

TELLURIUM IN ORGANIC SYNTHESIS

IV *. CARBONYLATION OF SOME AROMATIC TELLURIUM COMPOUNDS IN THE PRESENCE OF $\text{Ni}(\text{CO})_4$

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Summary

The reaction of ArTeCl_3 and Ar_2TeCl_2 with $\text{Ni}(\text{CO})_4$ in dimethylformamide followed by aqueous work-up readily gives the corresponding carboxylic acids. A mechanism is suggested in which the aromatic telluride adds oxidatively to nickel, and this is followed by insertion of a CO-unit yielding an ArCONi complex.

Introduction

Aromatic carbonylation reactions have been reported for substrates such as aromatic halides [1,2], aryldiazonium tetrafluoroborates [3] and organometallic compounds [1], with or without halogen on the metal, in the presence of various metal carbonyls. The products are carboxylic acid derivatives, ketones, or β -diketones depending on the reactants and the solvent.

In the palladium catalyzed carbonylation of iodobenzene [4] and arylmercuric halides [5] to carboxylic acid derivatives, a high pressure of CO is necessary. When $\text{Ni}(\text{CO})_4$ is used as a carbonylating agent, the reactions can be carried out under milder conditions at atmospheric pressure. In this way a number of aromatic halides have been converted into arylcarboxylic acids and their derivatives in alcoholic solution [6,7] or in dipolar aprotic solvents [8]. The reaction of $\text{Ni}(\text{CO})_4$ with arylmercuric halides in dimethylformamide yielded no carboxylic acid derivatives but almost exclusively diarylketones [9]. With an aryl halide present good yields of unsymmetrical diaryl ketones were reported [10].

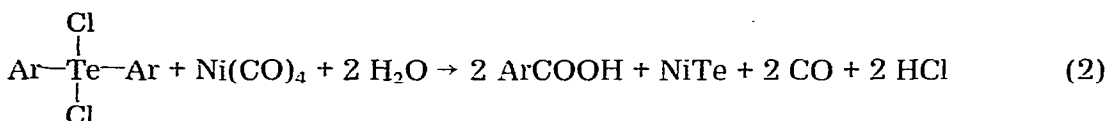
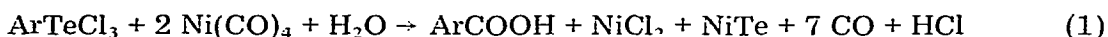
* For part III, see ref. 20.

In this paper we report carbonylation of aromatic tellurium halides to carboxylic acids in dimethylformamide under mild conditions in the presence of $\text{Ni}(\text{CO})_4$.

Results and discussion

Although aromatic tellurides have been used extensively as ligands in transition metal complexes [11,12], very few nickel complexes are known. Hieber and Kruck [13] observed that diphenyl telluride reacts with nickel carbonyl to deposit nickel and tellurium. No organic products were isolated. We have now found that aryltellurium trichlorides and diaryltellurium dichlorides react with nickel carbonyl in dimethylformamide at 70°C to give carboxylic acids, according to Scheme 1.

Scheme 1.



Thus diphenyltellurium dichloride gave benzoic acid (58%) together with benzophenone (10%) and diphenyl telluride (16%). Diaryl tellurides and diaryl ketones were formed in small amounts in all reactions of $\text{Ni}(\text{CO})_4$ with the aryltellurium trichlorides and diaryltellurium dichlorides (see Table 1). The yields of ketones, however, are strikingly different from those obtained with arylmercuric halides [9].

Although aliphatic alkylmercuric halides are known [9,14] to give dialkyl ketones by reaction with metal carbonyls, diethyl telluride failed to react under the usual conditions. Bis(2-chloropropyl)tellurium dichloride obtained from

TABLE I
CARBONYLATION OF TELLURIDES WITH $\text{Ni}(\text{CO})_4$

Substrate	Acid (%) ^a	Ketone (%)	Telluride (%)
4-Methoxyphenyltellurium trichloride (I)	4-Methoxybenzoic acid (51)	Bis(4-methoxyphenyl) ketone (trace)	Bis(4-methoxyphenyl) telluride (15)
2-Naphthyltellurium trichloride (II)	2-Naphthoic acid (35)	Di-2-naphthyl ketone (3)	Di-2-naphthyl telluride (trace)
Bis(4-methoxyphenyl)tellurium dichloride (III)	4-Methoxybenzoic acid (71)	Bis(4-methoxyphenyl) ketone (trace)	Bis(4-methoxyphenyl) telluride (15)
Diphenyltellurium dichloride (IV)	Benzoic acid (58)	Benzophenone (10)	Diphenyltelluride (16)
Diethyl telluride (V)	—	—	Diethyl telluride (100)
Bis(2-chloropropyl)tellurium dichloride (VI)	—	—	—

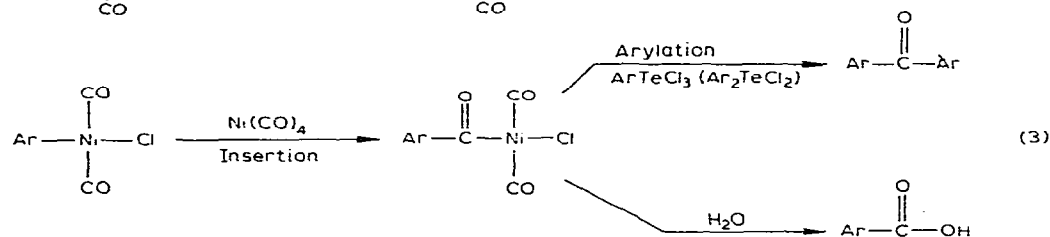
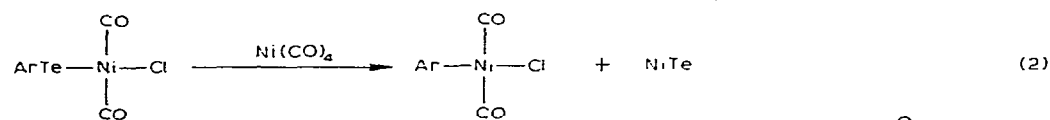
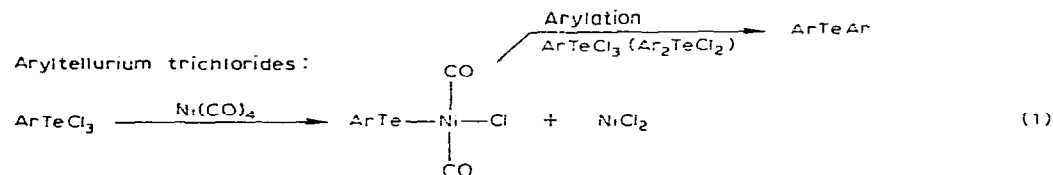
^a Isolated yield (of pure crystalline compound).

propene and TeCl_4 , on the other hand, when treated with $\text{Ni}(\text{CO})_4$ in DMF gave the usual black precipitate of NiTe , but the work up gave no acid, ketone, or telluride. The starting tellurium dichloride seems to be unstable under these reducing conditions, decomposing into propene, NiCl_2 and NiTe .

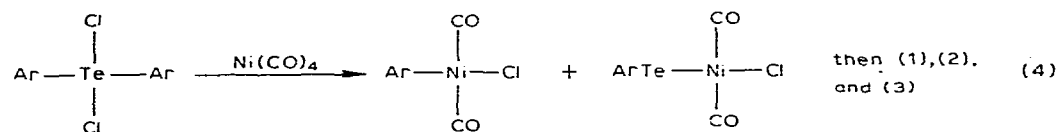
When $\text{Ni}(\text{CO})_4$ was replaced by $\text{Fe}_2(\text{CO})_9$ in the reaction with 4-methoxyphenyltellurium trichloride no carbonylation was observed. The only isolated product was bis(4-methoxyphenyl)ditelluride (40%), formed by reduction of the aryltellurium trichloride.

A probable scheme for carbonylation of aromatic tellurides involves several processes which are well established in organometallic chemistry. The reaction sequence may be rationalized as shown in Scheme 2.

Scheme 2.



Diaryltellurium dichlorides:



The initial step in both reactions is an oxidative addition, (1) and (4), in the former case combined with a reduction. A decomposition of the type shown in eq. 2, into an arynickel complex and NiTe , has been described for arylmercuric halides [9]. Low yields of diaryl ketones and diaryl tellurides in the product mixtures can be explained partly by the weak arylating ability of aryltellurium trichlorides and diaryltellurium dichlorides, and partly by the use of an aprotic dipolar solvent, which seems to promote insertion reactions [9].

The compounds ArTeCl_3 and Ar_2TeCl_2 can easily be synthesized from a variety of aromatics possessing an activating substituent [15,16], by reaction with TeCl_4 . Less activated substrates need catalysis by Lewis' acids, e.g. AlCl_3 .

TeCl_4 has a strong preference for attack at the *para* position of an activated aromatic ring, giving mono-adducts. This offers an advantage over those methods for introduction of a COOH group which start with aryl halides such as $\text{RMgX} + \text{CO}_2$ and $\text{RX} +$ a metal carbonyl, since the halogenations of the aromatics are less selective.

Experimental

Materials

Dimethylformamide was dried by distillation from calcium hydride. $\text{Ni}(\text{CO})_4$ and $\text{Fe}_2(\text{CO})_9$ were Merck products, diethyl telluride was an Alfa product. All other tellurium-containing starting materials were prepared by published methods: 4-methoxyphenyltellurium trichloride [16], 2-naphthyltellurium trichloride [17], diphenyltellurium dichloride [18], bis(4-methoxyphenyl)tellurium dichloride [15] and bis(2-chloropropyl)tellurium dichloride [19].

General procedure

Nickel carbonyl was added to a 3-necked round bottom flask containing the tellurium compound dissolved in dry dimethylformamide (50 ml) under nitrogen. After 24 h at 70°C the excess of nickel carbonyl was evaporated off in a stream of nitrogen. The mixture was then poured into 200 ml of water containing 10 ml of HBr (48%, aq.). The organic products were extracted with diethyl ether (3×75 ml) and the ether solution extracted with sodium hydroxide (2 M, aq.). The ether extract containing non-acid products was dried with CaCl_2 , the alkaline extract was acidified and the aromatic acid extracted with diethyl ether.

4-Methoxybenzoic acid from I. 2.0 g (5.9 mmol) 4-methoxyphenyltellurium trichloride and 2.6 ml (20 mmol) $\text{Ni}(\text{CO})_4$ were submitted to the general procedure described above. Work-up yielded 0.45 g (52%) 4-methoxybenzoic acid, m.p. 185°C ; 0.15 g (15%) bis(4-methoxyphenyl) telluride; and trace amounts of bis(4-methoxyphenyl) ketone.

4-Methoxybenzoic acid from III. Similarly, 2.0 g (4.8 mmol) bis(4-methoxyphenyl)tellurium dichloride and 1.5 ml (11.5 mmol) $\text{Ni}(\text{CO})_4$ gave 1.05 g (71%) 4-methoxybenzoic acid, m.p. 185°C ; 0.25 g (15%) bis(4-methoxyphenyl) telluride; and trace amounts of bis(4-methoxyphenyl) ketone.

Benzoic acid from IV. Similarly, 2.0 g (5.7 mmol) diphenyltellurium dichloride and 2.5 ml (19 mmol) $\text{Ni}(\text{CO})_4$ gave 0.80 g (58%) benzoic acid, m.p. 122°C ; 0.25 g (16%) diphenyl telluride; and 0.10 g (10%) benzophenone.

2-Naphthoic acid from II. Similarly, 1.5 g (4.2 mmol) 2-naphthyltellurium trichloride and 2.0 ml (15.5 mmol) $\text{Ni}(\text{CO})_4$ gave 0.25 g (35%) 2-naphthoic acid, m.p. 186°C ; 0.02 g (3%) di-2-naphthyl ketone, m.p. $165\text{--}166^\circ\text{C}$; and trace amounts of di-2-naphthyl telluride.

Bis(4-methoxyphenyl) ditelluride from I. Similarly, 1.0 g (2.4 mmol) 4-methoxyphenyltellurium trichloride and 1.5 g (4.1 mmol) $\text{Fe}_2(\text{CO})_9$ gave 0.25 g (40%) bis(4-methoxyphenyl) ditelluride, m.p. 59°C .

When diethyl telluride (V) was submitted to the general procedure described above no reaction was observed, and the starting material was recovered unchanged.

Bis(2-chloropropyl)tellurium dichloride (VI) gave a black precipitate of NiTe, but work-up yielded no organic material.

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