On the Mechanism of the Reaction between Cyclopentadienyl (Tributylphosphine)copper(I) and Benzoyl Chlorides

OLOF WENNERSTRÖM and ILONA RASTON

Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, S-402 20 Göteborg, Sweden

Organocopper compounds have been developed into useful synthetic reagents in the last decade.[1,2] Cuprates are now the preferred reagents for conjugate additions, and other organocopper compounds also show interesting reactivity and selectivity.[2,3] The mechanisms of these reactions are not fully understood, but the structure of the reactive organocopper compounds in solution is important. Available data indicate that clusters are often present.[4,5]

Cyclopentadienyl (tributylphosphine)copper-(I) (CpCuPBu₃) reacts with a variety of organic halides to form new C–C bonds.[6-8] The compound is thermally relatively stable and soluble in ethereal solvents. It is monomeric in solution[9] in contrast to most other organocopper compounds but shows the same general reactivity and selectivity.

CpCuPBu₃ is thus an attractive model compound for kinetic studies. It reacts slowly with benzoyl chloride in ether at room temperature to give a fulvene which is easy to detect by its intense colour (Scheme 1).[7] The rate of this reaction for some *para*-substituted benzoyl chlorides has now been studied so that further information on the mechanism could be obtained.
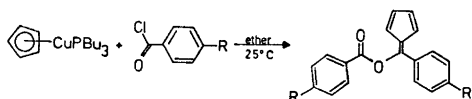

Scheme 1. R = H, CH₃, OCH₃, Cl.

Results and discussion. CpCuPBu₃ was reacted with *p*-methyl-, *p*-chloro-, *p*-methoxy- and unsubstituted benzoyl chloride in diethyl ether at 25 °C. The reactions were followed by UV spectroscopy. The observed relative rate constants for the second-order reactions were: benzoyl chloride 1, *p*-methylbenzoyl chloride 0.65, *p*-chlorobenzoyl chloride 2.8, and *p*-methoxybenzoyl chloride 0.30. The Hammett ϱ-value for the reaction was found to be $+1.7$ with a correlation coefficient of 0.89.

The formation of a fulvene from CpCuPBu₃ and benzoyl chlorides must occur in a multistep sequence in which the reaction steps are

not known with certainty. However, the assumption that the formation of the new C–C-bond is the rate-determining step is supported by the observed second-order kinetics and by the absence of any UV-absorbing intermediates in the reaction mixture. A suggested scheme for the overall reaction is shown in Scheme 2.
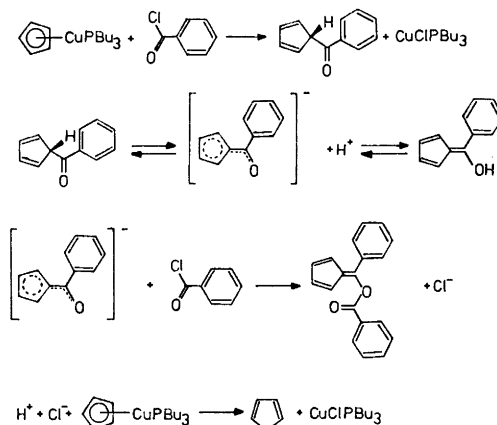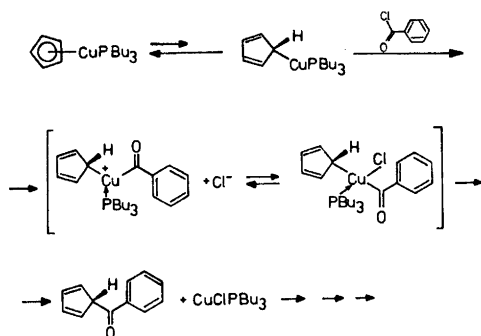

Scheme 2.

During the initial part of the reactions (conversion < 5 %) a small deviation from second-order kinetics was observed. The assumption that all reactions except the first one are very fast may not be strictly valid. At high conversions uncontrollable side-reactions, *e.g.* Diels-Alder reactions, may also be important.

The observed Hammett ϱ-value ($+1.7$) for the reaction between CpCuPBu₃ and benzoyl chlorides is typical for an S_N2 reaction.[10] Among the various mechanisms proposed for organocopper reactions,[1-3] nucleophilic substitution and a step-wise oxidative addition are likely in the present case. A copper-assisted S_N2 substitution of chlorine for a cyclopentadienyl group could well show the observed effect of substituents. Another reaction scheme, in which copper is the nucleophile which is inserted into the C–Cl bond in a two-step oxidative addition could also be consistent with the observed ϱ-value for the reaction (Scheme 3).

Experimental. All reactions were conducted in dried glass apparatus under oxygen-free nitrogen. Diethyl ether (Mallinckrodt, A.R.) was used as solvent. The acid chlorides were prepared by standard procedures and distilled before use. Cyclopentadienyl (tributylphosphine)-copper (I) was prepared from cyclopentadienylthallium and tributylphosphinecopper(I) iodide in diethyl ether.[9] The acid chlorides were added under stirring at 25 °C to the CpCuPBu₃-solution (100 ml). Small samples (*ca.* 30) were with-

Scheme 3.

drawn at intervals, diluted, and their UV spectra recorded (Bechman DK 2A).

The kinetic experiments were run with equivalent initial concentrations of $CpCuPBu_3$ and p-methoxy (0.2 and 0.1 M), p-methyl- (0.2 and 0.1 M), p-chloro- (0.1 and 0.05 M), and unsubstituted (0.1 and 0.05 M) benzoyl chloride, respectively. The concentration of the fulvene during the reaction was calculated directly from the UV spectrum of the small samples with minor corrections for the initial background absorption. Second-order kinetics, first-order in each reactant, was assumed and verified by the kinetic experiments. The following average rate constants, calculated from the rate equation $c_F/c_0(c_0 - 2c_F) = kt$ (c_F = concentration of the fulvene and c_0 = initial conc. of the reactants), were obtained; p-methoxy- (0.83×10^{-4} M^{-1} s^{-1}), p-methyl- (1.8×10^{-4} M^{-1} s^{-1}), p-chloro- (7.8×10^{-4} M^{-1} s^{-1}), and unsubstituted benzoyl chloride (2.8×10^{-4} M^{-1} s^{-1}). From the relative rate constant k/k_0 (k_0 = rate constant for the reaction with benzoyl chloride) and the σ-values for the different substituents,[11] the Hammet ϱ-value for the reaction was calculated to be $+1.7$ with a correlation coefficient of 0.89. The different fulvenes were isolated as previously reported.[7]

*6-p-Tolyl-6-*p-*toluoyloxyfulvene*. UV(ethanol): 313 nm (ε 18 600) and 242 nm (ε 21 000). NMR (270 MHz, $CDCl_3$): δ 8.08 (2 H, d), 7.56 (2 H, d), 7.31 (2 H, d, J 8 Hz), 7.22 (2 H, d, J 8 Hz), aromatic protons, 6.52 – 6.49 (4 H, m) fulvene protons, 2.46 (3 H, s), and 2.38 (3 H, s) methyl protons. MS (65 eV): m/e 302 (3.3 %, M+), 119 (100), 91 (23), 69.5 (metastable 119→91), and 65 (7).

*6-p-Chlorophenyl-6-*p-*chlorobenzoyloxyfulvene*. UV (ethanol): 306 nm (ε 20 400) and 245 nm (ε 21 300). NMR ($CDCl_3$): δ 8.09 (2 H, t of d), 7.55 (2 H, t of d), 7.46 (2 H, t of d, J 8.5 and 2 Hz), 7.37 (2 H, t of d, J 8.5 and 2 Hz), aromatic protons, 6.54 – 6.40 (4 H, m), fulvene protons. MS (65 eV): m/e 344 (2 %), 342 (3, M+), 141 (33), 139 (100), 113 (8), 111 (23), 92 (5), and 75 (10).

*6-p-Anisyl-6-*p-*anisoyloxyfulvene*. UV (ethanol): 330 nm (ε 19 500) and 265 nm (20 500). NMR ($CDCl_3$): δ 8.13 (2 H, d), 7.61 (2 H, d), 6.95 (2 H, d, J 8.5 Hz), 6.90 (2 H, d, J 8.5 Hz), aromatic protons, 6.53 – 6.47 (4 H, m), fulvene protons, 3.84 (3 H, s), and 3.78 (3 H, s), methoxyl protons. MS (65 eV): m/e 334 (3 %, M+), 136 (10), 135 (100), 92 (10), and 77 (11).

1. Posner, G. H. *Org. React.* **19** (1972) 1.
2. Posner, G. H. *Org. React.* **22** (1974) 253.
3. Jukes, A. E. *Adv. Organometal. Chem.* **12** (1974) 215.
4. van Koten, G., Leusink, A. J. and Noltes, J. G. *J. Organometal. Chem.* **84** (1975) 117.
5. Pearson, R. G. and Gregory, C. D. *J. Am. Chem. Soc.* **98** (1976) 4098.
6. Nilsson, M., Wahren, R. and Wennerström, O. *Tetrahedron Lett.* (1970) 4583.
7. Lundin, R., Moberg, C., Wahren, R. and Wennerström, O. *Acta Chem. Scand.* **26** (1972) 2045.
8. Månsson, J.-E., Nilsson, M. and Wennerström, O. *Acta Chem. Scand. B* **31** (1977) 47.
9. Cotton, F. A. and Marks, T. J. *J. Am. Chem. Soc.* **92** (1970) 5114.
10. Kivinen, A. In Patai, S., Ed., *The Chemistry of Acyl Halides*, Wiley, London 1972, pp. 192 – 194.
11. Hammett, L. P. *Physical Organic Chemistry*, 2nd Ed., McGraw-Hill, New York 1970, Chapter 11.