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THE PHOTOREACTION OF AMINES OR ENAMINES WITH METAL COMPLEXES OF β-DIKETONES

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The irradiation of amines or enamines with metal complexes of β-diketones in acetonitrile induced a coupling reaction to produce dihydrofuran derivatives.

In the course of our studies on the metal-catalyzed organic photoreactions, we proposed an electron transfer among ligands of the metal ions as a key process for the reaction (long-range electron transfer).[1)] Since amines are known to function as an efficient electron donor, we examined the photoreaction of aliphatic tertiary amines with some metal complexes of β-diketones, and found a novel type of coupling reaction between amines and β-diketones.

When a solution of tris(2,4-pentanedionato)cobalt(III) ($Co(acac)_3$) (2.50 mmol) and tri-n-propylamine (1a, 2.50 mmol) in acetonitrile (100 ml) was irradiated in a quartz tube under nitrogen atmosphere with a high pressure mercury lamp for 14 h, a dihydrofuran derivative 2a was obtained as a single product as well as the starting amine. The structure 2a was assigned from the following data. Mass spectrum showed a molecular ion at m/e 239. ^{1}H-NMR spectrum showed a doublet at δ 4.66 (J = 4.6 Hz, C5 - $\underline{H}$) and a doublet at δ 1.10 (J = 6.5 Hz, C4 - $C\underline{H}_3$). In view of the coupling constant (4.6 Hz) of C5 - $\underline{H}$, we assigned trans structure for the dihydrofuran. ^{13}C-NMR spectrum showed a doublet at δ 106.4 of $\underline{C}5$. Although tri-n-butylamine also underwent the same type reaction with some metal complexes of β-diketones as shown in the Table 1, N-alkyl derivatives of cyclic amines, such as piperidine, pyrrolidine, or morpholine, did not afford any amount of the dihydrofuran.

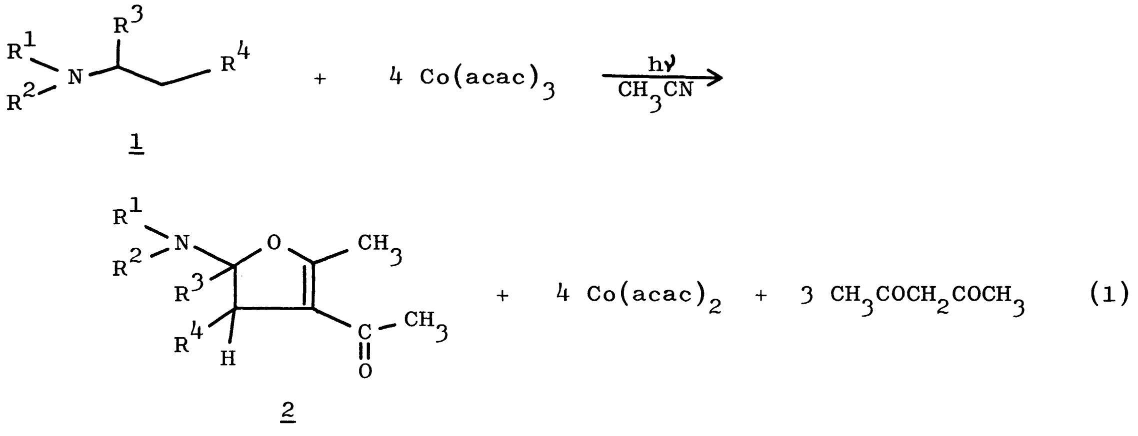
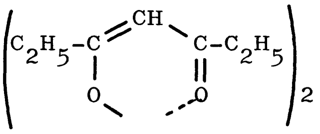


Table 1. Photoreaction of Amines with Metal Complexes of β-Diketones

Entry	Amine				Metal complex	Mol ratio (amine/metal)	Yield (%) of 2[a]
	R^1	R^2	R^3	R^4			
a	n-Pr	n-Pr	H	Me	$Co(acac)_3$	1/1	42
b	n-Bu	n-Bu	H	Et	"	1/1	61
c	"				"	1/2	75
d	"				"	1/4	57
e	"				$Cu(acac)_2$	1/1	66
f	"				$Cu(dpm)_2$[b]	1/1	74[c]
g	"				$Mn(acac)_3$	1/1	46

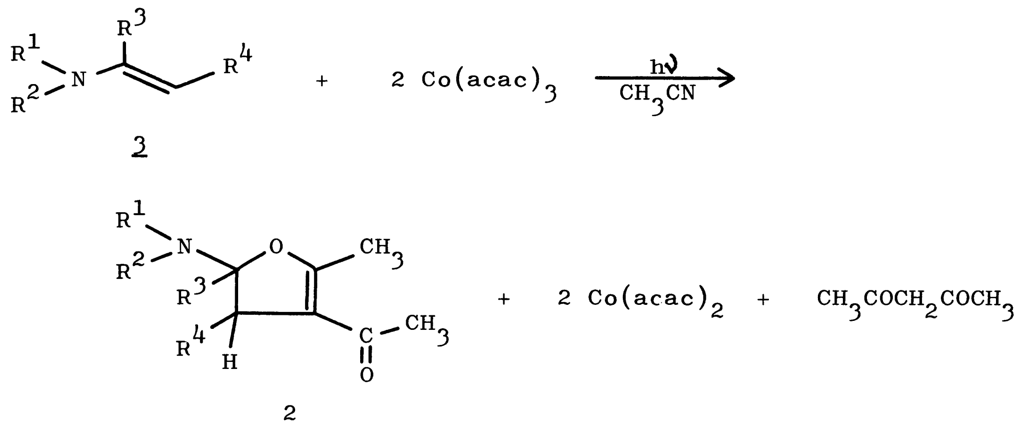
[a] Based on the metal compounds.

[b] Cu



[c] Product: 2-ethyl-3-propanoyl-4-ethyl-5-(N,N-dibutylamino)-4,5-dihydrofuran.

Both the metal complexes and light energy were requisite for the present reaction, because neither the irradiation of the amine and 2,4-pentanedione in acetonitrile in the absence of the metal complexes nor heating the amine and $Co(acac)_3$ in acetonitrile without irradiation gave the dihydrofuran derivatives. Although the UV irradiation of $Co(acac)_3$ in ether has been reported to produce biacetyl and acetic acid,[2)] no such products were identified in the present reaction. The UV absorption spectrum of $Co(acac)_3$ was not affected by the addition of tri-n-butylamine, indicating no complex formation between these species in the ground state.



(2)

Table 2. Photoreaction of Enamines with $Co(acac)_3$

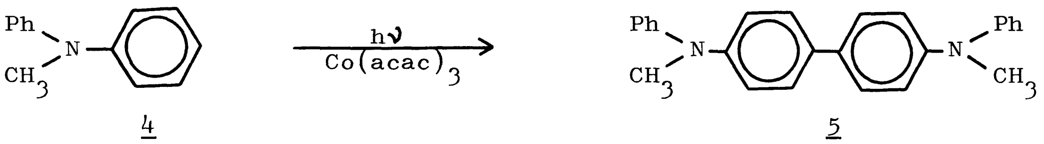
Entry	Enamine				Mol ratio (enamine/metal)	Yield (%) of 2[a]
	R^1	R^2	R^3	R^4		
a	n-Pr	n-Pr	H	n-Pr	1/2	56
b	n-Pr	n-Pr	H	Et	1/2	63
c	Et	Et	H	n-Pr	1/2	44
d	Et	Et	H	Et	1/1	58
e	Et	Et	H	Me	1/1	31
f	n-Bu	n-Bu	H	Et	1/1	78
g		"			1/2	62
h		"			1/3	34
i	$-(CH_2)_5-$		H	Me	1/1	33
j	$-(CH_2)_5-$		$-(CH_2)_4-$		1/2	30

a) Based on the metal compound.

Referring to the molecular formulae of the starting materials and the products, four-electron oxidation is speculated for the production of each molecule of the product, and thus we formulated the stoichiometric equation as shown in Eq. 1. The observation that the use of the amine in excess of that required from the equation (a quarter to the metal) did not change the cobalt-based yield of the product would be a support for the arguments (entries b and c *vs*. d).

The present reaction has a characteristic in that both α and β-positions of the amines are involved in the reaction. Assuming an enamine 3 as an intermediate in this reaction, some enamines were subjected to this coupling reaction in place of the amines. As expected, the same type of products was obtained, and the results are summarized in the Table 2. In contrast with the reactions of the amines, two equivalents of the metal compound are sufficient for the effective conversion of the enamine to the product (Table 2, entries f, g, and h), suggesting two-electron oxidation (Eq. 2). It should be noted that only the alkenyl moiety of the substrates was brought into reaction, although no significant difference in the reaction rate was observed between amines and enamines. The enhanced reactivity of the unsaturated group, however, was demonstrated by the findings that N-propenylpiperidine afforded the corresponding product in 33% yield (Table 2, entry i), in contrast to the inertness of its saturated analogue, N-propylpiperidine. N-Propylpyrrolidine neither suffered the reaction.

The progress of the reaction was accompanied by the color change from green (Co(III)) to violet (Co(II)). Evidently an electron transfer from the nitrogen compound to the metal ion to produce an aminium radical might be responsible for the reaction. Since the use of N-methyldiphenylamine 4 as an amine in the present reaction produced a dimer 5 in 70% yield, the intervention of the aminium radical is evident in view of the report$^{3)}$ that the anodic oxidation of aromatic amine induces a one-electron transfer producing the aminium radical, which affords the benzidine derivatives.



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References

1) A. Kohda, K. Nagayoshi, K. Maemoto, and T. Sato, J. Org. Chem., 48, 425 (1983); and references cited therein.

2) N. Filipescu and H. Way, Inorg. Chem., 8, 1863 (1969).

3) E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, J. Am. Chem. Soc., 88, 3498 (1966).

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