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EFFECT OF THE REACTION CONDITIONS ON THE INTERACTION OF $C_5H_5Fe(CO)_2Ar$ WITH PHOSPHINES AND PHOSPHITES

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SUMMARY

The reaction of $C_5H_5Fe(CO)_2Ar$ with PR_3 in benzene is independent of the nature of aryl group and the phosphine, but depends on the reaction conditions. The photochemical reaction with PR_3 results in $C_5H_5Fe(CO)(PR_3)Ar$, while the thermal reaction leads to $C_5H_5Fe(CO)(PR_3)COAr$.

The reaction of $C_5H_5Fe(CO)_2Ar$ with $P(OC_6H_5)_3$ is again independent of the nature of the aryl group but depends on the reaction conditions.

RESULTS AND DISCUSSION

Reaction of σ-arylcyclopentadienyliron dicarbonyl derivatives with phosphines in benzene is independent of the nature of the aryl group and the phosphine but depends on the reaction conditions[1-4]*.

Irradiation of the iron dicarbonyl at room temperature with a UV-source of varying intensity [lamps PRK-4 (150 W) and PRK-2 (375 W)] resulted in the substitution of a CO group by phosphine with the formation of (I):

$$C_5H_5Fe(CO)_2Ar + PR_3 \xrightarrow[25^\circ]{h\nu} \underset{\text{(I)}}{C_5H_5Fe(CO)(PR_3)Ar} + CO \qquad (1)$$

The reaction proceeds faster with the higher intensity.

In benzene refluxing in the absence of UV-light irondicarbonyl gives the aroyl derivative (II) as the main product, whereas (I) is produced only in small amounts:

$$C_5H_5Fe(CO)_2Ar + PR_3 \xrightarrow{80^\circ} \underset{\text{(II)}}{C_5H_5Fe(CO)(PR_3)COAr} + \underset{\text{(I)}}{C_5H_5Fe(CO)(PR_3)Ar} \qquad (2)$$

Thermal reaction (2) is much slower than the photochemical one. For example, after refluxing for 20 to 30 h in benzene the starting dicarbonyl complex may be isolated unchanged whereas under intensive irradiation the photochemical reaction is completed in 2–3 h.

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* Ref. 4 does not mention that PRK-2 lamp was employed under rigid conditions.

We have also found that aroyl derivative (II) ($Ar = C_6H_5$) decarbonylated to (I) under irradiation in benzene:

$$\underset{\text{(II)}}{C_5H_5Fe(CO)(PR_3)COAr} \xrightarrow{h\nu} \underset{\text{(I)}}{C_5H_5Fe(CO)(PR_3)Ar} + CO \quad (3)$$

This reaction is practically instantaneous under more intensive irradiation and refluxing. The decarbonylation is much slower at the refluxing and less intensive irradiation.

Formation of aroyl derivative (II) ($Ar = C_6H_5$, C_6H_4F-*p*) from the aryl (I) does not occur however under the action of CO. The reaction then involves replacement of PR_3 by CO.

When the reaction of $C_5H_5Fe(CO)_2Ar$ with phosphines in benzene is conducted under simultaneous irradiation and refluxing the composition of the products is dependent upon the intensity of UV-light. Less intensive light (lamp PRK-4, 150 W) and refluxing of the reaction mixture in benzene provide products (I) and (II) with the former predominating.

$$C_5H_5Fe(CO)_2Ar + PR_3 \xrightarrow[80°]{h\nu,\ 150\ W}$$

$$\underset{\text{(I)}}{C_5H_5Fe(CO)(PR_3)Ar} + \underset{\text{(II)}}{C_5H_5Fe(CO)(PR_3)COAr} \quad (4)$$

With higher intensity irradiation (lamp PRK-2, 375 W) and refluxing benzene, only σ-aryl derivative was isolated (I)

$$C_5H_5Fe(CO)_2Ar + PR_3 \xrightarrow[80°]{h\nu,\ 375\ W} \underset{\text{(I)}}{C_5H_5Fe(CO)(PR_3)Ar} + CO \quad (5)$$

and the reaction was completed in 1–2 h.

Apparently, under more intensive irradiation and refluxing the reaction (5) is so fast that it superceeds the slower formation of (II) [reaction (2)] and even if the latter could ever form these conditions would provide its immediate decarbonylation to (I) [reaction (3)].

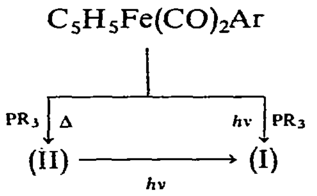
The products of reaction (4) may be explained in terms of two simultaneously proceeding reactions under these conditions: photochemical reaction giving (I) and the thermal yielding (II). Since less intensive irradiation does not provide complete decarbonylation of aroyl derivative (II), one can isolate both products in such case.

It is thus apparent that the aroyl derivative (II) can not originate from the aryl compound (I) via its carbonylation with carbon monoxide evolved in both the substitution and decomposition reactions of the starting dicarbonyl compound (usually occurring during the reaction).

Probably, the course of reaction of $C_5H_5Fe(CO)_2R'$ with phosphines in benzene for $R' = Ar$ is different from that for $R' = CH_3$ observed by Treichel *et al.*[5] in petroleum ether (90–100°) under reflux and UV-irradiation (150 W). They suggested formation of acyl derivative from the alkyl compound. [But for $C_5H_5Mo(CO)_3CH_3$ it was shown[6] that alkyl derivative results from the acyl compound].

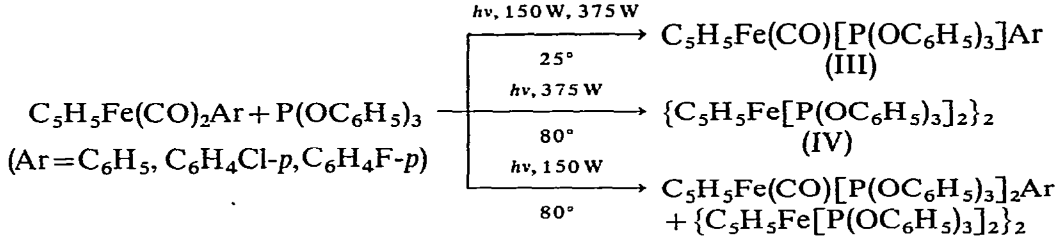
We assume that under our conditions both products (II) and (I) are formed directly from the dicarbonyl compound. The aryl compound (II) results from the thermal reaction (2) in accordance with the postulated mechanism[7]; the aryl compound (I) being generated in the photochemical reaction (1). Decarbonylation of the aroyl derivative (II) according to reaction (3) is an additional source for the compound (I).

The reactions occurring may be represented by the scheme:



We have also found that the previously investigated reaction of σ-arylcyclopentadienyliron dicarbonyl derivatives with triphenylphosphite in benzene[8] is independent of the nature of aryl group but depends upon intensity of the UV-source and the temperature.

At room temperature and UV-irradiation of any intensity formation of the exchange product (III) of one CO group with phosphite is observed only. Refluxing in benzene under more intensive irradiation affords the fully-substituted dimer (IV), whereas both products (III) and (IV) are formed under reflux and less intensive irradiation.



EXPERIMENTAL

Reaction of $C_5H_5Fe(CO)_2Ar$ with phosphines and phosphites

General procedure

The benzene solution of a mixture of $C_5H_5Fe(CO)_2Ar$ and phosphine was irradiated with the UV source located 10–15 cm away from the sample, or was refluxed without irradiation. The compounds obtained were separated by thin layer chromatography using alumina (benzene/light petroleum ether 1/1) and recrystallized from heptane.

Reactions of $C_5H_5Fe(CO)_2Ar$ with $P(OC_6H_5)_3$ and isolation of the products were conducted as described in ref. 8. All the reactions were carried out in an atmosphere of argon.

Reaction of $C_5H_5Fe(CO)_2C_6H_5$ with $P(C_6H_5)_3$

0.65 g of $C_5H_5Fe(CO)_2C_6H_5$ and 1.0 g of $P(C_6H_5)_3$ in 40 ml of benzene were irradiated for 2.5 h (lamp PRK-2) at 80°. 0.68 g (55%) of $C_5H_5Fe(CO)[P(C_6H_5)_3]$-$C_6H_5$ was isolated. Its m.p. and IR spectrum were identical to those described before[2].

Reaction of $C_5H_5Fe(CO)_2C_6H_5$ with $P(C_6H_4CH_3\text{-}p)_3$

(*a*). 0.55 g of $C_5H_5Fe(CO)_2C_6H_5$ and 0.77 g of $P(C_6H_4CH_3\text{-}p)_3$ in 40 ml of benzene were irradiated for 6.5 h (PRK-4) at 30°. 0.29 g (25%) of $C_5H_5FeCO[P(C_6H_4CH_3\text{-}p)_3]C_6H_5$ was isolated, red product, m.p. 171–173° (decompn.). (Found: C, 74.04, 73.92; H, 5.94, 5.94; Fe, 10.19, 9.98. $C_{33}H_{31}FeOP$ calcd.: C, 74.71; H, 5.85; Fe, 10.5%.) IR spectrum: ν(CO) 1923 cm^{-1} (terminal).

(*b*). 1.1 g of $C_5H_5Fe(CO)_2C_6H_5$ and 1.5 g of $P(C_6H_4CH_3\text{-}p)$ in 50 ml of benzene were irradiated for 2 h (PRK-2) at 80°. 2.3 g (96.5%) of $C_5H_5Fe(CO)[P(C_6H_4CH_3\text{-}p)_3]C_6H_5$ was obtained.

Reaction of $C_6H_5Fe(CO)_2C_6H_5$ with $P(C_6H_5)_2C_2H_5$

(*a*). 1.1 g of $C_5H_5Fe(CO)_2C_6H_5$ and 1.85 g of $P(C_6H_5)_2C_2H_5$ in 50 ml of benzene were irradiated for 3 h (PRK-2) at 80°. 1.68 g (87%) of $C_5H_5Fe(CO)[P(C_6H_5)_2C_2H_5]C_6H_5$ was obtained, red-yellow product, m.p. 119–121°. (Found: C, 70.96, 71.13; H, 5.97, 6.02; P, 6.45, 6.43. $C_{26}H_{25}FePO$ calcd.: C, 70.91; H, 5.68; P, 7.04%.) IR spectrum: ν(CO) 1916 cm^{-1} (terminal).

(*b*). 1.15 g of $C_5H_5Fe(CO)_2C_6H_5$ and 2 g of $P(C_6H_5)_2C_2H_5$ in 50 ml of benzene were irradiated for 14 h (PRK-4) at 80°. Two products were isolated: 1.04 g (52%) of $C_5H_5Fe(CO)[P(C_6H_5)_2C_2H_5]C_6H_5$ and 0.55 g (24.8%) of $C_5H_5Fe(CO)[P(C_6H_5)_2$- $C_5H_5Fe(CO)[P(C_6H_5)(C_2H_5)_2]COC_6H_5$ orange colored oily product IR spectrum: ν(CO) 1918 cm^{-1} (terminal), ν(CO) 1565 cm^{-1} (acyl).

Reaction of $C_5H_5Fe(CO)_2C_6H_5$ with $P(C_6H_5)(C_2H_5)_2$

0.86 g of $C_5H_5Fe(CO)_2C_6H_5$ and 0.98 g $P(C_6H_5)(C_2H_5)_2$ in 50 ml of benzene were irradiated for 11 h (PRK-4) at 80°. Two products were isolated: 0.81 g (61%) of $C_5H_5Fe(CO)[P(C_6H_5)(C_2H_5)_2]C_6H_5$, orange substance m.p. 140.5–141.5°. (Found: C, 66.63, 66.64; H, 6.79, 6.71; P, 8.04, 8.07. $C_{22}H_{25}FeOP$ calcd.: C, 67.36; H, 6.42; P, 7.90%.) IR spectrum: ν(CO) 1912 cm^{-1} (terminal), and 0.46 g (32.3%) of $C_5H_5Fe(CO)[P(C_6H_5)(C_2H_5)_2]COC_6H_5$ orange colored oily product IR spectrum: ν(CO) 1918 cm^{-1} (terminal), ν(CO) 1565 cm^{-1} (acyl).

Reaction of $C_5H_5Fe(CO)_2C_6H_4CH_3\text{-}p$ with $P(C_6H_5)_3$

1.38 g of $C_5H_5Fe(CO)_2C_6H_4CH_3\text{-}p$ and 1.8 g of $P(C_6H_5)_3$ in 60 ml of benzene were irradiated for 5.5 h (PRK-4) at 80°. Two compounds were isolated: 0.62 g (18.5%) of $C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_4CH_3\text{-}p$ and 0.45 g (12.60%) of $C_5H_5Fe(CO)[P(C_6H_5)_3]COC_6H_4CH_3\text{-}p$ yellow-orange product, m.p. 161–163° (decompn.). (Found: C, 72.57, 72.46; H, 5.22, 5.10. $C_{32}H_{27}FeO_2P$ calcd.: C, 72.46; H, 5.13%.) IR spectrum: ν(CO) 1922 cm^{-1} (terminal), ν(CO) 1573 cm^{-1} (acyl).

Reaction of $C_5H_5Fe(CO)_2C_6H_4Cl\text{-}p$ with $P(C_6H_5)_3$

0.2 g of analytically pure $C_5H_5Fe(CO)_2C_6H_4Cl\text{-}p$ and 0.36 g of $P(C_6H_5)_3$ in 30 ml of benzene were irradiated for 1 h (PRK-2) at 80°. 0.36 g (98.5%) of $C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_4Cl\text{-}p$ having m.p. and IR spectrum identical to those of an authentic sample[3] was obtained.

Reaction of $C_5H_5Fe(CO)_2C_6H_4F\text{-}p$ with $P(C_6H_5)_3$

1.18 g of $C_5H_5Fe(CO)_2C_6H_4F\text{-}p$ and 1.3 g of $P(C_6H_5)_3$ in 60 ml of benzene were irradiated for 6 h (PRK-4) at 80°. Two products were isolated. 0.7 g (32%) of $C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_4F\text{-}p$ and 0.18 g (7.84%) of $(C_5H_5Fe(CO)[P(C_6H_5)_3]COC_6H_4F\text{-}p$, yellow substance, m.p. 154.5–156°. (Found: C, 70.02, 70.66; H, 4.55, 4.34. $C_{31}H_{24}FFeO_2P$ calcd.: C, 69.68; H, 4.53%.) IR spectrum: ν(CO) 1923 cm^{-1} (terminal), ν(CO) 1562 cm^{-1} (acyl).

Reaction of $C_5H_5Fe(CO)_2C_6H_4F$-p with $P(C_2H_5)_3$.

0.45 g of $C_5H_5Fe(CO)_2C_6H_4F$-*p* and 0.2 g of $P(C_2H_5)_3$ in 40 ml of benzene were irradiated for 3 h (PRK-2) at 25–30°. The product was chromatographed on alumina column (benzene/light petroleum 1/4). 0.28 g (46%) of an orange colored oily product was isolated: $C_5H_5Fe(CO)[P(C_2H_5)_3]C_6H_4F$-*p*. IR spectrum ν(CO) 1911 cm^{-1} (terminal).

Reaction of $C_5H_5Fe(CO)_2C_6H_4F$-p with PFc_3 (Fc-ferrocenyl $C_5H_5FeC_5H_4$)

0.91 g of $C_5H_5Fe(CO)_2C_6H_4F$-*p* and 1.2 g of PFc_3 in 80 ml of benzene were irradiated for 1 h (PRK-2) at 30°. Apparently the reaction did not take place due to the poor solubility of PFc_3 in benzene. Irradiation was continued at 80° for 1.5 h. 1.07 g (38.6%) of yellow $C_5H_5Fe(CO)(PFc_3)C_6H_4F$-*p* was obtained, m.p. 140° (decompn.). (Found: C, 60.10, 60.57; H, 4.46, 4.21; Fe, 2.38, 2.39. $C_{42}H_{36}FFe_4OP$ calcd.: C, 60.72; H, 4.33; Fe, 2.29%.) IR spectrum: ν(CO) 1921 cm^{-1} (terminal).

Reaction of $C_5H_5Fe(CO)_2C_6H_5$ with $P(C_6H_5)_3$ under reflux in benzene without irradiation

0.8 g of $C_5H_5Fe(CO)_2C_6H_5$ and 1.2 g of $P(C_6H_5)_3$ in 40 ml of benzene were refluxed for 22 h. 0.48 g (29.2%) of $C_5H_5Fe(CO)[P(C_6H_5)_3]COC_6H_5$ and 0.03 g (1.95%) of $C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_5$ were isolated. The IR spectra and melting points were identical to those described before[2].

Reaction of $C_5H_5Fe(CO)_2C_6H_5$ with $P(OC_6H_5)_3$

1.59 g of $C_5H_5Fe(CO)_2C_6H_5$ and 3.88 g of $P(OC_6H_5)_3$ in 50 ml of benzene were irradiated for 9 h (PRK-4) at 80°. The products isolated were: 0.87 g of $C_5H_5Fe(CO)[P(OC_6H_5)_3]C_6H_5$ (26%) and 1.59% (34.2%) of $\{C_5H_5Fe[P(OC_6H_5)_3]_2\}_2$. Both products had m.p.'s and IR spectra identical to those described before[8].

Reaction of $C_5H_5Fe(CO)_2C_6H_4F$-p with $P(OC_6H_5)_3$

0.78 g of $C_5H_5Fe(CO)_2C_6H_4F$-*p* and 1.8 g of $P(OC_6H_5)_3$ in 50 ml of benzene were irradiated for 5.5 h (PRK-2) at 25–30°. 0.672 g (42.8%) of $C_5H_5Fe(CO)[P(OC_6H_5)_3]C_6H_4F$-*p* was obtained, yellow product, m.p. 130–132°. (Found: C, 65.15, 65.10; H, 4.55, 4.49; F, 3.24, 3.59. $C_{30}H_{24}FFeO_4P$ calcd.: C, 65.0; H, 4.33; F, 3.45%.) IR spectrum: ν(CO) 1949 cm^{-1} (terminal).

1 g of $C_5H_5Fe(CO)_2C_6H_4F$-*p* and 2.35 g of $P(OC_6H_5)_3$ in 50 ml of benzene were irradiated for 6.5 h (PRK-4) at 80°. Two compounds were isolated. 0.6 g (29.5%) of $C_5H_5Fe(CO)[P(OC_6H_5)_3]C_6H_4F$-*p* and 0.96 g (35.3%) of $\{C_5H_5Fe[P(OC_6H_5)_3]_2\}_2$ identical by their m.p.'s and IR spectra to those described before[8].

Decarbonylation of $C_5H_5Fe(CO)[P(C_6H_5)_3]COC_6H_5$

0.2 g of $C_5H_5Fe(CO)[P(C_6H_5)_3]COC_6H_5$ in 30 ml of benzene was irradiated at 25° (PRK-4 located 12 cm from the sample) for 5 h. Traces of $C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_5$ were detected by thin layer chromatography. Irradiation was continued for 5 h at 80°. Chromatography using (benzene/light petroleum 2/8) gave 0.050 g (25%) of $C_5H_5Fe(CO)[P(C_6H_5)_3]COC_6H_5$ and 0.025 g (17.7%) of $C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_5$.

0.14 g of $C_5H_5Fe(CO)[P(C_6H_5)_3]COC_6H_5$ in 25 ml of benzene was irradiated at 80° (PRK-2 located 15 cm from the sample) for 30 min. $C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_5$ was detected in 2 min. No starting material was found in the mixture after 30 min. 0.04 g (30.3%) of $C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_5$ was isolated having m.p. and IR spectrum identical to those described before[2].

Carbonylation of $C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_4F$-*p*

Carbon monoxide was bubbled through a solution of 0.26 g of $C_5H_5Fe(CO)$-$[P(C_6H_5)_3]C_6H_4F$-*p* in 30 ml of benzene under reflux and irradiation with PRK-4 for 11 h. 0.042 g (16.2%) of $C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_4F$-*p* and 0.093 g (66.4%) of $C_5H_5Fe(CO)_2C_6H_4F$-*p* were obtained and identified by thin layer chromatography.

Carbonylation of $C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_5$

Carbon monoxide was bubbled through a solution of 0.25 g of $C_5H_5Fe(CO)$-$[P(C_6H_5)_3]C_6H_5$ in 30 ml of benzene under reflux and irradiation (PRK-4) for 7 h. 0.12 g of $C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_5$ (48%) and traces of $C_5H_5Fe(CO)_2C_6H_5$ were isolated. The last product probably decomposed.

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