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METALS IN ORGANIC SYNTHESES

V *. THE GATTERMANN-KOCH SYNTHESIS OF AROMATIC ALDEHYDES PROMOTED BY $CuCl(PPh_3)_n$ (n = 0, 1 or 3). IS THE CUPROUS COMPLEX NECESSARY IN THE SYNTHESIS OF TOLUALDEHYDE?

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Summary

The use of $CuCl(PPh_3)$ in place of CuCl in the Gattermann-Koch synthesis slightly improves the yield of benzaldehyde but lowers the yield of tolualdehyde. The poorest yields are obtained in the presence of $CuCl(PPh_3)_3$. The formation of tolualdehyde from toluene and carbon monoxide in the presence of $AlCl_3$ and HCl is faster in the presence of CuCl, but higher yields are obtained in its absence and using an excess of hydrocarbon. In competitive experiments carried out using benzene and toluene together in equimolecular amounts, only tolualdehyde was formed, supporting the view that an electrophilic substitution is involved.

Introduction

The insertion of carbon monoxide into a C—H bond of an aromatic nucleus under the influence of aluminum chloride or bromide is known as the Gattermann-Koch reaction:

$$ArH + CO \xrightarrow[Cu_2Cl_2]{AlX_3,HCl} ArCHO$$

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* For part IV see ref. 1.

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In their original paper Gattermann and Koch passed a 2 : 1 CO : HCl mixture through 30 ml of toluene, 45 g of aluminum chloride, and 4 g of cuprous chloride. *p*-Tolualdehyde was obtained in 50% yield at 20—25°C [2]. Using this method, *o*- and *m*-xylylaldehyde, mesitylaldehyde, pseudocumyaldehyde and diphenylaldehyde were all prepared [2].

The synthesis fails with aromatic compounds bearing groups which are *meta* directing towards electrophilic attack, or groups capable of giving stable complexes with the aluminum halide, such as —OR or —NR_2. The synthesis fails also with benzene when $AlCl_3$ is used, but when the bromide is used, a 90% yield of benzaldehyde is claimed [3,4].

Gattermann and Koch suggested the use of cuprous chloride as promoter because it was known to absorb carbon monoxide under certain conditions [2]. Subsequently it was shown that cuprous chloride in benzene and in the presence of $AlBr_3$ absorbs carbon monoxide in the ratio 2 CO : 1 Cu_2Cl_2 * (hereafter indicated simply as CuCl). Conductivity measurements suggested the following equilibrium [5]:

$$CO + CuCl + AlBr_3 \rightleftharpoons [Cu(CO)]^+[AlBr_3Cl]^-$$

Using an excess of benzene (benzene : $AlCl_3$ 17 : 1) Dilke and Eley obtained 3% or 0.3% benzaldehyde using sublimed or commercial $AlCl_3$, respectively, in the presence of 20% equivalents of CuCl (with respect to $AlCl_3$) [5].

In a preliminary study, we found that when $CuCl(PPh_3)_n$, with $n = 1$ or 3, is used in place of CuCl, tolualdehyde is formed in 44% and 7% yield, respectively [7]. $CuCl(PPh_3)_n$ was used because it was also able to absorb CO in the presence of $AlCl_3$. Surprisingly we found that yield in tolualdehyde could be improved by lowering the amount of CuCl, and that the maximum yield was obtained in its absence.

We report below a full study on the carbonylation of benzene and toluene using the copper promoters mentioned above.

Results and discussion

Most of the experiments were carried out under 1 atm total pressure of carbon monoxide and dry HCl in the ratio 2 : 1, at temperature of 5—50°C, with 0.05 mol of $AlCl_3$ suspended in 0.05—0.20 mol of benzene or toluene, in the presence of $CuCl(PPh_3)_n$ ($n = 0, 1$, or 3) as catalyst precursor (0—100 mol % with respect to $AlCl_3$). These conditions (see Table 1) are close to those used by Gattermann and Koch, the most significant difference being a higher hydrocarbon/$AlCl_3$ molar ratio employed by us. This choice was suggested by the observation that when employing an excess of hydrocarbon it was easier to homogenize the reaction medium by mechanical stirring, whereas under Gattermann-Koch conditions, it is rather difficult to stir the reaction mixture efficiently. It should be noted that in the presence of an excess of hydrocarbon the aldehyde is formed in higher yields than under Gattermann-Koch conditions (compare

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* Recently various copper carbonyl complexes of general formula Cu(CO)X (X = Cl, F, HSO_4, ClO_4, HCOO, CH_3COO) have been synthesized by the action of carbon monoxide on the corresponding copper salts [6].

expts. 1 with 3 and 2 with 4). We ignore the interaction of $AlCl_3$ with the hydrocarbon, although it seems likely that the oil formed between these two reactants in the presence of HCl plays an important, although unknown role in this reaction. It is noteworthy that the yield in benzaldehyde is practically independent of the C_6H_6 : $AlCl_3$ ratio in the range of 3.3—1, at high carbon monoxide pressures (70 atm), in which case CuCl is not necessary [8].

Yields were calculated with respect to the amount of $AlCl_3$, employed since the reactions led to the stable complex $ArCHO \cdot AlCl_3$ with consequent subtraction of free and active $AlCl_3$ [5]. The highest yields were obtained with toluene. For example, when employing the hydrocarbon and $AlCl_3$ in the ratio 4 : 1, tolualdehyde and benzaldehyde were obtained in 76 and 3.8% yield, respectively, under the same experimental conditions (see expts. 1 and 2).

Tolualdehyde is formed in considerably lower yield when $CuCl(PPh_3)$ is used than when CuCl is used (compare expt. 1 and 5). This, and the fact that the same results are obtained when employing equimolar amounts of CuCl and PPh_3 in place of $CuCl(PPh_3)$ (compare expt. 5 and 6), suggest that $CuCl(PPh_3)$ dissociates to CuCl and PPh_3: this ligand is able to give stable complexes with $AlCl_3$ [9], thus reducing the amount of free and active $AlCl_3$ capable of giving the aldehyde. Even lower yields are obtained when $CuCl(PPh_3)_3$ is used probably because larger amounts of PPh_3 are produced by dissociation (see expt. 7).

With benzene, the aldehyde is formed in higher yield when $CuCl(PPh_3)$ is used in place of CuCl (compare expt. 8 with 2). (Note that the remaining amount of active $AlCl_3$, after dissociation (if any) and complexation with PPh_3, is still large in comparison with the yield of benzaldehyde).

In order to improve the yield of benzaldehyde, some experiments were carried out at various temperatures and CO/HCl ratios, and with increasing amounts of CuCl.

By comparing experiments 10—13 it can be seen that the temperature has little effect on the yield: rather similar yields are obtained between 10 and 40° C, the best results are obtained around room temperature. This indicates a low activation energy, as was found when $AlBr_3$ was used [5].

In CO : HCl ratio has little effect on the yield as long as HCl is present. In its absence the aldehyde is not formed (compare expts. 2, 14—16). It is interesting to observe that in the synthesis of benzaldehyde under higher pressures of carbon monoxide, in the absence of CuCl and of added HCl, added water acts as a promoter. It was suggested that the action of water is to generate some HCl from the anhydrous $AlCl_3$ present; an optimum water concentration is reached, above which the hydrolysis and consequent removal of $AlCl_3$ more than offset the benefit derived from the hydrogen chloride formed in the hydrolysis [8].

On increasing the amount of CuCl the yield in benzaldehyde increases up to 10% in the presence of 32% CuCl, and then decreases almost to zero when using $AlCl_3$: CuCl = 1 (compare expts. 2, 11, 16—22). Probably on increasing the amount of copper complex the beneficial effect of having larger amounts of CO carrier is surpassed by the removal of $AlCl_3$ to form $AlCl_4^-$.

It seems clear that toluene is more reactive than benzene. This observation was directly confirmed in competitive experiments between toluene and benzene, which were carried out by employing equimolar mixtures of the two hydrocarbons (see expt. 23). Under these conditions only tolualdehyde is formed

TABLE 1

GATTERMANN-KOCH SYNTHESIS OF BENZALDEHYDE AND TOLUALDEHYDE AT 22°C USING $CuCl(PPh_3)_n$ (n = 0, 1, 3) AS PROMOTER [a]

Run	Hydrocarbon [b]	ArH/$AlCl_3$	$CuCl(PPh_3)_n$/ $AlCl_3$ × 100	Reaction time (h)	Yield (%)	*para/ortho*
1	T	4	16	5	76	11.1
2	B	4	16	5	3.8	
3	T	1	16	5	55	11.1
4	B	1	20	5	traces	
5	T	4	14 (n = 1)	5	44	11.1
6	T	4	14 [c]	5	43	11.1
7	T	4	14 (n = 3)	6	7	10.5
8	B	4	14 (n = 1)	6	9	
9	B	4	14 (n = 3)	6	3	
10 [d]	B	4	32	5 (10°C)	7	
11 [d]	B	4	32	5 (20°C)	10	
12 [d]	B	4	32	5 (30°C)	11	
13 [d]	B	4	32	5 (40°C)	7	
14 [e]	B	4	16	5	3.9	
15 [e]	B	4	16	5	3.9	
16 [e]	B	4	16	5	traces	
17	B	4	0	7	—	
18	B	4	4	5	0.5	
19	B	4	8	5	1.5	
20	B	4	48	5	9	
21	B	4	64	5	3	
22	B	4	100	5	traces	
23	B, T	2, 2	16	5	78	12
24 [f]	T	1, 1	12	5	50	—
25 [f]	T	1, 1	15	7	54	—
26	T	1	16	5	55	11
27	T	1	16	2	53	11.0
28	T	4	16	2	59	11.1
29	T	4	16	5	76	11.1
30	T	4	64	5	24	11.7
31	T	4	100	5	traces	—
32	T	4	4	5	78	11.5
33	T	4	1	2	79	11.7
34	T	4	—	3	86	11.9
35	T	4	—	2	80	11.7
36	T	4	—	1	67	11.7
37	T	4	16 [g]	2	59	10.6
38	T	4	100 [g]	5	traces	—
39	T/B/Al = 2/2/1	—	—	5	86	11.7
40	T	1	—	5	44	11.9
41	T	1	—	2	30	11.2
42 [e]	T	3	—	3	—	—
43 [e]	T	3	—	2	67	11.1
44	T	3	—	2	72	11.3
45 [e]	T	3	—	3	61	11.7
46 [e]	T	3	—	4	64	11.7
47 [e]	T	3	—	4	47	11.3
48 [d]	T	3	—	2 (10°C)	71	12.1
49 [d]	T	3	—	2 (20°C)	80	11.1
50 [d]	T	3	—	2 (30°C)	75	10.2
51 [d]	T	3	—	2 (40°C)	63	9.3
52 [d]	T	3	—	2 (50°C)	42	9.1
53 [d]	T	3	—	2 (60°C)	26	8.9
54	T	1	—	5	44	11.9
55	T	2	—	3	63	11.8
56	T	3	—	3	86	11.8

[a] *Reaction conditions* (except when otherwise indicated): Temperature 22°C; CO/HCl ratio in mol 2; $n = 0$ except in runs 5 and 8 $n = 1$; and in runs 7 and 9 $n = 3$. In every case 6.7 g of $AlCl_3$ (0.05 mol) and a total volume of CO and gaseous dry HCl of 60 ml/min were used. [Except in runs 24 and 25 where a larger amount of $AlCl_3$ and hydrocarbon were used (~0.3 mol)]. [b] T = Toluene; B = benzene. [c] In the presence of an equimolar amount of PPh_3. [d] Reaction temperature: runs 10 and 48: 10°C; runs 11 and 49: 20°C; runs 12 and 50: 30°C; runs 13 and 51: 40°C; Run 52: 50°C; run 53: 60°C. [e] CO/HCl ratio. Run 43: 5; runs 14, 45 and 46: 1; runs 15 and 47: 0.5; runs 16 and 42 in the absence of HCl. [f] See refs. 2 and 12 for results of runs 24 and 25 respectively. [g] KCl was employed in place of CuCl.

with the usual *para* : *ortho* ratio. Since the earliest studies, it has been postulated that the formyl chloride is the active species in the reaction [2], but, although there is evidence for its existence [10], it has never been isolated. Conductivity and absorption measurements led Dilke and Eley [5] to postulate the presence of the formylium ion HCO^+ as the electrophile which attacks the hydrocarbon. The higher reactivity of toluene is in agreement with such a view. It has been suggested that the promoting role of CuCl consists in providing a higher concentration of HCO^+ [5].

The difference in reactivity between toluene and benzene towards electrophilic attacks in the closely related Friedel-Crafts reactions has been related with the *para* and *ortho* ratio in the products from toluene; a large selectivity between toluene and benzene in competitive experiments is associated with a high selectivity between the *para* and *ortho* positions. For example, in the $AlCl_3$ catalyzed acetylation with CH_3COCl of toluene and benzene in carbon disulfide at 25°C the relative rate is 141 and the *para* : *ortho* ratio is 95.5 : 2.5, while with the less selective $CH_2ClCOCl$ the corresponding values are 78.2 and 86.6 : 11.1 [11].

In connection with experiment 23, it should be noted that the unexpected high yield of *ortho* isomer relative to the great selectivity observed between toluene and benzene is not due to subsequent isomerization of the *para* derivative. Thus, in an experiment carried out with *p*-tolualdehyde, toluene, $AlCl_3$, and CuCl in the ratios 1 : 3 : 1 : 0.15, in the presence of only HCl and in the absence of CO, no isomerization to the *ortho* derivative was observed after 5 hours at room temperature. Thus our results seem anomalous, since a large selectivity between toluene and benzene is associated with a relatively small *p* : *o* ratio.

With the aim of gaining insight into the role played by CuCl, we ran several experiments in the presence of varying amounts of CuCl. An increase in the amount of CuCl lowers the yield (see expts. 29—31): for example in the presence of 100% of CuCl only traces of the aldehyde are formed (expt. 31). This is because of the reaction

$$CuCl + AlCl_3 \rightarrow Cu^+ + AlCl_4^-$$

as shown by electric conductivity measurements [5]. In the presence of stoichiometric amounts of CuCl the aldehyde is not formed because the Lewis acid is removed to form $AlCl_4^-$.

On lowering the amount of CuCl the yield is increased and the maximum yield is obtained in its absence (see expts. 29, 30 and 32—35). For example in 2 h the aldehyde is formed in 79% yield in the presence of 1% CuCl; in its absence the aldehyde is formed in 86% yield after 3 h, and the yield reaches 67% in only 1 h.

It should be emphasized that the isomeric composition, as expressed by the *p* : *o* ratio, is substantially the same whether or not CuCl is used. Moreover, yield and isomeric composition are practically the same irrespective of whether CuCl or KCl (which , in contrast with CuCl is unable to abosrb CO) is used. (Compare expts. 28 with 37 and 31 with 36). This suggests that the regioselective step is not controlled by a (electrophilic) copper complex and that CuCl does not play any major role in the carbonylation of toluene, even though it has been used because of its ability to absorb CO in the presence of $AlCl_3$.

In contrast, with benzene the aldehyde is formed only in the presence of CuCl. The minor reactivity of benzene is confirmed also in competitive experiments carried out using equimolar amounts of benzene and toluene together; only tolualdehyde is formed (expt. 39), as observed in the competitive experiments carried out in the presence of CuCl (expt. 23).

Since it was previously reported that the use of CuCl was unnecessary when operating under relatively high carbon monoxide pressure (50—100 atm) [8], we carried out other experiments with toluene and $AlCl_3$ in the ratio 1 : 1, as originally reported by Gattermann and Koch, but using the same amount of $AlCl_3$ (0.05 mol) as reported in this study, either in the presence or in the absence of CuCl, and for shorter reaction times, in order to seek evidence for a possible action of the copper complex. By comparing expt. 26 with expt. 40, it can be seen that the yield is lower in the absence of CuCl, though not greatly so: use of CuCl gives better results in experiments carried out for shorter reaction times: for example, after 2 h the yield is 53% or 30% in the presence or in the absence of CuCl, respectively (compare expt. 27 with expt. 41). In all cases the *p* : *o* ratio remains practically the same. Thus, when toluene and $AlCl_3$ are taken in the ratio 1 : 1, CuCl has a beneficial effect on the yield. As suggested by Dilke and Eley, in the presence of CuCl the concentration of the electrophile HCO^+ is higher than in the absence of the copper complex. With an excess of hydrocarbon the beneficial effect due to Cu^+ is outweighed by the detrimental effect due to the presence of the counter ion Cl^-, and the highest yield is obtained in the absence of CuCl.

Experiments 41—44 show that varying the CO : HCl ratio has little effect on the yield and selectivity. The highest yields are obtained by using an excess of CO in the presence of HCl; in the absence of the latter no aldehyde is formed (see expt. 42). Thus HCl is necessary to form HCO^+, probably via the very strong acid $HAlCl_4$ [11]. The highest yield is obtained with CO : HCl = 2, as originally suggested by Gattermann and Koch, though even with CO : HCl = 5 the aldehyde is formed in comparable yield (compare expt. 44 with expt. 43). With CO : HCl = 1 the yield is comparable after 4 h (expt. 46). With an excess of HCl the yield is 47% after 4 h (see expt. 47). Thus the yield decreases on decreasing the carbon monoxide pressure.

Experiments 48—53 show the effect of the temperature on the yield and selectivity. The highest yield is obtained at around room temperature (expt. 49) though rather similar yields are obtained at 10 or 30°C (expts. 48, 50), again suggesting that the reaction has a small activation energy. Lower yields are obtained above 40°C. For example, at 60°C the yield drops to 26%, probably because of secondary reactions of the aldehyde in the presence of $AlCl_3$ and excess hydrocarbon. A similar effect was found in the synthesis of benzaldehyde [5]. The decreased yields above 50° C might be due to a true thermodynamic effect and/or to decomposition of the aldehyde by side reactions. Moreover, it is interesting to note that the $p : o$ ratio is lowered on increasing the temperature. The possibility that the more abundant *p*-isomer undergoes side reactions may account for the observed variation of the $p : o$ ratio with temperature.

Finally, the comparison of expts. 54—56 and 34 reveals the effect of the toluene/$AlCl_3$ ratio on the yield. Higher yields are obtained when an excess of toluene is used (3 or 4 times, expts. 56 and 34), as was found in experiments carried out in the presence of CuCl (see expts. 26—29). It is noteworthy that in the synthesis of benzaldehyde under high pressures of carbon monoxide and in the absence of CuCl the yield is almost independent of the benzene : $AlCl_3$ ratio [8].

Experimental section

Materials

Benzene, toluene, anhydrous aluminum chloride and cuprous chloride were pure commercial reagents and were used without further purification. Carbon monoxide was the N 37 grade supplied by the SIO Company. Dry HCl was prepared by dropping conc. aqueous HCl into conc. H_2SO_4 [12]. $CuCl(PPh_3)_{1 \text{ or } 3}$ was prepared by published methods [13].

General procedures

Yields and isomeric composition of the products were determined by GLC, using a Hewlett-Packard gas chromatograph Model 5830A equipped with a Hewlett-Packard GC terminal Model 18850A. Analyses were carried out with a 6 ft long column 10 Pr. Uccw 982 Chrom. Awdmcs 80—100 mesh at 90°C using helium (20 ml/min) as carrier gas. Each sample was run at least three times to reduce problems associated with "memory's effects".

The aldehydes were isolated by distillation and by preparative GLC and identified by a combination of GLC, IR, NMR and elemental analysis techniques. IR and NMR spectra were recorded on Perkin-Elmer Model 457 and Bruker HFX-90 spectrometers.

Synthesis of the aldehydes

The general procedure described in the literature was followed [12]. In a typical experiment (see Table 1, expt. 2), benzaldehyde was produced as follows. In a 100 ml 3 neck flask, thermostated at 22° C and equipped with a mechanical stirrer, was placed benzene, $AlCl_3$, and CuCl (17.7 ml, 6.7 g, and 0.8 g, respectively) after the flask was flushed with a mixture of CO and dry HCl (2 : 1), total volume 60 ml/min) for 30 min. The gas was allowed to flow through the vigorously stirred liquid for 5 h, during which the solution first turned greenish and then reddish. The vessel was then cooled in an ice bath and the mixture was slowly treated with 50 g of ice under an atmosphere of CO/HCl. The organic layer was extracted with ether (50 ml in three portions), neutralized with $NaHCO_3$, and analyzed by GLC.

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