

A DUAL MECHANISTIC PATHWAY IN THE ALKYLATION OF PENTANE-2,4-DIONE THROUGH ITS Co(II) COMPLEX

J. Marquet,* M. Moreno-Mañas, P. Pacheco and A. Vallribera

Departamento de Química. Universidad Autónoma de Barcelona. Bellaterra. 08193-Barcelona. Spain.

Summary.- A mechanistic study on the alkylation of pentane-2,4-dione through its Co(II) complex has shown that a non radical chain mechanism initiated by an electron transfer step induced by Co(II) operates under certain experimental conditions.

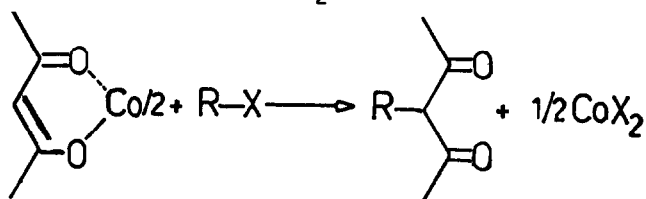
The α -alkylation of β -dicarbonyl compounds is an important carbon-carbon bond forming reaction.¹ The β -dicarbonyl compound is converted into the enolate anion which undergoes S_N2 reactions with appropriate alkyl halides or tosylates. We have previously reported that alkylations of β -dicarbonyl compounds by activation through their cobalt(II) complexes offer clear advantages over the classical methods for S_N1 active halides^{2,3} and others such as 1-bromoadamantane.^{3,4} These reactions do not show any sensitivity to the presence of radical scavengers and their general features and the halides involved suggest an ionic pathway (carbenium ion) with activation by the cobalt species as Lewis acids.³

We wish to report here the improvement of the original method by the elicitation of an alternative radical mechanism under certain experimental conditions as well as some preliminary mechanistic studies on this new reaction.

Preparative results of reactions between cobalt(II) bis(pentano-2,4-dionato) ($\text{Co}(\text{acac})_2$) and several benzyl and allyl halides are reported in Table I. Reactions were carried out by dissolving the reactants in chloroform and evaporating the solvent leaving the mixture at 120° in an open round-bottomed flask. This procedure produces very fast reactions (from 2 minutes for entry 5 to 4 hours for entry 7). Some halides unreactive under the conditions previously reported gave now good condensation yields in reasonable reaction times (e.g. 4-nitrobenzyl bromide, entry 1). It is clear that we are dealing with a new process interesting from the synthetic and mechanistic points of view. Therefore, we decided to carry out a preliminary mechanistic study.

The reactions between 1-bromo-1-phenylethane and $\text{Co}(\text{acac})_2$ in chloroform in a sealed vessel at 80°C were selected for the mechanistic studies. Figure 1 shows the reaction product formation with the time at different reactant concentrations. The less concentrated reaction shows an evolution that fits with our previously reported reactions which require times longer than 12h to be completed.³ However, in more concentrated solutions a second very fast process appears showing an induction period dependent on the concentration. Product analysis indicated the production of small amounts of *meso* and *d,l*-2,3-diphenylbutane, the radical dimers, only in the more concentrated reactions (2 and 3 in Fig. 1). The progress of the reactions can be followed by the change of colour, from dark purple to green.

In Fig. 2 we summarize the effect of additives in reaction 2 of Fig. 1 ($\text{Co}(\text{acac})_2 = 0.73\text{M}$). Addition of 0.25 equivalents of galvinoxyl (powerful radical scavenger) retarded the reaction making the induction period longer. Nevertheless, once the process started it exhibited a similar rate to that of the standard reaction. *m*-Dinitrobenzene had no effect.

TABLE 1.- Reactions of alkyl halides with $\text{Co}(\text{acac})_2$ at high concentration.^a

Entry	Alkyl halide	Reaction Product ^b	Reaction time	Yield (%)
1	$4\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Br}$	3-(4-Nitrobenzyl)- pentane-2,4-dione	1.5h	72
2	$4\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Cl}$	none	1h	0
3	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	3-Benzylpentane-2,4- -dione	15m	89
4	$4\text{-MeOC}_6\text{H}_4\text{CH}_2\text{Br}$	3-(4-Methoxybenzyl)- pentane-2,4-dione	12m	87
5	$\text{Me}_2\text{C}=\text{CHCH}_2\text{Br}$	3-(3,3-dimethylallyl)- pentane-2,4-dione	2m	66
6	$\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$	3-(1-Phenylethyl)- pentane-2,4-dione	6m	65
7	1-Bromoadamantane	3-(1-Adamantyl)- pentane-2,4-dione	4h	68

^a Standard conditions were: A round-bottomed flask containing 0.001 moles of $\text{Co}(\text{acac})_2$, 0.002 moles of alkyl halide and 2ml of chloroform was introduced in an oil bath at 120°C.

^b All products were previously known^{2,3,4} and were characterized by comparison with authentic samples.

The behaviour of the reactions reported in Table I suggest the possibility of an autocatalytic process. We have studied this point by adding anhydrous CoCl_2 (almost insoluble in chloroform) and $\text{CoCl}_2(\text{PPh}_3)_2$ ⁵ (soluble in chloroform). The results are also shown in Fig. 2. An almost complete elimination of the induction period was observed when $\text{CoCl}_2(\text{PPh}_3)_2$ was present. This alternative new process found in concentrated solutions has some similarities with the $\text{S}_{\text{RN}}1$ reactions⁶: absence of O-alkylation products, formation of radical dimers, increased reactions rates when compared with similar ionic processes, type of alkyl halides which can be used. However, the effects of galvinoxyl and of *m*-dinitrobenzene are not the expected for $\text{S}_{\text{RN}}1$ reactions.

A mechanistic proposal fitting all the available experimental data is depicted in Scheme 1. It involves a non radical chain mechanism initiated by an electron transfer step induced by CoX_2 . The cationic $\text{Co}(\text{II})$ is a d^7 species with radicaloid properties⁷ and coordinatively unsaturated even in the form of $\text{CoCl}_2(\text{PPh}_3)_2$. On the contrary, $\text{Co}(\text{acac})_2$ is known to be a tetramer⁸ in solid phase with the cobalt atoms coordinatively saturated. The induction period of the standard reaction is attributed to the time required for the slow ionic pathway to produce the initial concentration of CoX_2 needed to trigger the chain mechanism. The induction period is

absent in the presence of $\text{CoCl}_2(\text{PPh}_3)_2$. The second step of the initiation group is an electron transfer via atom transfer. Even though outer sphere⁹ electron transfer initiation has been recently reported¹⁰ for related processes catalyzed by Co^{II} species, our results indicate a sensitivity of the reaction to the coordinating ability of the leaving group (chlorides and N-benzylpyridinium salts are inert in our reactions). Moreover, the addition of *m*-dinitrobenzene that should have detected an outer sphere electron transfer step, had no noticeable effect. The third initiation step belongs to a class well known in the chemistry of $\text{Co}(\text{II})$ complexes, in particular in relation to vitamin B_{12} chemistry.^{11,12}

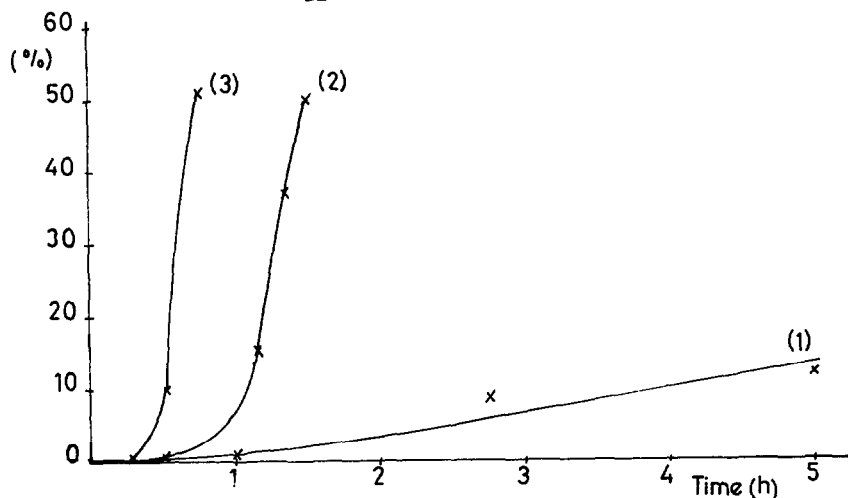


FIGURE 1.- Product yield vs. reaction time at different reactant concentrations in the reactions between $\text{Co}(\text{acac})_2$ and 1-bromo-1-phenylethane in chloroform. The indicated concentrations refer to $\text{Co}(\text{acac})_2$. The halide molar concentration was twice as high. (1): 0.18M; (2): 0.73M; (3): 2.92M.

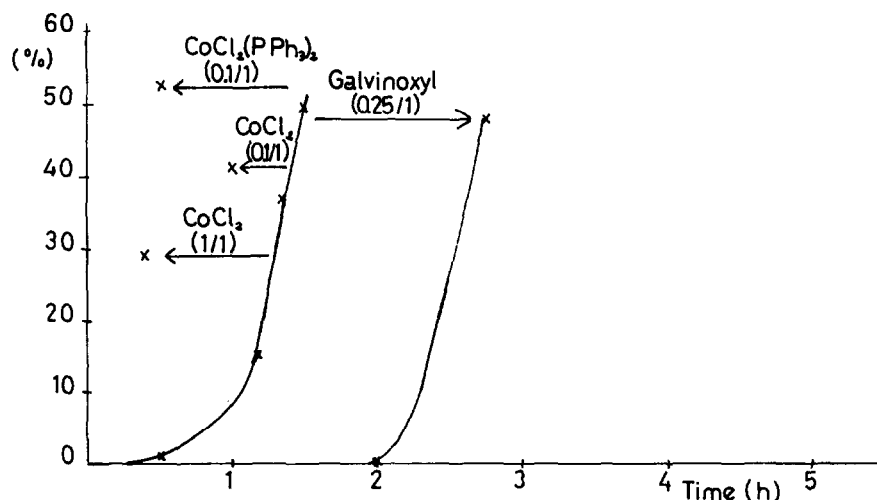
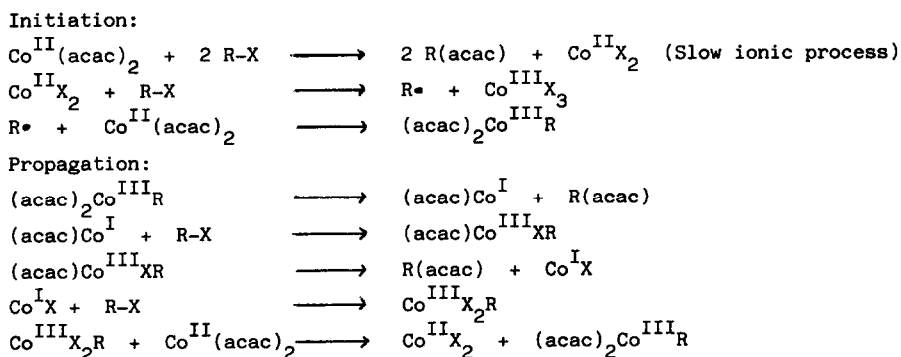


FIGURE 2.- Product yield vs. reaction time in the reactions of $\text{Co}(\text{acac})_2$ (0.73M) with 1-bromo-1-phenylethane (1.46M) in chloroform. Effect of additives. Numbers indicate the additive relative molar concentration with respect to $\text{Co}(\text{acac})_2$.



SCHEME I.- Mechanistic proposal

The isolation of radical dimers when the new mechanism operates and the effect of added galvinoxyl suggest that organic free radicals are only involved in the initiation steps. Thus, the propagation steps are based only on the ability of cobalt to undergo redox processes between Co^{I} and Co^{III} states. Catalytic reduction-oxidation cycles have been recently proposed for several processes in the presence of cobalt species.^{13,14,15}

Acknowledgements.- Financial support from CAICYT (Ministerio de Educación y Ciencia of Spain) through grant 2014/83 is gratefully acknowledged. One of us (A.V.) is also indebted to the "Ministerio de Educación y Ciencia" for a predoctoral grant. We are also indebted to Fluka AG and its representative in Spain, Alfonso Deselaers, S.A. for a generous gift of chemicals.

REFERENCES

- 1.- H.O. House; "Modern Synthetic Reactions", 2nd Ed. W.A. Benjamin. Menlo Park. 1972.
- 2.- J. Marquet, M. Moreno-Mañas; Synthesis, 1979, 348.
- 3.- A. González, F. Güell, J. Marquet, M. Moreno-Mañas; Tetrahedron Lett., 1985, 26, 3735.
- 4.- A. González, J. Marquet, M. Moreno-Mañas; Tetrahedron, 1986, 42, 4253.
- 5.- F.A. Cotton, O.D. Faut, D.M.C. Goodgame, R.H. Holm; J. Am. Chem. Soc., 1961, 83, 1781.
- 6.- a) M. Chanon, M.L. Tobe; Angew. Chem. Int. Ed. Eng., 1982, 21, 1.
b) M. Julia, M. Chanon; Chem. Rev., 1983, 83, 425.
c) J.F. Bunnett; Acc. Chem. Res., 1978, 11, 413.
- 7.- a) S. Miki, S. Matsumura, T. Ohno; Tetrahedron Lett., 1986, 27, 3669.
b) S. Miki, T. Ohno, H. Iwasaki; Tetrahedron Lett., 1985, 26, 3487.
- 8.- F.A. Cotton, R.C. Elder; J. Am. Chem. Soc., 1961, 86, 2294.
- 9.- J.K. Kochi; "Organometallic Mechanisms and Catalysis". Academic Press. 1974.
- 10.- S. Ahmad, J. Iqbal; J.C.S. Chem. Commun., 1987, 692.
- 11.- D. Dodd, M.D. Johnson; J. Organomet. Chem., 1973, 52, 1.
- 12.- J.M. Pratt, P.J. Craig; Adv. Organomet. Chem., 1973, 11, 331.
- 13.- S. Torii, T. Inokuchi, T. Yukawa; J. Org. Chem., 1985, 50, 5873.
- 14.- S. Uemura, S. Fukugawa, S.R. Patil; J. Organomet. Chem., 1983, 243, 9.
- 15.- H. Bhandal, G. Pattenden, J.J. Russell; Tetrahedron Lett., 1986, 27, 2299.

(Received in UK 21 January 1988)