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Synthesis of Ketones from Aroyl Chlorides and Nickel(0) Complexes

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Summary

Facile syntheses of ketones have been achieved starting from bis(1,5-cyclooctadiene)nickel(0) and aroyl halides containing *ortho*-substituents. Electrophilic or nucleophilic attack of aroyl groups upon organic substrates also give rise to other classes of ketones.

Introduction

In the course of our studies on organonickel chemistry, we attempted to devise simple procedures in order to obtain ketones from aroyl chlorides and readily accessible transition metal complexes in the homogeneous phase. Apart from Friedel-Crafts and related acylations$^{(1,2)}$, satisfactory syntheses involve the use of metal carbonyls$^{(3-6)}$ or of transition metals in association with organoalkali metal compounds$^{(7)}$. The use of nickel(0) complexes containing phosphine ligands mainly gives decarbonylation products$^{(8)}$ and low yields of ketones have been obtained in the latter case$^{(9)}$. We now report the use of bis(1,5-cyclooctadiene)nickel, $Ni(COD)_2$$^{(10)}$, in this context. This complex is now readily accessible by a very simple procedure$^{(11)}$.

If aroyl chlorides are reacted in tetrahydrofuran, THF, at room temperature under nitrogen with $Ni(COD)_2$ a variety of products is obtained. Under appropriate conditions however, one of the reactive intermediates is preferred and selective reactions result.

Results and Discussion

Benzoyl chloride reacts with $Ni(COD)_2$ in THF at room temperature to give a mixture of benzophenone, benzil and biphenyl. *m*- and *p*-Toluoyl chlorides do not easily give decarbonylation products under these conditions, but at higher temperatures partial decarbonylation occurs to give ketones and hydrocarbons. A concomitant reaction of the acyl group with THF then gives (*1*):

$$ArCOCl + THF \rightarrow ArCO_2CH_2CH_2CH_2CH_2Cl \quad (1)$$

Aliphatic acyl halides also react with THF, a process which may be attributed to the formation of anhydrous nickel chloride which acts as an electrophilic catalyst, as shown by a separate experiment carried out with anhydrous nickel chloride only. Moreover, benzoylation of anisole yields mainly the *p*-substituted benzoyl derivative (*2*), e.g.:

$$PhCOCl + PhOMe \xrightarrow{NiCl_2} p\text{-}PhCOC_6H_4OMe \ (2) + HCl$$

A comparison between different catalysts in Friedel-Crafts type acylations$^{(2)}$ places nickel after iron(III) and zinc(II) chloride and at *ca.* the same level as cobalt(II) chloride. After 17 h in benzene at the reflux temperature, using a ten-fold excess of anisole with respect to the catalyst, a 70% yield of product is obtained with $FeCl_3$ or $ZnCl_2$, 12% with $NiCl_2$ and 8% with $CoCl_2$.

In contrast to the behaviour of other acylnickel complexes, those derived from *o*-substituted benzoyl chlorides tend to decarbonylate in a controllable way at room and even at lower temperatures. It is thus possible to take advantage of these circumstances to obtain selective syntheses of diaryl ketones (*3*):

$$2\ o\text{-}RC_2H_4COCl + Ni(COD)_2 \rightarrow o\text{-}RC_6H_4COC_6H_4R\text{-}o \ (3) + NiCl_2 + CO + 2\ COD$$

A comparison between o-RC_6H_4COCl compounds show that aroyl chlorides having R = Cl, O_2CMe and Me give satisfactory syntheses of ketones.

o-Anisoyl chloride gives a lower yield, probably owing to the higher stability of the nickel complex and the diketone (*4*) (R = OMe) is formed in substantial amounts.

$$o\text{-}RC_6H_4COCl + Ni(COD)_2 \rightarrow o\text{-}RC_6H_4COCOC_6H_4R\text{-}o \ (4) + NiCl_2 + 2\ COD$$

The *o*-carbomethoxy compound easily leads to decarbonylation but the resulting arylnickel complex is rather stable and is weakly nucleophilic towards the acyl carbon. Thus, methyl benzoate is obtained upon treatment with acidified water. The diaryl derivative (*5*) (R = O_2CMe) is also formed by the coupling of two aryl groups.

$$2\ o\text{-}RC_6H_4COCl + Ni(COD)_2 \rightarrow o\text{-}RC_6H_4C_6H_4R\text{-}o \ (5) + NiCl_2 + 2\,CO + 2\,COD$$

Compounds (*4*), (*5*) and (*6*), together with the hydrolysis products of decarbonylated complexes, are always found in variable amounts. Free acids are also obtained after hydrolysis of the reaction mixture (unconverted aroyl chlorides and aroylnickel complexes).

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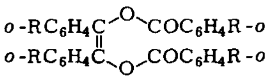
Table 1. Syntheses of diaryl ketones from $Ni(COD)_2$ (1 mol) and aroyl chloride (1 mol) in THF at 0°

R in o-RC_6H_4COCl	Yield of (3) (%)	Other products	o-RC_6H_4COCl recorded as free acid after acid hydrolysis (%)
H	13	(*4*), (*5*)	59
Cl	73	(*5*)	11
O_2CMe	65	(*5*), o-$HO(C_6H_4)_2O_2CMe$-o PhO_2CMe	10
Me	57	(*4*), (*6*), PhMe	12
OMe	29	(*4*), PhOMe	45
CO_2Me	39	(*5*), $PhCO_2Me$	22

(3) o-$RC_6H_4COC_6H_4R$-o; (4) o-$RC_6H_4COCOC_6H_4R$-o

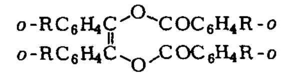
(5) o-$RC_6H_4C_6H_4R$-o;

(6) 

Better results are obtained when a 1 : 1 ratio of aroyl chloride to $Ni(COD)_2$ is employed. Nickel is found, in part, as a black powder under these conditions. Yields of diaryl ketones fall to 50, 10, 7 and < 1% for the o-Cl, o-Me, o-OMe and o-CO_2Me compounds respectively if a 2 : 1 ratio of chloride to $Ni(COD)_2$ is used.

$$4\ o\text{-}RC_6H_4COCl + 2\ Ni(COD)_2$$

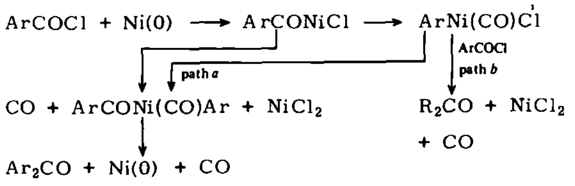
$$\downarrow$$



(*6*)

$$+\ 2\ NiCl_2 + 4\ COD$$

The behaviour observed can be rationalized according to the following Scheme. Path *a*, involves disproportionation, possibly *via* a chloro-bridged partially decarbonylated dimer. Path *b* involves direct attack of ArCOCl on the complex resulting from decarbonylation.



Scheme

The initially formed intermediate has been trapped with triphenylphosphine in the benzoyl chloride reaction and this aspect is currently being investigated$^{(12)}$.

We also tried to trap the coordinated acyl group by reaction of benzoyl chloride with methyl acrylate. This reaction does not occur significantly starting with $Ni(COD)_2$ only, however, addition of triphenylphosphine (2 moles) gave methyl benzoyl propionate in 33% yield (7):

$$PhCOCl + Ni(COD)_2 + 2\ PPh_3 + CH_2 = CHCO_2Me$$

$$\downarrow$$

$$Ni(OH)Cl + 2\ PPh_3 \xleftarrow{H_2O} PhCOCH_2CH(CO_2Me)Ni(PPh_3)_2Cl$$

$$+\ PhCOCH_2CH_2CO_2Me \qquad (7)$$

Thus nucleophilic-type additions of the acyl group can be obtained also without having recourse to anionic complexes as in the case of the lithium aroylnickel carbonylates employed by Tsutsumi$^{(5)}$.

Experimental

The acids (pure C. Erba products) were converted into the corresponding chlorides by standard procedures. $Ni(COD)_2$$^{(11)}$ and anhydrous metal chlorides$^{(13)}$ were prepared according to literature methods.

Separation and analysis of products was made by g.l.c. using Varian 1200 and 1400 chromatographs. Melting points were recorded on a Buchi apparatus and are uncorrected.

The i.r. spectra were recorded on a Perkin Elmer Infracord 137 instrument; n.m.r. spectra were recorded on a Varian EM 360 XL 100 machine and mass spectra on a Varian Mat CH 5 instrument.

General Acylation Procedure

The anhydrous metal halide (1 mmole), anisole (10 mmoles) and benzoyl chloride (10 mmole) in dry benzene (70 cm^3) were refluxed together for 17 h under dry nitrogen. Products, isolated by conventional procedures, were separated by g.l.c.

General Procedure for Decarbonylation and Coupling

The desired acid halide (10 mmoles) in dry freshly-distilled THF (25 cm^3) was added under nitrogen to $Ni(COD)_2$ (10 mmoles) cooled to −15°. The mixture was allowed to attain room temperature slowly with stirring. After some hours, metallic nickel separated. The solution was treated as usual and products were separated by g.l.c. and t.l.c. and were examined by i.r. and by mass spectroscopy and compared with authentic samples.

The main products obtained from various o-RC_6H_4COCl starting compounds are given in Table 1.

The following compounds were characterized (% of total g.l.c. peak areas are given in parentheses). Authentic samples were purchased from Schuchardt or were prepared according to the indicated literature method.

From PhCOCl: (*3*) (41) m.p. 48°; (*4*) (42.0) m.p. 95°; (*5*) (17) m.p. 70°. From o-ClC_6H_4COCl: (*3*) (87) m.p. 47° (lit$^{(14)}$. m.p. 45–56°); (*5*) (13) m.p. 60° (lit$^{(15)}$ 59.9°). From o-$MeCO_2C_6H_4COCl$: (*3*) (82) m.p. 95° (lit$^{(16)}$. 96°); (*5*) (8) m.p. 95° (lit$^{(17)}$. 95°); (*5*) o-hydroxy-o'-acetoxy (0.6) M^+ 228 (186, 158, 157, 139, 131, 128, 43); PhO_2CMe

(9). From *o*-$\mathrm{MeC_6H_4COCl}$: (*3*) (68) m.p. 69° (lit(18). 71°); (*4*) (16) m.p. 91° (lit(19). 92°); (*6*)(20) (16) m.p. 260°, i.r. 1750 cm^{-1} ($\mathrm{CO_2R}$), M$^+$ 476 (341, 239, 119, 91, 65). From *o*-$\mathrm{MeOC_6H_4COCl}$: (*3*) (62) m.p. 102° (lit(21). 103°); (*4*) (32) m.p. 130° (lit(22). 128–129°); PhOMe (6). From *o*-$\mathrm{MeO_2CC_6H_4COCl}$: (3) (60) m.p. 87° (lit(23). 83°); (*5*) (9) m.p. 74° (lit(24). 73–74°); $\mathrm{PhCO_2Me}$ (30). *m*-$\mathrm{MeC_6H_4COCl}$ in boiling THF gave 68% yields of the substituted analogues of: (*3*) (40)(25), (*4*) (16)(26), (*6*) (25) and (*1*) (19); M$^+$ 226 (190, 136, 119, 91, 65).

Benzoylation of Methyl Acrylate

The procedure was the same as for the syntheses of ketones from *o*-$\mathrm{RC_6H_4COCl}$ compounds but methyl acrylate was added in amount equivalent to the aroyl chloride.

This reaction failed to give the addition product of benzoyl to methyl acrylate. On adding triphenylphosphine (2 moles) to form a new complex before addition of methyl acrylate, a 33% yield of product was obtained, characterized as methyl benzoylpropionate (i.r. 1740, 1690 cm^{-1}, M$^+$ 192, m/e 161, 133, 105) as described in the literature(27). Most of the remaining product was identified as benzoic acid after treatment with acidified water.

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