CHEMISTRY LETTERS, pp. 713-714, 1973. Published by the Chemical Society of Japan

SIMPLE SYNTHESIS OF JASMONES
THE METAL ION PROMOTED REACTIONS OF 8-ACYLOXYQUINOLINE. II

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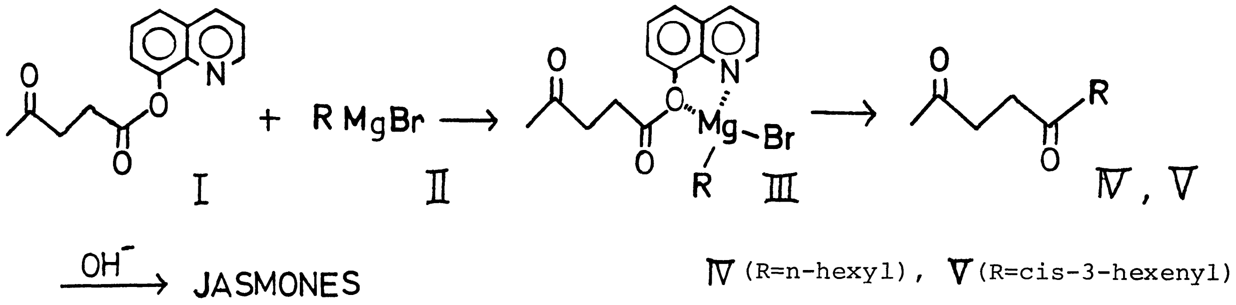
The known diketones, undecane-2,5-dione and cis-undec-8-ene-2,5-dione, are obtained by the reactions of 8-levulinyloxyquinoline with n-hexyl- and cis-3-hexenylmagnesium bromide, respectively, and converted to jasmones by base-catalyzed cyclization.

A number of synthetic routes of cis-jasmone, involving cyclization of cis-undec-8-ene-2,5-dione, were reported in recent years.[1~8] Now, as an application of the ketone synthesis by the use of 8-acyloxyquinoline,[9] we have carried out simple synthesis of jasmones, indicated in the following equation.



In our previous paper,[9] the rigid reaction matrix of 8-acyloxyquinoline complex with magnesium atom of Grignard reagent, for example III, has been considered to be a match-maker for the reaction of the activated acyl group with the nucleophilic organic group of the organometallic reagent. Therefore, the regiospecific reaction between the ester carbonyl of I and the Grignard reagent II shown in the above scheme seems to be possible even in the presence of the reactive γ-carbonyl group, providing a new synthetic design for 1,4-diketone.

We examined a reaction of I in 1,2-dichloroethane with equimolar amount of n-hexylmagnesium bromide in ether at 0°C by reverse addition, but the desired undecane-2,5-dione, IV, was obtained in only 15% yield and γ-n-hexyl-γ-methylbutyrolactone in 10%, which was formed by the attack of the Grignard reagent on γ-carbonyl of I.

Addition of 0.25 molar amount of $SiCl_4$ to the solution of I was found to be effective for the increase of yield of the diketone. In Table I, the yields of products at three different reaction temperatures are listed.

Table I. The reaction of I with n-hexylmagnesium bromide

solvent	addendum	temperature(°C)	diketone,IV,%	lactone %
dichloroethane	$SiCl_4$	-15~-20	15	3
dichloroethane	$SiCl_4$	-40	30	6
dichloromethane	$SiCl_4$	-90	42	9
dichloromethane	(without $SiCl_4$)	-90	29	12

Furthermore, in the reaction of I with cis-3-hexenylmagnesium bromide in dichloromethane, it was observed that 0.25 molar amount of PBr_3 gives a considerable effect to the formation of the diketone V as shown in Table II.

Table II. The reaction of I with cis-3-hexenylmagnesium bromide

solvent	addendum	temperature(°C)	diketone,V,%	lactone %
dichloromethane	$SiCl_4$	-78	38	11
dichloromethane	PBr_3	-78	28	trace

Base-catalized cyclization of the diketones, IV and V, gave dihydro- and cis-jasmone, respectively,[10] and they were identified by comparison (IR, NMR, UV, GLC, odor) with the authentic samples.

Finally, we report that a trace amount of PBr_3 is effective as an initiator for the preparation of Grignard reagents.

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(Received May 7, 1973)