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Cyclopentadienylcopper Reactions with Some Benzylic Halides, α-Haloketones and Pyrylium Ion

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Cyclopentadienylcopper(I) tributylphosphine ($CpCuPBu_3$) reacts with chlorotriphenylmethane and dibromodiphenylmethane under mild conditions to give cyclopentadienyltriphenylmethane and dicyclopentadienyldiphenylmethane, respectively. With 2-bromo-2-phenylacetophenone and trimethylpyrylium perchlorate it gives 2-cyclopentadienyl-2-phenylacetophenone and trimethylazulene, respectively. The mechanism of these reactions are briefly discussed.

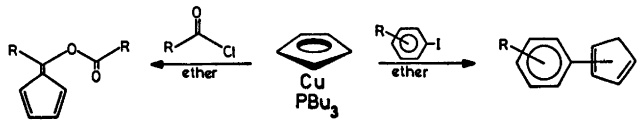
During the last decade organocopper reactions have been developed into valuable synthetic tools by several groups. Various lithium cuprates have been successfully applied as conjugate-addition reagents for the synthesis of natural products. Other organocopper compounds often generated "*in situ*" in the presence of suitable ligands also show promising utility as new and selective reagents. The field has been reviewed recently.[1–4] In contrast to most other organocopper compounds cyclopentadienylcopper(I) tributylphosphine is monomeric and is reasonably stable.[5–7] It is a weak base but rather reactive towards organic halides. Previously we have reported on the reactions of $CpCuPBu_3$ with iodoarenes [8,9] and with acid chlorides [10] to give arylcyclopentadienes and acyloxyfulvenes, respectively (Scheme 1).

The reactivity of $CpCuPBu_3$ towards these organic halides has prompted us to investigate its reaction with other organic halides.

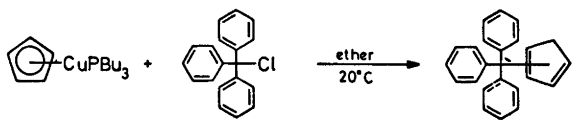
RESULTS AND DISCUSSION

Cyclopentadienylcopper(I) tributylphosphine ($CpCuPBu_3$) reacts at room temperature with chlorotriphenylmethane in ether to give cyclopentadienyltriphenylmethane in a good yield (Scheme 2). The product is a mixture of isomers with the cyclopentadienyl ring bonded in the 1- and 2-positions. A report on an analogous reaction with nickelocene has been published.[11]

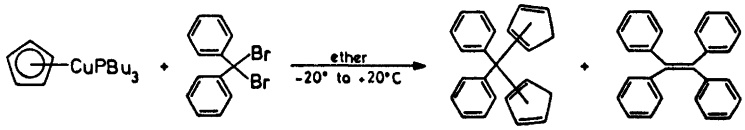
More interesting is the reaction of $CpCuPBu_3$ with dibromodiphenylmethane which gives dicyclopentadienyldiphenylmethane and tetraphenylethene (Scheme 3).



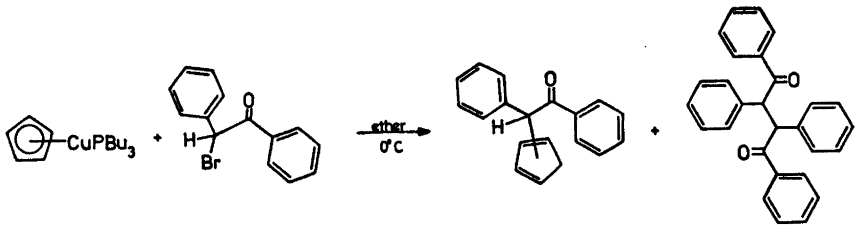
Scheme 1.



Scheme 2.



Scheme 3.



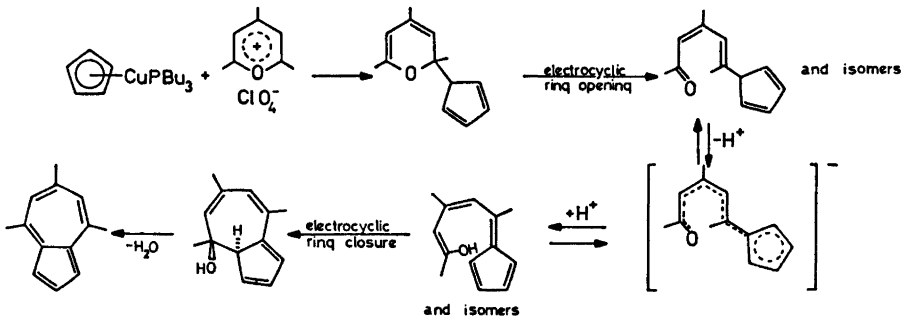
Scheme 4.

In the reaction between $CpCuPBu_3$ and dibromodiphenylmethane two reaction paths with different mechanisms seem to compete. One leads to tetraphenylethene *via* an initial one-electron transfer reaction followed by a radical dimerisation or possibly by a carbene dimerisation. The other reaction path leads to dicyclopentadienyldiphenylmethane by a route that is more likely to involve an oxidative addition of a carbon-bromine bond to copper or a nucleophilic substitution of bromine by a cyclopentadienyl group originally bonded to copper.

We have also reacted $CpCuPBu_3$ with various α-halocarbonyl compounds. Reduction and reductive dimerisation of the α-halocarbonyl compounds occur frequently. However 2-bromo-2-phenylacetophenone reacts with $CpCuPBu_3$ to give 2-cyclopentadienyl-2-phenylacetophenone as the major product, together with some 1,2,3,4-tetraphenylbutan-1,4-dione (Scheme 4).

So far the reactions described have been specific for cyclopentadienylcopper or in a few cases nickelocene. However, other less specific reactions can still be of some interest when discussing reaction mechanisms. Cyclopentadienyl sodium is known to react with trimethylpyrylium perchlorate to give trimethylazulene in 60 % yield.[14] No detailed mechanism has been proposed for this reaction, although the initial attack of a cyclopentadienide ion on the pyrylium ring and a subsequent ring opening has several analogies. With trimethylpyrylium perchlorate, $CpCuPBu_3$ gives trimethylazulene in 60 % yield. The following reaction scheme is suggested since $CpCuPBu_3$ is a weak base and is not expected to undergo metal-hydrogen exchange reactions (Scheme 5).

The initial nucleophilic attack is followed by an electrocyclic ring opening (6 π-system) to give a mixture of ketones. These are isomerized to the enols one of which can undergo an un-



Scheme 5.

usual electrocyclic ring closure (10 π-system) to form the azulene skeleton. The last reaction is the elimination of water "releasing" the resonance energy of azulene.

We have found that $CpCuPBu_3$ is a rather selective reagent for the introduction of cyclopentadienyl groups by reaction with organic halides, such as iodoarenes, acid chlorides, benzyl halides and some α-halocarbonyl compounds. The reactions are run under neutral conditions in ether from -25 °C to reflux.

Several mechanisms have been proposed for organocopper reactions, the more common ones being the oxidative addition of a substrate to an organocopper compound followed by reductive elimination,[12,13] one-electron transfer reaction with oxidation and reduction of copper(I) and copper(II) species [18] and "copper-assisted nucleophilic substitution" where the organic part of the organocopper compound acts as a nucleophile.[19]

No single mechanism seems to fit our experimental results. Tetraphenylethylene and tetraphenylbutandione are most likely formed *via* one-electron transfer processes whereas nucleophilic substitutions or alternatively oxidative additions occur during the formation of the cyclopentadienyl derivatives.

EXPERIMENTAL

Melting points were determined on a Reichert Termophan hot stage melting point apparatus. NMR spectra were recorded on a Varian A60 or a Bruker WH 270, UV spectra on a Beckman DK-2A, IR spectra on a Beckman IR-10 and MS on an AEI MS 902 instrument.

Cyclopentadienylcopper(I) tributylphosphine ($CpCuPBu_3$) was prepared by the method suggested by Cotton and Marks.[15] All reactions with $CpCuPBu_3$ were run in a dried apparatus under dry, oxygen-free nitrogen.

$CpCuPBu_3$ and chlorotriphenylmethane. A solution of chlorotriphenylmethane (0.01 mol) in ether (50 ml) was added dropwise to a freshly prepared solution of $CpCuPBu_3$ (0.01 mol) in dry diethyl ether (200 ml). The mixture was stirred at room temperature for 5 h. The white precipitate of cyclopentadienyltriphenylmethane (1.0 g) was formed slowly and collected. The filtrate was concentrated and chromatographed on silica gel (Merck. Kieselgel 60, 70–230 mesh ASTM) with tetrachloromethane as eluent to give more cyclopentadienyltriphenylmethane (0.8 g, m.p. 190–194 °C lit.[11] 199–200 °C, total yield 58 %). The product, which was identified by IR and NMR spectra, was an isomeric mixture of 1- and 2-triphenylmethylcyclopentadienes. NMR (270 MHz, $CDCl_3$): δ 7.29–7.15 (15, m, aromatic protons), 6.41, 6.34, 6.27, 6.21, and 6.06 (3, m, olefinic protons) and 3.03, 2.90 (2, m, methylene protons).

$CpCuPBu_3$ and dibromodiphenylmethane. A solution of dibromodiphenylmethane (0.01 mol) in ether (50 ml) was added dropwise to a freshly prepared solution of $CpCuPBu_3$ (0.02 mol) in ether (150 ml). The mixture was stirred for 15 h at -25 °C and placed in a refrigerator (+5 °C) for another 24 h. The precipitate was removed and the filtrate was concentrated to 10 % of the starting volume. A second filtration yielded tetraphenylethene (0.61 g). The resulting filtrate was evaporated and chromatographed on silica gel with tetrachloromethane giving an isomeric mixture of di(1,3-cyclopentadien-1-yl)- or di(1,4-cyclopentadien-1-yl),- and (1,3-cyclopentadien-1-yl)-(1,4-cyclopentadien-1-yl)diphenylmethane in a 3:2 ratio, as faintly yellow crystals (0.63 g, 21 %, m.p. 115–127 °C). NMR ($CDCl_3$): δ 7.25–7.15 (25, m, aromatic protons), 6.45–6.29 (10, m, cyclopentadienyl olefinic protons), 6.19 (1, sextet, cyclopentadienyl olefinic protons), 5.98 (3, quintet, cyclopentadienyl olefinic protons), 5.87 (1, quintet, cyclopentadienyl olefinic protons), 3.00 (6, quintet, methylene protons), 2.97 (2, q, methylene protons), 2.93 (2, q, methylene protons). IR (KBr): 3350 (s), 1598 (m), 1490 (s), 1448 (s), 1376 (m), 1350 (s), 1036 (m), 905 (s), 755 (m), 734 (s), 703 (s), 662 (s) and 652 cm^{-1} (s). MS (70 eV): *m/e* 296 (M^+, 100 %), 205 (42), 167 (53) and 155 (42).

Later fractions yielded more tetraphenylethene (0.72 g, total yield 43 %, m.p. 224–225 °C, lit.[17] 225 °C). The structure was checked by IR and NMR spectra. The same reaction, run at +25 °C, gave essentially the same results.

$CpCuPBu_3$ and 2-bromo-2-phenylacetophenone. A solution of 2-bromo-2-phenylacetophenone (0.036 mol) in ether (50 ml) was added to a freshly prepared solution of $CpCuPBu_3$ (0.036 mol) in ether (150 ml) at 0 °C. After 1.5 h the stirred mixture was placed in a refrigerator (+5 °C) for another 15 h. The reaction mixture was filtered, the filtrate evaporated, and the residue chromatographed on silica gel with tetrachloromethane/toluene as eluent to give an isomeric mixture of 2-(1,3-cyclopentadien-1-yl)- and 2-(1,4-cyclopentadien-1-yl)-2-phenylacetophenone as faint yellow crystals (4.39 g, 47 %, m.p. 73–76 °C). NMR ($CDCl_3$): δ 8.0 (4, m, aromatic protons), 7.3 (16, m, aromatic protons), 6.4 (4, m, cyclopentadienyl olefinic protons), 6.3 (1, m, cyclopentadienyl olefinic protons), 5.8 (2, m, methine proton) and 3.1 ppm (4, m, cyclopentadienyl methylene protons). IR (KBr): 3250 (m), 1715 (m), 1675 (s), 1598 (s), 1580 (s), 1496 (m), 1447 (m), 1215 (s), 765 (m), 725 (s), 702 (s) and 646 cm^{-1} (s). UV (EtOH): $\lambda = 207$ nm (log $\varepsilon = 4.34$) and 246 (4.15). MS (70 eV): *m/e* 260 (M^+, 8 %), 155 (19), 105 (base peak) and 72 (71). Abs.

mass; found 260.120, calc.for $C_{19}H_{16}O$ 260.120.

Later fractions yielded 1,2,3,4-tetraphenylbutan-1,4-dione (0.9 g, 13 %, m.p. 158 °C, lit.[15] 159–160 °C).

CpCuPBu$_3$ and trimethylpyrylium perchlorate. In a series of experiments trimethylpyrylium perchlorate (0.01 mol) was suspended in ether (100 ml) together with cyclopentadienylthallium and copper(I) iodide tributylphosphine (0.02, 0.01, 0.005, and 0.0025 mol) and stirred at room temperature for 48 h. The solvent was evaporated and the residue chromatographed on silica gel with dichloromethane as eluent to give violet 4,6,8-trimethylazulene (spectroscopic yields, based on CpCuPBu$_3$, were 14, 26, 56, and 60 %, respectively). The product was identified by its NMR and mass spectra.

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