SOME NEW REACTIONS OF NICKEL CARBONYL

WITH ORGANIC HALIDES
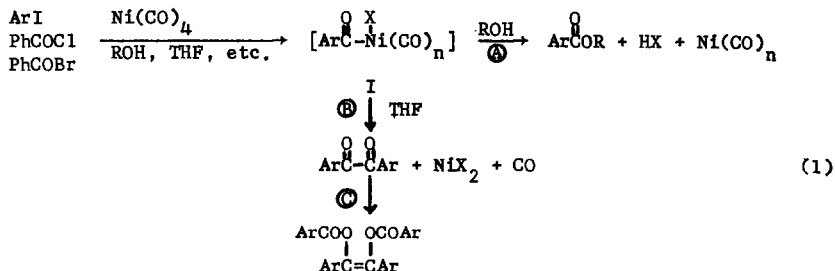
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Scheme (1), below, summarizes several new reactions of organic hal-
ides with nickel carbonyl which have been found in this laboratory. As
indicated, aryl iodides are converted to aroate esters (path A) in alco-
holic solvents (methyl, ethyl, and isopropyl alcohols have been studied).

$$
\begin{array}{l}
ArI \\
PhCOCl \\
PhCOBr
\end{array}
\xrightarrow[\text{ROH, THF, etc.}]{Ni(CO)_4}
\left[Ar\overset{O}{\underset{}{C}}-\overset{X}{\underset{}{Ni}}(CO)_n \right]
\xrightarrow[\text{\textcircled{A}}]{ROH}
Ar\overset{O}{\underset{}{C}}OR + HX + Ni(CO)_n
$$

$$
\text{\textcircled{B}} \downarrow \text{ THF}
$$

$$
Ar\overset{O}{\underset{}{C}}-\overset{O}{\underset{}{C}}Ar + NiX_2 + CO \qquad (1)
$$

$$
\text{\textcircled{C}} \downarrow
$$

$$
\underset{ArC=CAr}{ArCOO \; OCOAr}
$$

Yields are nearly quantitative; conversions for equimolar amounts of
nickel carbonyl and aryl iodide are listed in column one of Table I for
several representative examples.

In aprotic solvents (THF is preferable) the products are arils (B),
again in excellent yield and fair conversion (column two, Table I).

Two slightly hindered aryl iodides, o-iodotoluene and 1-naphthyl
iodide, give, in addition to the expected arils, endiol diesters (path C,
column three, Table I).

TABLE I

Iodide	% Conversion to Methyl Aroate Ester in Methanol	% Conversion to Aril in THF	% Conversion to Endiol Diester in THF
Phenyl	60	80	0
p–Chlorophenyl	-	47	0
m–Tolyl	-	50	0
m–Chlorophenyl	70	-	-
1–Naphthyl	80	35	29
o–Tolyl	-	10	26
Mesityl	0	0	0

Benzoyl chloride and bromide are converted (40%) to 1,2-dibenzoyloxy-
stilbene (also path C) in the aprotic solvents THF and hexane.

All of the aforementioned reactions proceed under mild conditions,
viz., refluxing a solution of equimolar quantities of nickel carbonyl
(b.p. 42°) and the organic substrate in the appropriate solvent until the
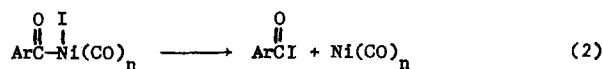reflux temperature reaches that of the pure solvent.

Aryl chlorides and bromides and alkyl halides do not react with
nickel carbonyl under these conditions, nor with triphenylphosphine
nickel tricarbonyl or bistriphenylphosphine nickel dicarbonyl at temper-
atures ranging up to 140° in various solvents. The especial reactivity
of aryl as contrasted to alkyl iodides is being studied further.

Mechanism. - All of the observed products can be viewed as arising
from transformations of postulated intermediate I, each of which transfor-
mations bears a formal similarity to previously observed reactions of more
stable organometallics of analogous structure (Table II). Reaction A is

TABLE II

Reaction	Analogy	Reference

A $\quad CH_3\overset{\overset{O}{\|}}{C}Co(CO)_4 \quad \xrightarrow{MeO^-} \quad CH_3CO_2Me + {}^-Co(CO)_4 \quad$ 1

B (reaction scheme)

$$\underset{Me}{\overset{Me}{>}}Pt\underset{PEt_3}{\overset{PEt_3}{<}} \quad \xrightarrow{CO} \quad \left[\underset{Me}{\overset{Me\overset{O}{\overset{\|}{C}}}{>}}Pt\underset{PEt_3}{\overset{PEt_3}{<}}\right] \quad \longrightarrow \quad CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}CH_3 \quad 2$$

C $\quad Ph\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}Ph \xrightarrow{Na} Ph\overset{\overset{O}{\cdot}}{C}\overset{\overset{\cdot O}{:}}{C}Ph \xrightarrow{Na} Ph\overset{\overset{O}{:}}{C}\overset{\overset{O}{:}}{C}Pn \xrightarrow{2BzCl} Ph\overset{OBz}{\overset{|}{C}}=\overset{OBz}{\overset{|}{C}}Ph \quad 3$

an alcoholysis effected by the addition of alcohol nucleophiles to the aroyl carbonyl group. The latter should be more activated toward nucleo-philic attack in I than in the cobalt analogy because of the presence of the positively charged nickel ion alpha to the carbonyl group in the former. That it is I and not benzoyl iodide formed via (2) that is

$$\underset{Ar\overset{\|}{C}-\overset{|}{Ni}(CO)_n}{\overset{O\quad I}{}} \quad \longrightarrow \quad \underset{Ar\overset{\|}{C}I + Ni(CO)_n}{\overset{O}{}} \quad (2)$$

alcoholyzed is inferred from the fact that benzoyl iodide gives no benzil or 1,2-dibenzoyloxystilbene upon reaction with nickel carbonyl in THF (only a trivial ether cleavage results). Since reaction (2) does not occur in THF it is improbable in the more polar alcoholic solvents [ions are destroyed in (2)].

[1] R. F. Heck and D. S. Breslow, _J. Am. Chem. Soc._, **84**, 2499 (1962)

[2] G. Booth and J. Chatt, _Proc. Chem. Soc._, **1961**, 67

[3] N. L. Bauld, _J. Am. Chem. Soc._, **84**, 4345 (1962)

The details of B cannot be specified with any assurance, but a bi-molecular reaction of I molecules seems to be involved, since free aroyl and aryl radicals could not be detected; yields of aril were not sub-stantially diminished when the reactions were run in the presence of large excesses of cyclohexene and benzaldehyde, two acyl radical traps. Process (3) seems most likely.

$$2\text{"I"} \longrightarrow \quad\quad \longrightarrow (ArCO)_2 + (CO)_2Ni \underset{I}{\overset{I}{\diagdown\diagup}} Ni(CO)_n \xrightarrow{etc.}$$

(3)
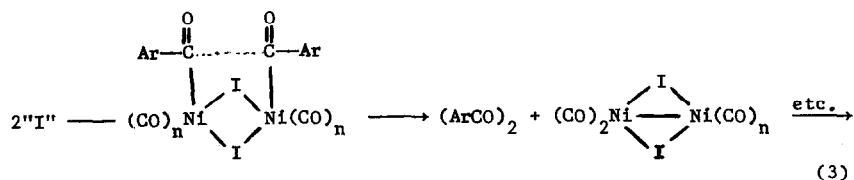
Our suggestion for C follows in detail the cited analogy (4). This

(4)
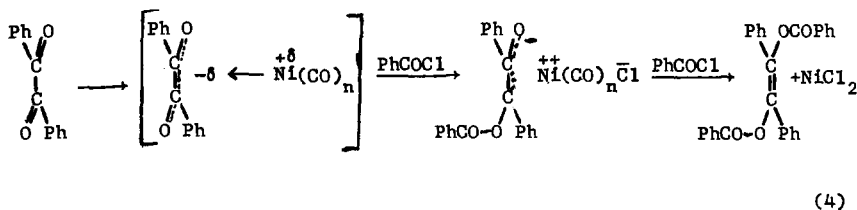
formulation is strongly supported by three observations: (1) benzil is converted to the endiol diester by nickel carbonyl and benzoyl chloride in THF (2) benzil and nickel carbonyl form a transient red complex upon refluxing in THF (3) the endiol diester formed from benzoyl chloride is 90% cis when prepared in hexane but 60% trans from THF. Item (1) indi-cates benzil is a precursor for the endiol diester. The remaining items show a detailed similarity to the cited analogy, where the cis ester is also strongly preferred in nonpolar solvents and the trans fraction in-creases with solvent polarity, as fixed by the geometry of the metal → benzil adduct.

With the hindered iodides aroylation of the aril ← nickel carbonyl complex cannot be effected by an acid chloride molecule originally present. A likely aroylating agent is I, which already has been averred to aroylate alcohols. The greater tendency of the hindered iodides to react further via path C is unexpected. However, Chatt and Shaw[4] have shown that bistriethylphosphine arylnickel bromides are stable enough to isolate when Ar = o-tolyl and 1-naphthyl, but not when Ar = phenyl or m- or p-substituted phenyl groups. It is inferred that bimolecular couplings may be sensitive to steric effects, thereby allowing alternate reactions to compete more successfully.

[4]J. Chatt and B. L. Shaw, J. Chem. Soc., 1960, 1718