The Reaction of Arylcoppers with Diazo-compounds

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Summary The reaction of an arylcopper with an aliphatic diazo-compound gives the corresponding aryl derivative of the aliphatic group.

SINCE the publication by Costa *et al.*[1] on phenylcopper, a number of studies of its reactions have been reported.[2] Recently, Cairncross and Sheppard[3] reported that the reaction of ethyl diazoacetate and pentafluorophenylcopper, followed by hydrolysis, afforded ethyl (pentafluorophenyl)-acetate by formal insertion of a carbene into the carbon–copper bond (eqn. 1).

$$C_6F_5Cu + N_2CH{\cdot}CO_2Et \xrightarrow{\text{hydrolysis}} C_6F_5{\cdot}CH_2{\cdot}CO_2Et \qquad (1)$$

In connection with our studies on the reactions of diazo-compounds with copper-containing compounds,[4] we found that the reaction between arylcoppers and diazo-compounds could be used to substitute an aromatic ring (eqn. 2).

$$ArCu + N_2CR^1R^2 \xrightarrow{\text{hydrolysis}} ArCHR^1R^2 \qquad (2)$$

As a general procedure, an ethereal suspension of arylcopper was prepared from the reaction of ethereal aryllithium (from aryl bromide and lithium) with copper(I) bromide (molar ratio 0·98:1) at −15 to −17° under nitrogen.[1]. The reaction of the arylcopper with diazo-compound was performed at −17° to room temperature with 1·43 moles of the copper compound per mole of diazo-compound. When evolution of nitrogen had ceased, the reaction mixture was hydrolysed with dilute HCl. (See footnote to Table.) The results are summarized in the Table. In reactions 1 and 5, ethyl maleate was obtained as by-product in 38·8 and 40·0% yield, respectively.

Arylcoppers permit the use of diazo-compounds containing such functional groups as ester or carbonyl, unlike aryllithiums; no compound could be isolated in a pure state from the reaction of phenyl-lithium and ethyl diazoacetate. The reaction of phenyl-lithium and diphenyldiazomethane afforded benzophenone phenylhydrazone and triphenylmethanol in a ratio of 3·5:1. It should be noted that 4-nitrodeoxybenzoin, previously available only from complicated sequences of reactions,[5] can easily be prepared by the use of the reaction 4.

TABLE

Reaction	Diazo-compound	Copper compound	Reaction temperature	Product	Yield
1	$N_2CH{\cdot}CO_2Et$	PhCu	−15 to −17°	$PhCH_2{\cdot}CO_2Et$	51·5
2	$N_2CH{\cdot}COPh$	PhCu	−15 to −17°	$PhCH_2{\cdot}COPh$	34·8
3[a]	N_2Ph_2	PhCu	room temp.	Ph_3CH	41·0
				Ph_3COH	38·5
4	$N_2CH{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$-*p*	PhCu	−15 to −17°	*p*-$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Ph$	86·5
5	$N_2CH{\cdot}CO_2Et$	*p*-MeC_6H_4Cu	−15 to −17°	*p*-$MeC_6H_4{\cdot}CH_2{\cdot}CO_2Et$	45·5
6	$N_2CH{\cdot}COPh$	*p*-MeC_6H_4Cu	−15 to −17°	*p*-$MeC_6H_4{\cdot}CH_2{\cdot}COPh$	31·0

[a] Triphenylmethane resulted when the reaction mixture was treated with anhydrous HCl under nitrogen, while triphenylmethanol resulted when oxygen gas was bubbled into the reaction mixture just before the hydrolysis with dilute HCl. The direct hydrolysis of the reaction mixture (without addition of oxygen) afforded an unidentified crystalline product, m.p. 178·5—182°.

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