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ORGANOMETALLIC DERIVATIVES

VII*. THE LITHIATION OF (FERROCENYLMETHYL)DIPHENYLPHOSPHINE OXIDE AND SULPHIDE

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Summary

(Ferrocenylmethyl)diphenylphosphine oxide and sulphide have been lithiated with n-butyllithium under mild conditions. Metallation occurred on the α-carbon atom with both the oxide and the sulphide, and condensation of the lithiated intermediates with electrophiles gave a series of α-substituted ferrocenylmethylphosphines.

Introduction

Recently we have been investigating the formation and stability of α-ferrocenylcarbanions, compounds which previously had received little attention. Ferrocenylmethyl cyanide and ferrocenylmethyl phenyl sulphone were lithiated readily with n-butyllithium and condensation of the lithiated intermediates with electrophiles gave the corresponding α-disubstituted ferrocenylmethyl cyanides and sulphones [1,2]. The isolation of these α-substituted derivatives indicated that carbanions could be formed adjacent to the ferrocene nucleus provided an electron withdrawing group was present to assist in the delocalization of the negative charge.

In the benzene series the diphenylphosphine oxide group stabilized anion formation adjacent to itself in the lithiation of benzyldiphenylphosphine oxide [3]. Recently we have reported a convenient route to the corresponding ferrocene derivative (ferrocenylmethyl)diphenylphosphine oxide [4]. We now report the lithiation of this oxide (I) and the corresponding phosphine sulphide (IV, R = H).

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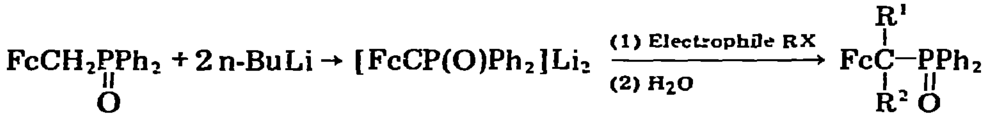
* For Part VI see ref. 4.

Results and discussion

The reaction of (ferrocenylmethyl)trimethylammonium iodide with diphenylphosphine in water gave (ferrocenylmethyl)diphenylphosphine, and treatment of this ferrocenylphosphine with aqueous hydrogen peroxide [4] or sulphur in benzene gave the corresponding oxide I and sulphide IV (R = H). The sulphide IV (R = H) was prepared also in good yield by the direct reaction of diphenylphosphine sulphide with (ferrocenylmethyl)trimethylammonium iodide.

The phosphine oxide I was treated with two mole equivalents of n-butyllithium at room temperature and the solution almost immediately turned deep red (Scheme 1). After thirty minutes the red solution was quenched with deuterium oxide and the PMR spectrum of the deuterated ferrocene showed that both the hydrogen atoms on the α-carbon atom had been removed by lithium. The ease of formation of the dicarbanion II was assisted presumably by charge delocalization onto the diphenylphosphine oxide group and also by the presence of the ferrocenyl group which behaved as a typical aromatic nucleus. The lithiated intermediate II was condensed with methyl iodide to give the α-dimethyl derivative III ($R^1 = R^2 = Me$). This compound was identical with an authentic sample of the dimethyl compound III ($R^1 = R^2 = Me$) prepared by the reaction of the tertiary alcohol 2-ferrocenylpropan-2-ol with diphenylphosphine [4]. This confirmed that the α-ferrocenylmethyl dicarbanion II was formed via lithiation of the oxide I. Condensation of the lithiated intermediate II with benzyl chloride gave the mono- and di-α-substituted ferrocenes III ($R^1 = CH_2Ph$, $R^2 = H$) and III ($R^1 = R^2 = CH_2Ph$). Similarly, reaction of the lithioferrocene II with butyl bromide and 1,2-dichloroethane gave the α-substituted ferrocenes III ($R^1 = Bu$, $R^2 = H$), III ($R^1 = R^2 = Bu$) and the cyclopropane V respectively (see Table 1).

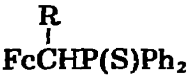
SCHEME 1



$$FcCH_2\underset{\underset{O}{\|}}{P}Ph_2 + 2\,n\text{-}BuLi \rightarrow [FcCP(O)Ph_2]Li_2 \xrightarrow[(2)\ H_2O]{(1)\ \text{Electrophile RX}} Fc\overset{R^1}{\underset{R^2}{C}}-\underset{\underset{O}{\|}}{P}Ph_2$$

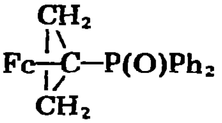
(I) (II) (III)

($Fc = C_{10}H_9Fe$)



$$Fc\overset{R}{C}HP(S)Ph_2$$

(IV)



(V)

$$Fc\overset{Me}{C}HNMe_3I$$

(VI)

The phosphine sulphide IV (R = H) was treated with two mole equivalents of n-butyllithium at room temperature and the colour of the solution immediately turned deep red. After twenty minutes the solution was quenched with deuterium oxide.

TABLE 1

YIELDS OF (FERROCENYLMETHYL)PHOSPHINES FROM THE REACTIONS OF LITHIATED (FERROCENYLMETHYL)DIPHENYLPHOSPHINE OXIDE AND SULPHIDE WITH SOME ELECTROPHILES

Reactants	Reaction time (h)	Products	Yield (%)
II + MeI	6.0[a]	III (R^1 = R^2 = Me)[c]	89
		III (R^1 = R^2 = Bu)	58
II + n-BuBr	24[a]	III (R^1 = H, R^2 = Bu)	40
II + $ClCH_2CH_2Cl$	18[a]	V	57
IV (R = Li) + $PhCH_2Cl$	0.5[b]	IV (R = CH_2Ph)	53
IV (R = Li) + BuBr	1.0[b]	IV (R = Bu)	44
IV (R = Li) + MeI	16[a]	IV (R = Me)	95

[a] Room temperature. [b] Heated under reflux. [c] M.p. and infrared identical with those of an authentic sample.

The PMR spectrum of the deuterated product showed that one of the hydrogen atoms on the α-carbon had been replaced by deuterium. The lithiated intermediate IV (R = Li) was condensed with methyl iodide to give the ferrocenylethane IV (R = Me). This compound was identical with a sample of the monomethyl derivative IV (R = Me) prepared by the reaction of diphenylphosphine sulphide with the ferrocenylammonium salt VI. This confirmed that monolithiation had occurred on the α-carbon atom of the sulphide IV (R = H) and not on the cyclopentadienyl or phenyl rings. The lithiated intermediate was condensed also with benzyl chloride and butyl bromide to give the α-substituted ferrocenes IV (R = CH_2Ph) and IV (R = Bu) respectively (see Table 1).

Experimental

For general directions see Part I [5] and Part VI [4].

Lithiation and deuteration of (ferrocenylmethyl)diphenylphosphine oxide

n-Butyllithium (0.00525 mol) was added to a yellow solution of (ferrocenylmethyl)diphenylphosphine oxide (1.0 g, 0.0025 mol) in a mixture of ether (60 ml) and tetrahydrofuran (40 ml), and the colour of the solution immediately turned deep red. The mixture was stirred at room temperature for 30 min and quenched by the addition of deuterium oxide, extracted with ether and the dried ($MgSO_4$) ether extracts were evaporated to leave a yellow solid. The solid was chromatographed on alumina and ether/methanol eluted the deuterated ferrocenylphosphine III (R^1 = R^2 = D), (0.78 g, 78%), PMR [τ, $(CD_3)_2CO$] 2.33 (10H, m, 2 × Ph) 5.95 and 6.10 (9H, s and m, ferrocene); the PMR spectrum [$(CD_3)_2CO$] of the undeuterated phosphine III (R^1 = R^2 = H) showed resonances at τ 2.34 (10H, m, 2 × Ph) 5.90 and 6.04 (9H, s and m, ferrocene) and a doublet centred at 6.42 (J 20.3 Hz) (2H, CH_2).

(Dibenzylferrocenylmethyl)diphenylphosphine oxide (III, R^1 = R^2 = CH_2Ph) and (benzylferrocenylmethyl)diphenylphosphine oxide (III, R^1 = H, R^2 = CH_2Ph)

The lithioferrocene II was prepared from the ferrocenylphosphine I (1.0 g, 0.0025 mol) and n-butyllithium (0.00525 mol). Benzyl chloride (1.27 g, 0.01

mol) was added slowly. The resultant mixture was heated under reflux for 1 h, poured into an aqueous slurry of sodium bicarbonate, extracted with ether and the dried ether extracts were evaporated to leave a red oil. The oil was chromatographed on alumina, ether/methanol eluted the dibenzyl derivative III (R^1 = R^2 = CH_2Ph) (0.455 g, 31%) which crystallized from ether/light petroleum as orange needles, m.p. 174-176° (found: C, 76.29; H, 5.82; Fe, 9.35. $C_{37}H_{33}FeOP$ calcd.: C, 76.55; H, 5.73; Fe, 9.62%). Ether/methanol then eluted the benzyl derivative III (R^1 = H, R^2 = CH_2Ph) (0.65 g, 53%) which crystallized from ether/light petroleum as yellow needles, m.p. 235-238° (found: C, 73.53; H, 5.60. $C_{30}H_{27}FeOP$ calcd.: C, 73.48; H, 5.55%).

Reaction of the lithioferrocene II with methyl iodide, 1,2-dichloroethane and n-butyl bromide

The reactions of the lithioferrocene II with methyl iodide, 1,2-dichloroethane and n-butyl bromide were carried out as described. The reaction times, products and yields are given in Table 1, and analyses and m.p.'s in Table 2.

(Ferrocenylmethyl)diphenylphosphine sulphide IV (R = H)

(a) Reaction of (ferrocenylmethyl)diphenylphosphine with sulphur. (Ferrocenylmethyl)diphenylphosphine (2.0 g, 0.0052 mol) was heated under reflux with sulphur (0.83 g, 0.026 mol) for 24 h in benzene. The benzene was evaporated to leave a red oil which was chromatographed on alumina. Ether eluted the product IV (R = H) (1.11 g, 51%) which crystallized from ether/light petroleum as yellow needles, m.p. 119-120° (found: C, 66.54; H, 5.09; S, 7.57; mol. wt., 416 by mass spectrometry. $C_{23}H_{21}FePS$ calcd.: C, 66.35; H, 5.08; S, 7.70%; mol. wt., 416).

(b) The reaction of (ferrocenylmethyl)trimethylammonium iodide with diphenylphosphine sulphide. (Ferrocenylmethyl)trimethylammonium iodide (3.85 g, 0.01 mol) and diphenylphosphine sulphide (5.0 g, 0.023 mol) [6] were added to water (100 ml) and heated under reflux for 3 h, and extracted with ether. The dried ($MgSO_4$) ether extracts were evaporated to leave a yellow solid which was chromatographed on alumina. Ether eluted the product IV (R = H) (3.5 g, 83%), which had identical m.p. and IR spectrum to those of the compound prepared as in (a).

(1-Ferrocenylethyl)diphenylphosphine sulphide (IV, R = Me)

The quaternary salt VI (1.5 g, 0.00375 mol) and diphenylphosphine sulphide (3.3 g, 0.015 mol) were added to water (50 ml) and heated under reflux for 3 h. The work-up was as described above and on chromatography ether eluted the product IV (R = Me) (1.15 g, 71%); its m.p. and IR spectrum were identical to those of the compound prepared from the lithio derivative IV (R = Li) and methyl iodide (see Table 1).

Lithiation and deuteration of (ferrocenylmethyl)diphenylphosphine sulphide

n-Butyllithium (0.0050 mol) was added to a yellow solution of (ferrocenylmethyl)diphenylphosphine sulphide (1.04 g, 0.0025 mol) in a mixture of ether (60 ml) and tetrahydrofuran (40 ml), the colour of the solution immediately turned red. The mixture was stirred at room temperature for 20 min and quenched

TABLE 2

ANALYTICAL DATA FOR SOME (FERROCENYLMETHYL)PHOSPHINES

Compound	M.p. (°C)	Empirical formula	Found (calcd.) (%)		
			C	H	Fe
III ($R^1 = R^2 = Bu$)	170-172	$C_{31}H_{37}FeOP$	72.81 (72.65)	7.49 (7.27)	10.67 (10.89)
III ($R^1 = H, R^2 = Bu$)	153-155	$C_{27}H_{29}FeOP$	71.55 (71.06)	6.60 (6.40)	
V	130-133	$C_{25}H_{23}FeOP$	70.50 (70.50)	5.36 (5.44)	13.96 (13.10)
IV ($R = CH_2Ph$)	158-160	$C_{30}H_{27}FePS$	70.54 (71.10)	5.67 (5.37)	9.46 (11.00)
IV (R = Bu)	132-134	$C_{27}H_{29}FePS$	68.40 (68.60)	6.10 (6.10)	11.46 (11.80)
IV (R = Me)	174-176	$C_{24}H_{23}FePS$	67.30 (67.00)	5.51 (5.38)	

by the addition of deuterium oxide, extracted with ether and the dried ($MgSO_4$) ether extracts were evaporated to leave a yellow solid. The solid was chromatographed on alumina, ether/light petroleum eluted an unstable purple oil (0.38 g) which was not characterised. Ether then eluted the deuterated ferrocenylphosphine IV (R = D) (0.64 g, 62%). PMR [τ, $CDCl_3$]: 2.48 (10H, m, 2 × Ph), 5.93 and 6.03 (9H, two overlapping singlets, ferrocene) and a doublet centred at 6.39 (*J* 12.0 Hz) (1H); the PMR spectrum (CCl_4) of the undeuterated phosphine IV (R = H) showed resonances at 2.43 (10H, m, 2 × Ph), 6.03 and 6.10 (9H, two overlapping singlets, ferrocene) and a doublet centred at 6.50 (*J* 12.1 Hz) (2H, CH_2).

Reaction of the lithioferrocene IV (R = Li) with benzyl chloride, methyl iodide and n-butyl bromide

The lithioferrocene IV (R = Li) was prepared as described and condensed with benzyl chloride, methyl iodide and n-butyl bromide. The reaction times, products and yields are given in Table 1 and the analyses and m.p.'s in Table 2.

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