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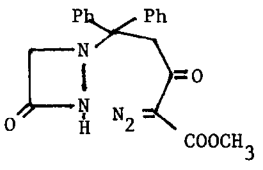
RHODIUM(II) ACETATE-CATALYZED REACTION OF ETHYL 2-DIAZO-3-OXOPENT-4-ENOATES: SIMPLE ROUTES TO 4-ARYL-2-HYDROXY-1-NAPHTHOATES AND β,γ-UNSATURATED ESTERS. THE DIANION OF ETHYL 4-(DIETHYLPHOSPHONO)ACETOACETATE AS A PROPIONATE HOMOENOLATE EQUIVALENT

Edward C. Taylor* and Huw M. L. Davies
Department of Chemistry, Princeton University
Princeton, New Jersey 08544

ABSTRACT: Rhodium(II) acetate-catalyzed decomposition of ethyl 2-diazo-3-oxopent-4-enoates results in the formation of either 4-aryl-2-hydroxy-naphthoates or β,γ-unsaturated esters. In the latter transformation, the dianion of 4-(diethylphosphono)acetoacetate functions as a propionate homoenolate equivalent.

In the course of our investigations of diazetidinone chemistry, aimed at the preparation of highly strained aza analogs of the β-lactam antibiotics, we attempted an acid catalyzed cyclization of the α-diazoketone 1.[1] However, the only product obtained (72% yield) upon treatment of 1 with TFA was 2, formed by elimination of diazetidinone (an excellent if somewhat esoteric leaving group). Subsequent investigation of 2 revealed that it was smoothly converted in 99% yield to methyl 4-phenyl-2-hydroxy-1-naphthoate upon treatment with rhodium(II) acetate in benzene. The extraordinary efficiency of this transformation of 2 to 3 led us to develop a general synthesis of compounds of type 2 and to investigate their reactions with rhodium(II) acetate. Our results are described herein.



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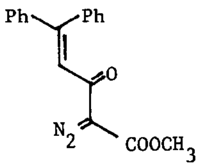

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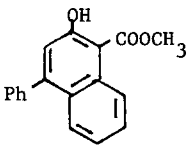
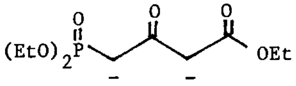


3

It has recently been reported that the dianion of ethyl 4-(diethylphosphono)acetoacetate (4) condenses both with aldehydes and with ketones in high yield.[2] By using this procedure we have prepared a series of ethyl 3-oxopent-4-enoates (5: see Table 1). Reasonable yields of condensation products between 4 and substituted benzophenones could only be obtained using the dipotassium salt of 4 rather than the disodium salt. Condensation of 4 with aldehydes gave only the E isomers of 5.[2] The conversion of 5 to the diazoketones 6 was most conveniently effected by diazo transfer utilizing p-(n-dodecyl)benzenesulfonyl azide.[3]



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Rhodium(II) acetate-catalyzed decomposition of 6a-c was carried out by adding a solution of 6 in fluorobenzene to a stirred suspension of rhodium(II) acetate in refluxing fluorobenzene, followed by heating the mixture under reflux for 1 h. The 4-aryl-2-hydroxy-1-naphthoates 7 were isolated in excellent yield after chromatography on silica gel (see Table 1). The formation of naphthalenes rather than cycloheptatrienes[4] is presumably a consequence of the lower energy pathway leading to aromatization.

The α-diazo esters 6d-g, derived from the condensation of aldehydes with 4, would appear to have the wrong geometry to undergo rhodium(II) acetate-catalyzed decomposition to give naphthalenes, although double bond isomerizations in the presence of transition metals are known.[5] However, heating 6d

Scheme 1

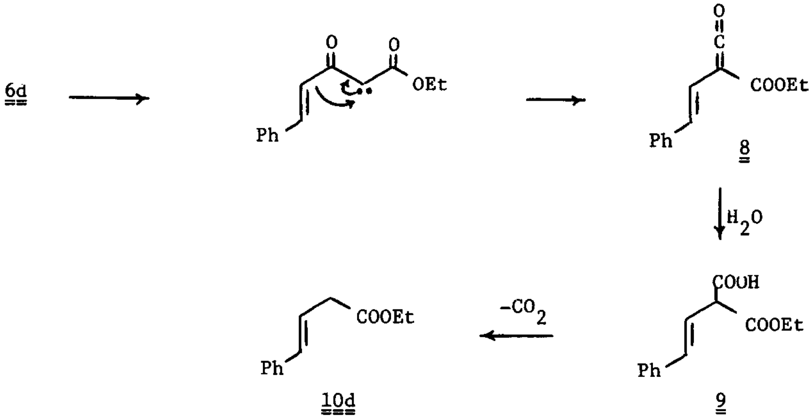
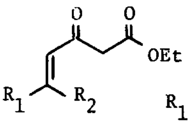
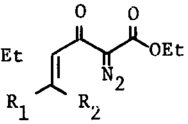
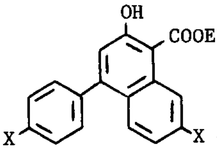
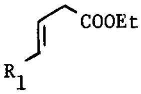


Table 1. Synthesis and Rhodium(II) Acetate Decompositon of Alkyl 2-diazo-3-oxopent-4-enoates.

	R_1	R_2	 5 Yield,%	 6 Yield,%	 7 Yield,%	 10 Yield,%
a	C_6H_5	C_6H_5	74	94	90(X=H)	
b	$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	65	84	76(X=OCH_3)	
c	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	74	67	97(X=Cl)	
d	C_6H_5	H	72	67		67
e	$4\text{-}CH_3OC_6H_4$	H	72	71		56
f	$4\text{-}ClC_6H_4$	H	71	69		52
g	$C_6H_5CH=CH$	H	15	71		55

with rhodium(II) acetate in fluorobenzene for 5 min resulted in the formation of the malonic acid half ester 9, which must have been formed by a Wolff rearrangement[6] to the ketene 8 which was then hydrated under the reaction conditions (see Scheme 1). Deliberate addition of water to the above reaction mixture followed by continued heating for 12 h in fact led to the formation of the β,γ-unsaturated ester 10d in 67% yield. In analogous fashion, the α-diazo esters 6e-g were smoothly transformed into the unsaturated esters 10e-g under the same reaction conditions. The transformation of aryl aldehydes via 5 and 6 to 10 represents the equivalent of an aldol condensation with the beta anion of ethyl propionate; the dianion 4 can thus be considered as a propionate homoenolate equivalent.[7]

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