

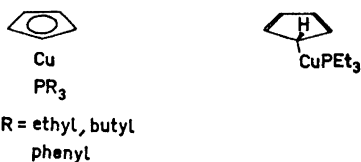
Reactions of Cyclopentadienylcopper(I) Tributylphosphine with Some Acid Chlorides

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Cyclopentadienylcopper(I) tributylphosphine reacts with benzoyl chloride to give 6-benzoyloxy-6-phenylfulvene. The organocopper compound reacts analogously with cinnamoyl chloride, phenylpropynoyl chloride and phthaloyl chloride.

Cyclopentadienylcopper(I) phosphine complexes are among the more stable organocopper compounds. Their structures have been determined recently by X-ray investigations,^{1,2} showing the copper atom to be equidistant from the five carbon atoms in the cyclopentadienyl ring. Infrared data had previously pointed to this highly symmetric structure³ (1).



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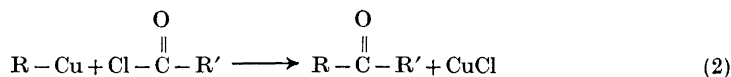
At low temperatures in sulphur dioxide solution, cyclopentadienylcopper(I) triethylphosphine is less symmetric and may contain a fluxional carbon-copper σ -bond, which undergoes a sequence of fast 1,2 or 1,3 shifts around the ring⁴ (2).

We have previously found that the reaction between cyclopentadienylcopper(I) tributylphosphine and some iodobenzenes gives phenylcyclopentadienes (reaction 1, R = 2- and 3-cyclopentadienyl).⁵

Alkyl-,⁶ alkenyl-,⁷ alkynyl-,⁸ and arylcopper⁹ compounds react analogously.



Alkyl-,^{10,11} alkynyl-,¹² and arylcopper^{13,14} compounds also react with acid chlorides to ketones (reaction 2).



R = alkyl, alkynyl, aryl

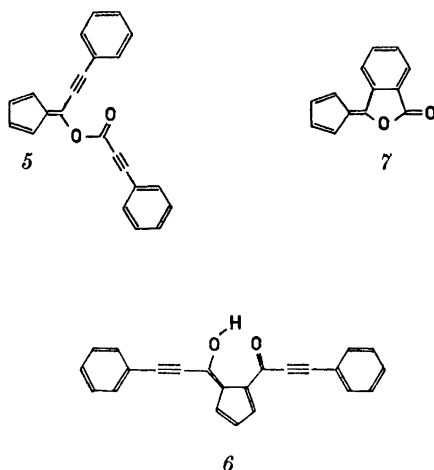
We have now investigated the reaction between cyclopentadienylcopper(I) tributylphosphine and some acid chlorides.

RESULTS

Cyclopentadienylcopper(I) tributylphosphine reacts smoothly with benzoyl chloride in ether at 0° to give a good yield (67 %) of 6-benzoyloxy-6-phenylfulvene, **3**, the enol ester of the primarily acylated cyclopentadiene. The analogous reaction with cinnamoyl chloride gives 6-cinnamoyloxy-6-styrylfulvene, **4**, but in a lower yield (26 %).



Phenylpropynoyl chloride reacts faster with cyclopentadienylcopper(I) tributylphosphine than do benzoyl or cinnamoyl chlorides. An unstable product, 6-phenylpropynoyloxy-6-phenylethynylfulvene, **5** (20%), was obtained when the reaction was run at -20°. A higher temperature (0°) resulted in a low yield of the enol of the diacylated cyclopentadiene, 1,2-diphenylpropynoylcyclopentadiene, **6** (6 %).



Cyclopentadienylcopper(I) tributylphosphine was also reacted with phthaloyl chloride to give a lactone, 3-cyclopentadienylidene-phthalide, 7 (11 %).

The compounds 4, 5, 6, and 7 are unstable in solution and give white precipitates on warming. In the case of 7, the mass spectrum of the precipitate indicates a dimer.

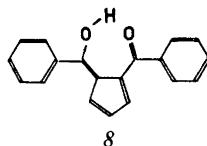
Preliminary attempts to react cyclopentadienylcopper(I) tributylphosphine with the following acid chlorides gave dark tarry product mixtures from which no pure compounds were isolated; acetyl, trimethylacetyl, trichloroacetyl, glutaroyl, oxalyl, thionyl, 3-methyl-2-butenoyl, thienoyl, and furanoyl chlorides.

p-Toluenesulphonyl chloride reacts with cyclopentadienylcopper(I) tributylphosphine and gives *p*-toluthiosulphonic acid *S*-*p*-tolyl ester. This compound has also been observed in the direct reaction of *p*-toluenesulphonyl chloride with copper powder in pyridine.¹⁵

DISCUSSION

Cyclopentadienylthallium, used to prepare the organocopper compound, does not react with benzoyl chloride in ether. Nor does a mixture of cyclopentadiene and benzoyl chloride in pyridine produce any coupling products.

In contrast to the copper compound, cyclopentadienyllithium reacts with benzoyl chloride to give the enol of 1,2-dibenzoylcyclopentadiene, 8.¹⁶



A similar reaction between cyclopentadienylsodium and acetyl chloride has been reported to give approximately equal amounts of the enol of 1,2-diacetylcyclopentadiene and 6-acetoxy-6-methylfulvene.¹⁷ The copper, lithium, and sodium derivatives of cyclopentadiene all give diacylated products when reacted with acid chlorides.

Acylation of ferrocene with aluminium chloride and excess acid chloride gives mainly 1,1'-diacylferrocene and only minor amounts of 1,2-diacylferrocene.¹⁸ The latter product is somewhat unexpected, as acyl groups usually deactivate the β carbon in electrophilic substitutions, but it is consistent with the experimental results obtained in the reactions with copper, lithium, and sodium derivatives of cyclopentadiene.

The initial product on acylation of a metal cyclopentadienide should be a cyclopentadiene ketone. There is little literature about this type of compound. Acetylcyclopentadiene has been described as a mixture of three tautomeric ketones. No enol was detected by IR and NMR.¹⁹ Cyclopentadienyl ketones should undergo metal-hydrogen exchange with metal cyclopentadienides. The resulting salt would then react with another molecule of acid chloride to give a diacylated cyclopentadiene.¹⁶ When the metal is lithium, *C*-acylation occurs¹⁶ and when it is copper the *O*-acylated product dominates. The *C*-acylated

product is thermodynamically more stable. Rearrangement of isomer 3 to isomer 8 does not, however, occur easily either on heating or under acidic or basic conditions. Some results have been reported of the reaction between an organic halide and the metal salt of cyclopentadienecarbaldehyde, leading to 6,6'-difulvenyl ether.²⁰

We consider that the influence of metals on the acylation of salts of cyclopentadienecarbonyl derivatives deserves further investigation. Metal-carbon and metal-oxygen interactions could be responsible for the changes observed in reaction rates for *C*- and *O*-acylation.

EXPERIMENTAL

Melting points were determined on a micro hot stage. Infrared spectra were recorded on a Perkin Elmer No. 421 spectrometer, ultraviolet spectra with a Beckman DK 2 instrument, NMR spectra on a Varian A 60 A spectrometer (TMS internal standard), and mass spectra on an LKB 9000 instrument.

Reactions involving organometallic compounds were performed anhydrously under purified nitrogen. Diethyl ether was freshly distilled from lithium aluminium hydride. The acid chlorides were distilled before use. Cyclopentadienylcopper tributylphosphine was prepared from cyclopentadienylthallium as described earlier⁵ (*cf.* Ref. 21).

General procedure for the coupling reactions. A reaction flask (250 ml) fitted with a gas inlet tube and a magnetic stirrer was charged with acid chloride in dry diethyl ether (100 ml) at 0°. Cyclopentadienylcopper tributylphosphine in about 100 ml dry ether was added during 30 min. Orange or red colours presently appeared. The reactions were followed with thin-layer chromatography tests and were worked up when no acid chloride could be detected. Products were isolated by chromatography on silica gel (eluted with mixtures of carbon tetrachloride and methylene chloride).

Cyclopentadienylcopper tributylphosphine and benzoyl chloride. Cyclopentadienylcopper (about 12.5 mmol) was added to benzoyl chloride (10 mmol). Reaction time 23 h. Chromatography gave 6-phenyl-6-benzoyloxyfulvene, orange crystals, m.p. 95–101° (0.92 g, 67 %); recrystallized from glacial acetic acid. (Found: C 83.3; H 5.2. Calc.: C 83.2; H 5.1.) IR spectrum (KBr): carbonyl absorption at 1735 cm⁻¹. UV spectrum (ethanol) $\lambda = 234$ nm, $\epsilon = 34\,700$ l mol⁻¹ cm⁻¹, $\lambda = 304$ nm, $\epsilon = 35\,000$. NMR (CDCl₃) showed the fulvene protons as a singlet at $\tau = 3.49$ (relative area 4). Mass spectrum (70 eV) gave the molecular ion at $m/e = 274$ (22 %) and the base peak at $m/e = 105$ (ArCO⁺).

Cyclopentadienylcopper tributylphosphine and cinnamoyl chloride. Cyclopentadienylcopper (about 12.5 mmol) was added to cinnamoyl chloride (10 mmol). Reaction time 6.5 h. Chromatography gave 6-cinnamoyloxy-6-styrylfulvene, red crystals (0.42 g, 26 %) m.p. 112–120°, decomp.

IR spectrum (KBr): carbonyl absorption at 1730 cm⁻¹. UV spectrum (ethanol) $\lambda = 287$ nm, $\epsilon = 34\,600$ l mol⁻¹ cm⁻¹; $\lambda = 353$ nm, $\epsilon = 42\,200$. NMR (C₆D₆NO₂) showed the fulvene protons as a doublet at $\tau = 3.45$. Due to the low solubility of this and the compounds described below, no integrals could be recorded. Mass spectrum (20 eV) gave the molecular ion at $m/e = 326$ (24 %) and the base peak at $m/e = 131$ (ArCHCHCO⁺).

Cyclopentadienylcopper tributylphosphine and phthaloyl chloride. Cyclopentadienylcopper (about 25 mmol) was added to phthaloyl chloride (12.5 mmol). Reaction time 2.5 h. Chromatography and sublimation gave 3-cyclopentadienyldienephthalide, red crystals (0.26 g, 11 %) m.p. 75–80°, decomp. IR spectrum (KBr): carbonyl absorption at 1780 and 1800 cm⁻¹. Double carbonyl bands have also been observed for some other unsaturated lactones.²² UV spectrum (ethanol) $\lambda = 257$ nm, $\epsilon = 6700$ l mol⁻¹ cm⁻¹; $\lambda = 267$, $\epsilon = 6700$; $\lambda = 302$, $\epsilon = 12\,500$; $\lambda = 315$, $\epsilon = 14\,000$, $\lambda = 340$, $\epsilon = 16\,000$.

NMR (CCl₄) showed the fulvene protons as multiplets around $\tau = 3.24$ and 3.51. Mass spectrum (70 eV) gave the molecular ion at $m/e = 196$ (100 %). Attempted recrystallization of 3-cyclopentadienyldienephthalide, 7, in carbon tetrachloride, glacial acetic acid or nitrobenzene gave an insoluble yellow-white crystalline material. Mass spectrum (70 eV) was identical with that of 7 except for a small peak at $m/e = 392$ (1 %) corresponding to a dimer.

Cyclopentadienylcopper tributylphosphine and phenylpropynoyl chloride. Cyclopentadienylcopper (about 12.5 mmol) was added to phenylpropynoyl chloride (10 mmol) at -20° . Reaction time 2.8 h. Chromatography gave 6-phenylpropynoyloxy-6-phenylethynylfulvene, impure red crystals (0.33 g, 20 %). Infrared (neat): carbonyl absorption at 1725 cm^{-1} . NMR ($\text{C}_6\text{D}_6\text{NO}_2$) showed the fulvene protons as a doublet at $\tau = 3.51$. Mass spectrum (20 eV) gave the molecular ion at $m/e = 322$ (1 %) and the base peak at $m/e = 129$ (ArCCCO^+).

The same reaction run 4.5 h at 0° gave the enol of 1,2-diphenylpropynoylcyclopentadiene, 6, red crystals (0.10 g, 6 %), m.p. $135-145^{\circ}$, decomp. NMR (CCl_4) gave a triplet at $\tau = 3.56$ and a complex region between $\tau = 2.30$ and 2.85 . The NMR of 6-hydroxy-2-fulvenecarbaldehyde (CCl_4) has been reported to show the fulvene protons as a triplet at $\tau = 3.63$ and a doublet at $\tau = 2.83$.²³ Mass spectrum (70 eV) showed the molecular ion at $m/e = 322$ (100 %), and $m/e = 321$ (62 %), and $m/e = 129$ (30 %, ArCCCO^+).

Cyclopentadienylcopper tributylphosphine and p-toluenesulfonylchloride. Cyclopentadienylcopper (about 10 mmol) was added to *p*-toluenesulfonylchloride (10 mmol). A white precipitate presently formed. The IR spectrum (KBr) of the precipitate was in accordance with that of *p*-toluthiosulfonic acid-*S-p*-tolylester.²⁴ NMR (CDCl_3) showed no ethylenic protons. Mass spectrum (70 eV) gave the molecular ion at $m/e = 278$ (10 %).

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