

COBALT(II) CHLORIDE BISTRIPHENYLPHOSPHINE CATALYZED ALKYLATIONS OF β -DICARBONYL COMPOUNDS

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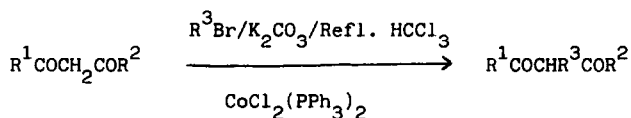
Summary.— The alkylation of β -dicarbonyl compounds with several benzyl halides in chloroform and in the presence of potassium carbonate is accelerated by the presence of cobalt(II) chloride bistrisphenylphosphine, thus broadening the scope of this alkylation method.

The preceding paper in this journal¹ describes a dual mechanistic pathway in the reactions of cobalt(II) pentano-2,4-dionato ($\text{Co}(\text{acac})_2$) and some alkyl halides. These reactions offer clear synthetic advantages for some alkyl halides when compared with classical procedures. An interesting catalytic effect of cobalt(II) chloride reducing the induction period of the reaction between $\text{Co}(\text{acac})_2$ and 1-bromo-1-phenylethane has been recognized. In our continuing effort to improve this methodology we have studied the direct alkylation of β -dicarbonyl compounds using catalytic amounts of cobalt² without previous formation of the cobalt chelates. In this work we report that alkylation of β -dicarbonyl compounds catalyzed by cobalt(II) chloride bistrisphenylphosphine³ in the presence of potassium carbonate efficiently gives the corresponding α -substituted products as indicated in Table I. A typical procedure is as follows: A mixture of 1.5g (0.015 mole) of pentane-2,4-dione, 2.78g (0.015 mole) of 1-bromo-1-phenylethane, 8.28g (0.36mole) of potassium carbonate and 30ml of chloroform was stirred at room temperature for 5 minutes. 0.98g (1.5 mmole) of $\text{CoCl}_2(\text{PPh}_3)_2$ were then added at once and the mixture refluxed under stirring for 6h. No precautions to exclude oxygen were taken. The reaction mixture was worked up in a conventional manner. Column chromatography on silica gel afforded 3-(1-phenylethyl)pentane-2,4-dione (2.39g, 78%) (Table I, entry 2).

This alkylation procedure has been successfully applied to several β -diketones and to ethyl acetoacetate giving preparatively useful yields on C-alkylation products for benzylic and allylic bromides. Furthermore, the reaction rates are remarkably increased in the catalyzed processes as indicated in Table II.

The alkyl halides active in the present reactions are almost the same as those active in the reactions reported in the preceding paper¹. 4-Nitrobenzyl halides (Table I, entries 4 and 6) that were unreactive towards $\text{Co}(\text{acac})_2$ in refluxing chloroform⁴ give good yields of C-alkylation products using the present or the just described¹ methods. Comparative experiments in the presence of the catalyst showed enhanced reactivity of the pentane-2,4-dione anion (Table II). By analogy with the results of the preceding paper we suggest an electron transfer initiation step (probably of the atom transfer type due to the radicaloid character and the redox ability of Co^{II}) to elicit a chain mechanism^{1,5}

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Table I.- Cobalt(II) catalyzed alkylation of β -dicarbonyl compounds.^a

Entry	R ¹	R ²	R ³	Time(h) ^b	Yield(%) ^c	Mp(°C) ^d
1	CH ₃	CH ₃	Ph ₂ CH	2	75	114-5 (116) ⁶
2	CH ₃	CH ₃	Ph(CH ₃)CH	8	78	48-9 (48-9) ⁷
3	CH ₃	CH ₃	1-(2-Naphthyl)ethyl	3	83	91-2
4	CH ₃	CH ₃	4-O ₂ N-Ph(CH ₃)CH	12	40	83-4
5	CH ₃	CH ₃	PhCH ₂	4	62	Bp 95-8/1mmHg (135-6/7mmHg) ⁸
6	CH ₃	CH ₃	4-O ₂ N-PhCH ₂	3	61 ^e	88-9 (90-1) ⁹
7	Ph	CH ₃	Ph ₂ CH	3	89	149-50
8	Ph	Ph	Ph ₂ CH	3	83	230-1
9	Ph	CH ₃	Ph(CH ₃)CH	3	88	79-80
10	Ph	Ph	Ph(CH ₃)CH	4	61	126-7
11	CH ₃	EtO	Ph(CH ₃)CH	12	52	Bp 125-30/2mmHg

^a The reactions were carried out under normal atmosphere.

^b Optimal reaction time was determined by glc.

^c Yields refer to isolated products.

^d All new compounds were characterized by spectroscopic methods and elemental analysis. Figures in parentheses are literature mp.

^e 3,3-bis-(4-Nitrobenzyl)pentane-2,4-dione, mp 225-7°C was also isolated (12%).

Table II.- Comparison between the Co(II) catalyzed and the uncatalyzed alkylations^a

Entry	R ¹	R ²	R ³	Time(h)	Conversion ^b	
					Catalyzed ^c	Uncatalyzed
1	CH ₃	CH ₃	Ph(CH ₃)CH	5	14/82	76/12
2	CH ₃	EtO	Ph(CH ₃)CH	6	6/66	55/9
3	CH ₃	CH ₃	CH ₂ =CHCH ₂	5	23/63	49/51
4	CH ₃	CH ₃	PhCH ₂	4	3/97	80/20
5	CH ₃	CH ₃	Ph ₂ CH	2	15/70	81/13
6	CH ₃	CH ₃	4-O ₂ NPhCH ₂	5	0/99	41/57

^a Experiments within rows were performed simultaneously.

^b Ratios of starting bromide to final product chromatographic areas.

^c In the presence of 0.1 equivalent of catalyst.

REFERENCES

- 1.- J. Marquet, M. Moreno-Mañas, P. Pacheco, A. Vallibera; Tetrahedron Lett., preceding letter.
- 2.- J. Marquet, M. Moreno-Mañas; Chem. Lett., 1981, 173.
- 3.- F.A. Cotton, O.D. Faut, D.M.C. Goodgame, R.M. Holm; J. Am. Chem. Soc., 1961, **83**, 1781.
- 4.- A. González, F. Güell, J. Marquet, M. Moreno-Mañas; Tetrahedron Lett., 1985, **26**, 3537.
- 5.- a) N. Kornblum; Angew. Chem. Int. Ed. Eng., 1975, **14**, 734.
b) M. Chanon, M.L. Tobe; Angew. Chem. Int. Ed. Eng., 1982, **21**, 1.
- 6.- M.R. Fosse; C.R. Acad. Sci., 1907, **145**, 1290.
- 7.- J. Marquet, M. Moreno-Mañas; Synthesis, 1979, 348.
- 8.- N.K. Kochentov, S.D. Sokolvo, V.E. Zhibirblis; Zh. Obshch. Khim., 1960, **30**, 3675.
- 9.- I.P. Sword; J. Chem. Soc.(C), 1970, 1916.