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GRIGNARD-TYPE REACTIONS WITH TRANSITION METALS: ALKYLATION OF CARBON COMPOUNDS IN PROTIC SOLVENTS

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SUMMARY

Allylic halides react with reduced cobalt or nickel halides and with carbonyl compounds according to a pattern analogous to that of a Grignard reaction but with the difference that protic solvents can be used.

In the course of our studies, aimed at finding conditions for the formation of C–C bonds in organometallic complexes, we observed that carbonyl compounds in general and aromatic aldehydes in particular are subject to attack by allyl and some alkyl groups formed by reaction of the corresponding alkyl halides with cobalt or nickel. The latter are obtained in alcoholic solutions, even in the presence of small amounts of water, by reduction with a manganese/iron alloy. The reaction is carried out simply by dissolving the aldehyde, organic halide and nickel or cobalt halide in methanol at room temperature, then adding gradually and with stirring an excess of the powdered alloy. Certain ligands are necessary in order for the reaction to occur. Various types of compounds such as amides or nitriles are effective. Among these, thiourea has been chosen for the present study. The results obtained are presented in Table 1.

The reaction has also been carried out with Raney cobalt, which had been previously treated with thiourea.

The overall reaction for benzaldehyde and allyl chloride can be written as in eqn. (1).

$$CH_2{=}CHCH_2X + C_6H_5CHO + M \xrightarrow{H_2O} \underset{(I)}{C_6H_5CHOHCH_2CH{=}CH_2} + M(X)OH$$

$$(M = Co \text{ or } Ni; X = Cl, Br, I) \qquad (1)$$

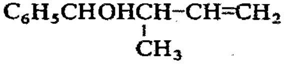
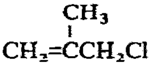
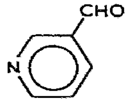
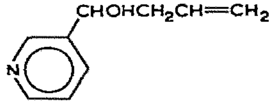
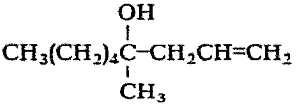
1,5-Hexadiene, the coupling product of two allyl radicals, is formed as a by-product of the reaction.

It is noteworthy that eqn. (1) suggests a pattern analogous to that of a Grignard reaction, and the product obtained from the reaction of crotyl bromide and benzaldehyde is the same branched isomer as can be obtained by a Grignard procedure[1].

The fact that the reactions described here take place in a protic medium indicates that a metal–carbon bond is formed which is quite stable to hydrolysis. To

TABLE 1

ALKYLATION OF CARBONYLIC COMPOUNDS

Starting materials		*Metal*	*Product*	*Yield*[a] *(%) (based on benzaldehyde)*
$CH_2=CHCH_2Cl$	C_6H_5CHO	Co	$C_6H_5CHOHCH_2CH=CH_2$	11
$CH_2=CHCH_2Cl$	C_6H_5CHO	Co	$C_6H_5CHOHCH_2CH=CH_2$	22[b]
$CH_3CH=CHCH_2Cl$	C_6H_5CHO	Co	 $C_6H_5CHOH\underset{CH_3}{CH}-CH=CH_2$	8.4
 $CH_2=\overset{CH_3}{C}CH_2Cl$	C_6H_5CHO	Co	 $C_6H_5CHOHCH_2\overset{CH_3}{C}=CH_2$	4
$CH_2=CHCH_2Cl$	p-Cl-C_6H_4-CHO	Co	p-Cl-$C_6H_4CHOHCH_2CH=CH_2$	9.6
$CH_2=CHCH_2Cl$	p-CH_3O-C_6H_4CHO	Co	p-$CH_3OC_6H_4CHOHCH_2CH=CH_2$	2.7
$CH_2=CHCH_2Cl$		Co		9.3
$CH_2=CHCH_2Cl$	$CH_3(CH_2)_4COCH_3$	Co	 $CH_3(CH_2)_4\overset{OH}{\underset{CH_3}{C}}-CH_2CH=CH_2$	< 1
$H_3COOCCH_2Cl$	$CH_3CH=CHCHO$	Co	$CH_3CH=CHCH=CHCOOCH_3$[c]	0.8
$CH_2=CHCH_2Cl$	C_6H_5CHO	Ni	$C_6H_5CHOHCH_2CH=CH_2$	13.5

[a] Selectivity is in general higher than 90%. In some cases a small amount of the aldehyde was recovered as acetal. Only in the case of crotonaldehyde several by-products formed, which were not identified. [b] Benzaldehyde in excess (10 mol/mol allyl chloride). [c] From dehydration of the alcohol.

establish the mechanism of the reaction we treated allyltricarbonylcobalt[2] with benzaldehyde in methanol. The product is the same alcohol (I) obtained according to the procedure described above.

The reactions of π-methallylnickel halides[3] and of π-allylnickel complexes[4] with aldehydes and ketones have already been described.

(Cyanomethyl)nickel bromide and iodide react in an analogous manner with benzaldehyde[5]. When π-allylbromobis(thiourea)nickel[6] was treated with benzaldehyde in methanol only very low yields of the expected product were obtained, the use of dimethylformamide in the presence of zinc, however, resulted in a better yield.

These experiments suggest that the reaction involves a π-allylic derivative of cobalt similar to allyltricarbonylcobalt or a π-allylic derivative of nickel, possibly one which does not contain halogen.

After coordination the carbonyl compound is likely to insert at a position *cis* to the allyl group, as observed in several other instances (see for example ref. 7).

EXPERIMENTAL

The method reported below for the reaction between benzaldehyde and allyl chloride is general and can be used for homologous allylic halides and for aldehydes and ketones. The reactions were carried out under nitrogen. All the compounds obtained were identified by comparison with authentical samples. Allyl chloride was 98.5% pure.

Preparation of 1-*phenyl*-3-*buten*-1-*ol*

A powdered (50 mesh) manganese iron alloy (5g) containing 80% of manganese was gradually added at 20° to a stirred solution of benzaldehyde (4.33 g, 40 mmol), allyl chloride (3.06 g, 40 mmol), $CoCl_2 \cdot 6H_2O$(9.52 g, 50 mmol) and thiourea (6.12 g, 80 mmol) in 70 ml of methanol. After 4 h methanol was distilled off and the residue was treated with water and extracted with diethyl ether. 1-Phenyl-3-buten-1-ol[8] (0.69 g, 4.4 mmol) was obtained by distillation (yield 11% based on benzaldehyde). Benzaldehyde was recovered almost completely (in part as dimethyl acetal).

Reaction of allyltricarbonylcobalt with benzaldehyde

Benzaldehyde (0.3 g, 3 mmol) was added under nitrogen to a stirred solution of 0.3 g (1.6 mmol) of allyltricarbonylcobalt[2].

Little gas evolution was observed during 5 h. Analysis of the mixture at this point showed the formation of 0.017 g (0.12 mmol) of (I) (in 7% yield based on the allyltricarbonylcobalt) (GLC data). 1,5-Hexadiene (10% yield) was also detected. Most of the benzaldehyde and allyltricarbonylcobalt were recovered unchanged by distillation under reduced pressure.

Reaction of π-allylnickel bromide with benzaldehyde

Under the above conditions π-allylnickel bromide[9] and π-allylbromobis-(thiourea)nickel[6] behaved in the same way as allyltricarbonylcobalt giving (I) in 5% yield (GLC data). (I) formed in yields of up to 20% when the reaction was run in dimethylformamide in presence of some zinc powder.

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