.2 (d, $^1J_{CP}$ = 181.8); 55.4; 55.3; 53.0 (d, $^2J_{CP}$ = 4.7). Anal. Calcd. for $C_{20}H_{21}O_6P$: C, 61.86; H, 5.45; P, 7.98. Found: C, 61.87; H, 5.53; P, 8.09.

Dimethyl 1-hydroxy-7-chloro-4-(4-chlorophenyl)-2-naphthalenephosphonate (3e)

Yield 76 %. Mp 182°C. IR ($CHCl_3$): 3500-2500, 1570, 1055, 1030. ^{1}H-NMR: δ 11.18 (large, 1H); 8.44 (d, 1H, J = 2.2); 7.71 (d, 1H, J = 8.9); 7.47 (dd, 1H, J = 8.9, J = 2.2); 7.45 (d, 2H, J = 8.4); 7.35 (d, 2H, J = 8.4); 7.18 (d, 1H, $^3J_{HP}$ = 11.9); 3.80 (d, 6H, $^3J_{HP}$ = 11.4). ^{13}C-NMR: δ 160.1 (d, $^2J_{CP}$ = 7.4); 137.8; 133.7; 133.4 (d, J_{CP} = 2.4); 132.3 (d, J_{CP} = 2.1); 131.3; 130.7 (d, $^3J_{CP}$ = 13.5); 130.2; 128.7; 127.3; 126.2 (d, $^2J_{CP}$ = 6.5); 125.8 (d, $^3J_{CP}$ = 14.3); 123.2 (d, $^4J_{CP}$ = 2.0); 100.2 (d, $^1J_{CP}$ = 183.4); 53.1 (d, $^2J_{CP}$ = 4.9). Anal. Calcd. for $C_{18}H_{15}Cl_2O_4P$: C, 54.43; H, 3.81; Cl, 17.85; P, 7.80. Found: C, 53.99; H, 3.85; Cl, 17.56; P, 7.66.

Dimethyl 1-hydroxy-4-methyl-2-naphthalenephosphonate (3f)

Yield 94%. Oil. IR ($CHCl_3$): 3400-2700, 1625, 1055, 1030. ^{1}H-NMR: δ 11.68 (d, 1H, J = 1.2); 8.44 (dd, 1H, J = 8.1, J = 1.4); 7.90 (d, 1H, J = 8.1); 7.66 (ddd, 1H, J = 8.1, 6.9, 1.4); 7.56 (ddd, 1H, J = 8.1; 6.9, 1.4); 7.10 (dd, 1H, $^3J_{HP}$ = 12.7, J = 0.7); 3.78 (d, 6H, $^3J_{HP}$ = 11.5); 2.58 (s, 3H). ^{13}C-NMR: δ 160.2 (d, $^2J_{CP}$ = 7.0); 136.3 (d, $^4J_{CP}$ = 2.3); 129.1; 125.6 (d, $^4J_{CP}$ = 2.3); 125.4 (d, $^3J_{CP}$ = 13.4); 124.9 (d, $^3J_{CP}$ = 14.9); 124.6 (d, $^2J_{CP}$ = 6.4); 124.0; 123.9; 98.1 (d, $^1J_{CP}$ = 182.4); 52.8 (d, $^2J_{CP}$ = 4.6); 18.7. Anal. Calcd. for $C_{13}H_{15}O_4P$: C, 58.65; H, 5.68; P, 11.63. Found: C, 58.87; H, 5.69; P, 11.05.

Dimethyl 1-hydroxy-4-trifluoromethyl-2-naphthalenephosphonate (3g)

Yield 73 %. Oil. IR (neat): 3600-2400, 1630, 1575, 1050, 1030. ^{1}H-NMR: δ 11.62 (s, 1H); 8.48 (d, 1H, J = 7.8); 8.10 (d, 1H, J = 8.2); 7.78-7.54 (m with a doublet with $^3J_{HP}$ ~13, 3H); 3.81 (d, 6H, $^3J_{HP}$ = 11.4). ^{13}C-NMR: δ 164.6 (d, $^2J_{CP}$ = 7.7); 132.5; 130.8; 126.9; 125.4 (m); 125.4 (d, $^3J_{CP}$ = 13.2); 124.6 (q, $^1J_{CF}$ = 272.5); 124.5 (d, J_{CP} = 1.1); 124.3 (d, J_{CP} = 2.0); 118.0 (qd, $^2J_{CF}$ = 30.7, $^3J_{CP}$ = 13.8); 97.9 (d, $^1J_{CP}$ = 186.9); 53.3 (d, $^2J_{CP}$ = 4.9). Anal. Calcd. for $C_{13}H_{12}F_3O_4P$: C, 48.76; H, 3.78; F, 17.80; P, 9.67. Found: C, 49.10; H, 3.87; F, 17.62; P, 9.57.

Dimethyl 3-fluoro-1-hydroxy-2-naphthalenephosphonate (3h)

Yield 88 %. Mp 70°C. IR ($CHCl_3$): 3600-2400, 1635, 1610, 1570, 1065, 1020. ^{1}H-NMR: δ 11.92 (s, 1H); 8.34 (d, 1H, J = 8.3); 7.70-7.30 (m, 3H); 6.96 (dd, 1H, $^2J_{HF}$ = 10.8, $^4J_{HP}$ = 5.4); 3.83 (d, 6H, $^3J_{HP}$ = 11.8). ^{13}C-NMR: δ 163.4 (dd, $^3J_{CF}$ = 8.4, $^2J_{CP}$ = 4.2); 158.9 (dd, $^1J_{CF}$ = 246.7, $^2J_{CP}$ = 1.8); 136.7 (dd, $^3J_{CF}$ = 11.9, $^4J_{CP}$ = 1.0); 130.3; 126.9 (d, $^4J_{CF}$ = 5.8); 125.0 (dd, $^5J_{CF}$ = 3.6, $^4J_{CP}$ = 1.4); 124.1; 122.2 (d, $^3J_{CP}$ = 12.6); 101.9 (dd, $^2J_{CF}$ = 21.9, $^3J_{CP}$ = 6.9); 91.4 (dd, $^1J_{CP}$ = 181.1, $^2J_{CF}$ = 26.6); 53.4 (d, $^2J_{CP}$ = 5.4). Anal. Calcd. for $C_{12}H_{12}FO_4P$: C, 53.34; H, 4.48; F, 7.03; P, 11.46. Found: C, 53.93; H, 4.64; F, 6.60; P, 10.80.

Dimethyl 3-hydroxy-2-fluoranthenephosphonate (3i)

Yield 91 %. Mp 137°C. IR ($CHCl_3$): 3400-2700, 1625, 1055, 1030. ^{1}H-NMR: δ 11.50 (s, 1H); 8.22 (d, 1H, J = 8.2); 8.03 (d, 1H, J = 7.0); 7.91-7.79 (m, 2H); 7.73 (d, 1H, $^3J_{HP}$ = 12.5); 7.64 (d, 1H, J = 7.9); 7.41-7.30 (m, 2H); 3.82 (d, 6H, $^3J_{HP}$ = 11.5). ^{13}C-NMR: δ (Only 15 resonances were observed) 163.2 (d, $^2J_{CP}$ = 8.7); 138.9; 138.5 (d, $^4J_{CP}$ = 1.6); 136.7; 128.6 (d, $^3J_{CP}$ = 14.8); 127.8; 126.9; 122.9 (d, $^4J_{CP}$ = 1.8); 122.7; 122.3 (d, $^3J_{CP}$ = 15.1); 121.6; 120.9; 120.6 (d, $^2J_{CP}$ = 7.0); 100.8 (d, $^1J_{CP}$ = 180.0); 53.1 (d, $^2J_{CP}$ = 4.7). Anal. Calcd. for $C_{18}H_{15}O_4P$: C, 66.26; H, 4.63; P, 9.49. Found: C, 66.47; H, 4.84; P, 8.96.

RHODIUM(II) ACETATE CATALYSED DECOMPOSITION OF α-DIAZO-β-KETO-γ,δ-ALKENYLPHOSPHONATES (1)

A mixture of rhodium(II) acetate (40 mg, 3 % mol), diazophosphonate **1** (3 mmol) and anhydrous benzene (80 ml) was refluxed with stirring under nitrogen for 1 h (**1c**), 1.5 h (**1d,f**), 2.5 h (**1b,g**), 3 h (**1e**), 4 h (**1i**) or 5 h (**1h**) until the disappearance of compound **1** was completed as judged by TLC. The solvent was evaporated and the residue was purified by chromatography eluting with diethyl ether/pentane 80:20 (**b**), diethyl ether/pentane 67:33 (**d,h,i**), diethyl ether/pentane 60:40 (**f**) or diethyl ether/pentane 50:50 (**c,e,g**) to afford mixtures of **3b+ 5b**, **3c+ 5c**, **3e+ 5e**, **3f+ 5f**, **3h+ 5h** or pure **3d**, **3i** or **5g**; the **3**:**5** ratios were determined by ^{1}H-NMR (for yields and **3**:**5** ratios, see table 1). Pure compounds **5b,f** were obtained after a second purification by chromatography.

Dimethyl 2-hydroxy-1-naphthalenephosphonate (5b)

Isolated yield 53%. Mp 66°C. IR ($CHCl_3$): 3600-2500, 1615, 1595, 1045, 1020. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 11.75 (d, 1H, J = 1.3); 8.02 (brd, 1H, J = 8.7); 7.92 (pd, 1H, J = 9.1); 7.76 (dt, 1H, J = 8.0, J = 1.7); 7.52 (m, 1H); 7.36 (m, 1H); 7.12 (dd, 1H, J = 9.0, $^4J_{HP}$ = 5.8); 3.72 (d, 6H, $^3J_{HP}$ = 11.8). ^{13}C-NMR (75 MHz, CD_2Cl_2): δ 165.3 (d, $^2J_{CP}$ = 6.8); 136.9 (d, $^4J_{CP}$ = 2.7); 133.7 (d, $^2J_{CP}$ = 7.8); 129.2 (d, $^4J_{CP}$ = 1.5); 128.7 (d, $^3J_{CP}$ = 11.8); 128.5; 124.8 (d, $^3J_{CP}$ = 4.6); 124.1; 119.9 (d, $^3J_{CP}$ = 13.6); 97.5 (d, $^1J_{CP}$ = 176.6); 53.0 (d, $^2J_{CP}$ = 4.4). Anal. Calcd. for $C_{12}H_{13}O_4P$: C, 57.15; H, 5.20; P, 12.28. Found: C, 56.75; H, 5.30; P, 11.91.

Dimethyl 2-hydroxy-4-phenyl-1-naphthalenephosphonate (5c):

A pure sample (yield ~ 10%) was separated for spectroscopic characterization. Mp 112-114°C. IR ($CHCl_3$): 3500-2500, 1610, 1595, 1570, 1050, 1020. ^{1}H-NMR : δ 11.79 (d, 1H, J = 1.3); 8.13 (brd, 1H, J = 8.5); 7.73 (brd, 1H, J = 8.3); 7.60-7.45 (m, 6H); 7.32 (ddd, 1H, J = 8.3, 7.2, 1.0); 7.14 (d, 1H, $^4J_{HP}$ = 5.9); 3.80 (d, 6H, $^3J_{HP}$ = 12.0). ^{13}C-NMR : δ 164.2 (d, $^2J_{CP}$ = 6.8); 148.8 (d, $^4J_{CP}$ = 2.8); 139.3 (d, $^5J_{CP}$ = 0.7); 134.0 (d, $^2J_{CP}$ = 8.1); 129.5; 128.4; 128.1; 127.9 (d, $^3J_{CP}$ = 10.6); 127.2; 127.1 (d, $^3J_{CP}$ = 10.6); 124.6 (d, $^3J_{CP}$ = 4.8); 123.7; 120.4 (d, $^3J_{CP}$ = 13.7); 96.4 (d, $^1J_{CP}$ = 177.8); 52.8 (d, $^2J_{CP}$ = 4.3).

Dimethyl 2-hydroxy-7-chloro-4-(4'-chlorophenyl)-1-naphthalenephosphonate (5e)

^{1}H-NMR: δ (partial data obtained from the spectrum of the 92:8 mixture of **5d/7d**) 11.81 (s, 1H); 8.12 (d, H-8, J ~ 8); 7.06 (d, H-3, $^4J_{HP}$ = 5.8).

Dimethyl 2-hydroxy-4-methyl-1-naphthalenephosphonate (5f)

Isolated yield 48%. Oil. IR (neat): 3600-2500, 1615, 1605, 1595, 1045, 1020. ^{1}H-NMR: δ 11.59 (d, 1H, J = 1.2); 7.96 (dd, 1H, J = 8.0); 7.84 (dd, 1H, J = 8.2, 1.7); 7.44 (ddd, 1H, J = 8.2, 6.9, 1.2); 7.31 (ptd, 1H, J = 6.9, 1.2); 6.95 (d, 1H, $^4J_{HP}$ = 5.9); 3.65 (d, 6H, $^3J_{HP}$ = 11.8); 2.58 (s, 3H). ^{13}C-NMR: δ 164.7 (d, $^2J_{CP}$ = 6.7); 144.1 (d, $^4J_{CP}$ = 2.7); 133.5 (d, $^2J_{CP}$ = 8.2); 128.1 (d, $^3J_{CP}$ = 11.8); 128.0; 124.9 (d, $^3J_{CP}$ = 5.2); 124.8; 123.7; 120.3 (d, $^3J_{CP}$ = 13.6); 95.0 (d, $^1J_{CP}$ = 178.8); 52.7 (d, $^2J_{CP}$ = 4.3); 20.0. Anal. Calcd. for $C_{13}H_{15}O_4P$: C, 58.65; H, 5.68; P, 11.63. Found: C, 58.69; H, 5.28; P, 11.51.

Dimethyl 2-hydroxy-4-trifluoromethyl-1-naphthalenephosphonate (5g)

Yield 83 %. Oil. IR (neat): 3600-2500, 1620, 1590, 1050, 1030. ^{1}H-NMR: δ 11.87 (s, 1H); 8.14-8.10 (m, 2H); 7.64-7.44 (m, 3H); 3.79 (d, 6H, $^3J_{HP}$ = 12.8). ^{13}C-NMR: δ 163.2 (d, $^2J_{CP}$ = 6.9); 134.4 (d, $^2J_{CP}$ = 8.0); 133.6 (qd, $^2J_{CF}$ = 30.6, $^4J_{CP}$ = 3.0); 128.9; 125.3; 125.2 (d, $^2J_{CP}$ = 4.5); 125.1; 123.5 (d, $^3J_{CP}$ = 11.8); 119.4 (dq, $^3J_{CP}$ = 14.0, $^3J_{CF}$ = 6.1); 118.2 (q, $^1J_{CF}$ = 274.7); 101.6 (d, $^1J_{CP}$ = 175.9); 53.1 (d, $^2J_{CP}$ = 4.5). Anal. Calcd. for $C_{13}H_{12}F_3O_4P$: C, 48.76; H, 3.78; F, 17.80; P, 9.67. Found: C, 48.89; H, 3.86; F, 17.21; P, 9.70.

Dimethyl 3-fluoro-2-hydroxy-1-naphthalenephosphonate (5h)

Isolated yield 40 %. Mp 104-106°C. IR ($CHCl_3$): 3600-2400, 1630,1610, 1580, 1055, 1015. ^{1}H-NMR: δ 12.02 (s, 1H); 8.00 (d, 1H, J = 8.4); 7.74-7.37 (m, 4H); 3.78 (d, 6H, $^3J_{HP}$ = 11.8). ^{13}C-NMR: δ 155.6 (dd, $^2J_{CF}$ = 14.9, $^2J_{CP}$ = 7.7); 151.5 (dd, $^1J_{CF}$ = 252.2, $^3J_{CP}$ = 21.6); 130.0 (d, $^2J_{CP}$ = 6.9); 128.4 (dd, $^4J_{CF}$ = 5.3, $^4J_{CP}$ = 2.0); 127.7 (dd, $^3J_{CP}$ = 14.3, $^3J_{CF}$ = 7.5); 127.6 (d, $^5J_{CF}$ = 2.5); 124.8; 124.5 (dd, $^3J_{CP}$ = 4.5, $^5J_{CF}$ = 1.9); 118.7 (dd, $^2J_{CF}$ = 17.2, $^4J_{CP}$ = 2.7); 100.2 (dd, $^1J_{CP}$ = 176.4, $^3J_{CF}$ = 1.8); 53.2 (d, $^2J_{CP}$ = 4.5). Anal. Calcd. for $C_{12}H_{12}FO_4P$: C, 53.34; H, 4.48; F, 7.03; P, 11.46. Found: C, 53.53; H, 4.39; F, 5.89* P, 11.04. * No better analysis could be obtained.

SYNTHESIS OF ETHYL 2-DIAZO-3-OXOPENT-4-ENOATES (9)

A solution of ester **7** (9.3 mmol) in a 3 M methanolic solution of potassium hydroxide (15 ml, 44.6 mmol) was refluxed for 1 h (**c**) or allowed to stay at room temperature for 30 mn (**g**). The solution was acidified to pH 5 with Dowex W50X8 H^+ and filtrated. The solvent was evaporated under vacuum. Anhydrous toluene (30 ml) was added and then evaporated under reduced pressure. Anhydrous toluene (50 ml) was added and the suspension was treated with freshly distilled oxalyl chloride (5 ml, 55.8 mmol) at room temperature. The mixture was refluxed for 3 h. The solvent was evaporated under reduced pressure, anhydrous toluene (50 ml) was added and evaporated; this operation was repeated once again to remove oxalyl chloride completely and afforded a crude acid chloride. A mixture of this crude acid chloride and ethyl diazoacetate (5.3 g, 46.4 mmol) under nitrogen was kept at room temperature for 10 days with occasional shaking. Volatile materials were removed under 1 Torr vacuum at room temperature. The crude residue was purified by chromatography, eluting with diethyl ether/pentane 5:95 .

Ethyl 2-diazo-5,5-diphenyl-3-oxopent-4-enaote (9c)

Yield: 65%. Oil. IR (neat): 2130, 1700, 1640. ^{1}H-NMR: δ 7.54 (s, 1H); 7.41-7.21 (m, 10H); 4.32 (q, 2H, J = 7.1); 1.34 (t, 3H, J = 7.1). Anal. Calcd. for $C_{19}H_{16}N_2O_3$: C, 71.24; H, 5.03; N, 8.74. Found: C, 70.95; H, 5.28; N, 8.51.

Ethyl (E)-2-diazo-3-oxo-5-phenyl-5-trifluoromethylpent-4-enaote (9g)

Yield: 54%. Oil. IR (neat): 2140, 1710, 1640. ^{1}H-NMR : δ 7.74-7.25 (m, 6H); 4.33 (q, 2H, J = 7.1); 1.35 (t, 3H, J = 7.1). ^{13}C-NMR : δ 181.4; 160.7; 139.4 (q, $^2J_{CF}$ = 30.8); 131.1; 129.4; 128.9; 128.7 (q, $^3J_{CF}$ = 5.2); 128.3; 122.7 (q, $^1J_{CF}$ = 274.7); 78.5; 62.1; 14.2. LRMS (EI) m/z (rel int) 284 (4), 239 (24), 238 (100), 212 (42), 211 (88), 210 (48), 199 (43), 183 (28), 182 (35). HRMS (EI) m/z Calcd. for $C_{14}H_{11}F_3O_3$ (M^+- N_2) 284.0660, found 284.0660.

THERMOLYSIS OF ETHYL 2-DIAZO-3-OXOPENT-4-ENOATES (9)

A solution of diazo ester **9** (1.5 mmol) in anhydrous toluene (20 ml) was refluxed with stirring under nitrogen for 3.5 h (**c**) or 15 h (**g**). The solvent was then evaporated in vacuo and the residue was purified by chromatography eluting with diethyl ether/pentane 5:95. The diazo **9c** gave pure **11c**; the diazo **9g** gave a 13:78:9 mixture of **10g, 11g** and **12g** in a total yield of 73 % (see the following paragraph for the spectral data of **10g** and **12g**)

Ethyl 1-hydroxy-4-phenyl-2-naphthalenecarboxylate (11c)

Yield 68 %. Mp 118-120°C. IR ($CHCl_3$): 3400-2600, 1665, 1630, 1580. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 12.09 (s, 1H); 8.52-8,48 (m, 1H); 7.82-7.79 (m, 1H); 7.74 (s, 1H); 7.55-7.51 (m, 7H); 4.43 (q, 2H, J = 7.1); 1.42

(t, 3H, J = 7.1). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 171.1; 160.4; 140.2; 135.5; 131.2; 130.2; 129.5; 128.4; 127.2; 125.9; 125.7; 125.0; 124.9; 124.2; 105.4; 61.5; 14.3. Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.73; H, 5.78.

Ethyl 1-hydroxy-4-trifluoromethyl-2-naphthalenecarboxylate (11g)

Isolated yield 56 %. Mp 78-80°C. IR ($CHCl_3$): 3400-2500, 1660, 1635, 1580. ^{1}H-NMR : δ 12.45 (s, 1H); 8.50 (dd, 1H, J = 8.1, 1.4); 8.20 (s, 1H); 8.10 (pd, 1H, J = 8.4); 7.74 (ddd, 1H, J = 8.4, 7.0, 1.4); 7.61 (m, 1H); 4.50 (q, 2H, J = 7.1); 1.48 (t, 3H, J = 7.1). ^{13}C-NMR : δ 170.4; 163.7; 132.4; 130.8; 126.5; 125.3; 124.6 (q, $^1J_{CF}$ = 272.4); 124.5; 124.3 (q, $^3J_{CF}$ = 6.4); 124.2 (q, $^4J_{CF}$ = 2.6); 117.0 (q, $^2J_{CF}$ = 30.9); 103.9; 61.9; 14.1. Anal. Calcd. for $C_{14}H_{11}F_3O_3$: C, 59.16; H, 3.90; F, 20.05. Found: C, 59.11; H, 4.02; F, 19.84.

RHODIUM(II) ACETATE CATALYSED DECOMPOSITION OF ETHYL 2-DIAZO-3-OXOPENT-4-ENOATES (9)

A mixture of rhodium(II) acetate (20 mg, 3 % mol), diazo ester **9** (1.5 mmol) and anhydrous fluorobenzene (20 ml) was refluxed with stirring under nitrogen for 1 h (**c**) or 2 h (**g**). The solvent was evaporated and the residue was purified by chromatography eluting with diethyl ether/pentane 5:95. The diazo ester **9c** gave pure **11c**; the sample of **11c** for X-ray Analysis was obtained by recrystallisation from ethyl acetate. The diazo ester **9g** gave a 74:26 mixture of **10g** and **12g**.

Ethyl 1-hydroxy-4-phenyl-2-naphthalenecarboxylate (11c)

Yield 77 %. The spectral data were identical with those of the product obtained by thermolysis (*vide supra*). Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.53; H, 5.75.

Ethyl 2-hydroxy-4-trifluoromethyl-1-naphthalenecarboxylate (10g)

Isolated yield 57 %. Oil. IR ($CHCl_3$): 3500-2500, 1655, 1620, 1585. ^{1}H-NMR : δ 12.04 (s, 1H); 8.84 (pd, 1H, J = 8.2); 8.14-8.06 (s, 1H); 7.66-7.56 (m, 2H with a singlet at 7.58); 7.48 (ddd, 1H, J = 8.4, 6.9, 1.3); 4.62 (q, 2H, J = 7.1); 1.55 (t, 3H, J = 7.1). ^{13}C-NMR : δ 171.4; 161.8; 133.1 (q, $^2J_{CF}$ = 30.5); 132.8; 128.8; 125.8; 125.0 (2C); 125.0 (q, $^3J_{CF}$ = 2.8); 123.6 (q, $^1J_{CF}$ = 274.6); 119.1 (q, $^3J_{CF}$ = 6.2); 108.4; 62.7; 14.3. Anal. Calcd. for $C_{14}H_{11}F_3O_3$: C, 59.16; H, 3.90; F, 20.05. Found: C, 58.87; H, 3.78; F, 19.47.

Ethyl 1,8a-dihydro-1-oxo-3-trifluoromethyl-8a-azulenecarboxylate (12g)

Isolated yield 13 %. Oil. IR (neat): 1745, 1715, 1590. ^{1}H-NMR : δ 6.60-6.33 (m, 5H); 5.86 (pd, 1H, J = 8.5); 4.00 (q, 2H, J = 7.1); 1.07 (t, 3H, J = 7.1). ^{13}C-NMR : δ 198.3; 165.1; 156.6 (q, $^2J_{CF}$ = 34.8); 133.9; 130.7 (q, $^3J_{CF}$ = 0.6); 129.5 (q, $^3J_{CF}$ = 3.5); 129.2; 128.6; 128.2; 123.7; 121.2 (q, $^1J_{CF}$ = 273.6); 63.6; 62.2; 13.7. Anal. Calcd. for $C_{14}H_{11}F_3O_3$: C, 59.16; H, 3.90; F, 20.05. Found: C, 58.87; H, 3.96; F, 20.08.

Ethyl 2-hydroxy-4-phenyl-1-naphthalenecarboxylate (10c)

About 2 mg of a sample of 95 % pure **10c** was isolated from the rhodium(II) acetate decomposition of **1a** in dichloromethane at room temperature (15 h) allowing a proton NMR spectrum to be obtained.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 12.22 (s, 1H); 8.81 (d 1H, J = 8.7); 7.70 (dd, 1H, J = 8.3, 1.3); 7.48 (ddd, 1H, J = 8.7, 6.8, 1.5); 7.47-7.35 (m, 5H); 7.22 (ddd, 1H, J = 8.3, 6.8, 1.3); 7.06 (s, 1H); 4.54 (q, 2H, J = 7.2); 1.49 (t, 3H, J = 7.2).

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28. Chemical shifts and coupling constants reported in Tables 2 and 3 were attributed as follows. The dimethyl hydroxynaphthalenephosphonates **3b** and **5b** served as reference compounds. Their H-3 and H-4 resonances were established by proton decoupling experiments. Attribution of the C-1 and C-2 resonances was evident because these carbons are bonded to the hydroxy and dimethylphosphono groups. *CH* COSY spectra permitted us to establish the H-3/C-3 and H-4/C-4 connectivities. Attribution of C-4a and C-8a resonances was based on the expected shielding effect produced by a hydroxy group on *ortho* and *para* carbons. All attributed resonances were consistent with the H-P and C-P coupling constants values observed in the NMR spectra. Chemical shifts and coupling constants of other compounds **3** and **5** were deduced on the basis of their spectral similarities with **3b** and **5b**.
29. We observed in the case of compounds **3** (except for **3h**) $^{1}J_{CP}$ = 179.8-186.9 Hz for C-2, $^{2}J_{CP}$ = 6.3-8.7 Hz for C-1 and C-3 , $^{3}J_{CP}$ = 13.2-15.1 Hz for C-4 (or C-10b) and C-8a and $^{4}J_{CP}$ = 0-2.4 Hz for C-4a (or C-10c) and in the case of compounds **5** $^{1}J_{CP}$ = 175.9-178.8 Hz for C-1, $^{2}J_{CP}$ = 6.7-8.2 Hz for C-2 and C-8a, $^{3}J_{CP}$ = 11.8-21.6 Hz for C-3 and C-4a and $^{4}J_{CP}$ = 2.7-3.0 Hz for C-4.
30. Pouchert, C. J.; Behnke, J. *The Aldrich Library of ^{13}C and ^{1}H FT NMR spectra*, 1993, Edition I, *vol. 2*, spectra 1169 B (1-hydroxy-2-naphthoic acid) and 1169 C (2-hydroxy-1-naphthoic acid).
31. Crystal data: $C_9H_{16}O_3$, M = 292.3, monoclinic, space group $P2_1/c$, a = 5.881(1), b = 21.197(3), c = 13.740(3) Å, V = 1510.4(5)Å^3, Z = 4, D_C = 1.286 g.cm^{-3}. Data were collected on a Nonius CAD4 diffractometer. Of 3010 unique reflections measured ($2\theta_{max}$ = 146°, μ(CuKα) = 7.1 cm^{-1}), 2491 had I > 3σ(I) and were used for all calculations with the Structure Determination Package (Frenz, B.A. and Associates Inc., "SDP Structure Determination Package", College Station, Texas, USA, 1982). All the hydrogen atoms were located from ΔF syntheses and their coordinates were refined. The final refinement gave R = 0.058 and R_W = 0.083.
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