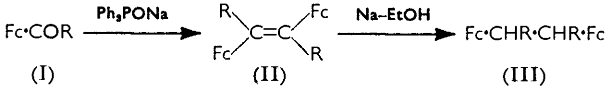
552. *Ferrocene Derivatives. Part XIII.* Some Ferrocenylethylene and -acetylene Derivatives.*

By P. L. Pauson and W. E. Watts.

Ferrocenecarboxyaldehyde and benzoylferrocene have been converted into 1,2-diferrocenylethylene derivatives; and (ferrocenylmethylene)triphenylphosphorane has been used for the preparation of a range of related olefins and acetylenes.

In an earlier paper[1] of this series we reported the use of ferrocenecarboxyaldehyde in a Wittig reaction with allyltriphenylphosphinylide to give ferrocenylbutadiene. We now report a series of reactions in which the ferrocenyl group is present as the phosphorane. We also report the use of ferrocenecarboxyaldehyde (I; R = H) and benzoylferrocene (I; R = Ph) in the related synthesis[2] of the symmetrical olefins (II; R = H or Ph) employing sodium diphenylphosphinite.



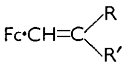
(Fc = ferrocenyl)

The olefins were characterised by reduction to the known saturated derivatives (III; R = H or Ph). 1,2-Diferrocenylethylene (II; R = H) was also obtained by a Wittig reaction between ferrocenecarboxyaldehyde (I; R = H) and the phosphorane (VI). That the olefin prepared by both these routes has the *trans*-configuration is indicated by the preparation of the *cis*-isomer described below.

The intermediate phosphorane (VI) was readily formed by the action of phenyl-lithium on the corresponding phosphonium salt (V), but was employed in the above and other reactions without isolation. The phosphonium salt (V) was itself obtained in quantitative yield from (ferrocenylmethyl)trimethylammonium iodide (IV) and triphenylphosphine. While our work was in progress, Helling and Schumacher[3] independently employed analogous reactions for the preparation of phosphonium salts.

$$\underset{\text{(IV)}}{\mathrm{Fc{\cdot}CH_2{\cdot}NMe_3{}^+I^-}} \xrightarrow[\mathrm{PPh_3}]{} \underset{\text{(V)}}{\mathrm{Fc{\cdot}CH_2{\cdot}PPh_3{}^+I^-}} \xrightarrow[\mathrm{PhLi}]{} \underset{\text{(VI)}}{\mathrm{Fc{\cdot}CH{:}PPh_3}}$$

Apart from the symmetrical olefin (II; R = H), the unsymmetrical olefins (VII; R = Ph, R′ = H; R = R′ = Ph; and R = C:CH, R′ = H) were prepared from the phosphorane (VI) by analogous reactions with benzaldehyde, benzophenone, and propynal, respectively. The acetylene (VII; R = C:CH, R′ = H) was converted into the dienediyne (VIII) by oxidative coupling,[4] and all these unsaturated derivatives (VII and VIII) were smoothly reduced to the corresponding saturated compounds with sodium and ethanol.

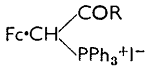


$$\mathrm{Fc{\cdot}CH{=}C(R)(R')}$$

(VII)

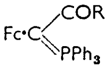
$$\mathrm{(Fc{\cdot}CH{=}CH{-}C{\equiv}C{-})_2}$$

(VIII)



$$\mathrm{Fc{\cdot}CH(COR)(PPh_3{}^+I^-)}$$

(IX)



$$\mathrm{Fc{\cdot}C(COR){:}PPh_3}$$

(X)

Phosphoranes react with acid chlorides to give, initially, the corresponding acyl-substituted phosphonium salts[5] and in the present case the benzoyl (IX; R = Ph) and the ferrocenoyl (IX; R = Fc) derivative were obtained in good yield. Further reaction

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* Part XII, Pauson and Watts, *J.*, 1962, 3880.

[1] Osgerby and Pauson, *J.*, 1961, 4604.

[2] Horner, Beck, and Toscano, *Chem. Ber.*, 1961, **94**, 1323.

[3] Helling and Schumacher, *Annalen*, 1961, **640**, 79.

[4] Eglinton and Galbraith, *J.*, 1959, 889.

[5] Trippett and Walker, *J.*, 1961, 1266.

of these products with the phosphorane (VI), to give the phosphonium salt (V) and acylphosphorane (X) (as observed in other cases[6]), could not have been a significant side reaction under our conditions. However, the acylphosphoranes (X; R = Ph or Fc) were very readily formed on treatment of the salts (IX; R = Ph or Fc) with dilute aqueous sodium hydroxide. Conversion of such acylphosphoranes into acetylenes by pyrolysis has been described by Gough and Trippett,[7] and application of their method readily afforded the acetylenes (XI; R = Ph or Fc).

$Fc{\cdot}C{\equiv}CR$	$Fc{\cdot}CH_2{\cdot}COR$	$Fc{\cdot}CH_2{\cdot}PPh_2$	$Fc{\cdot}CH_2{\cdot}C{\equiv}CR$
(XI)	(XII)	(XIII)	(XIV)

Catalytic hydrogenation converted diferrocenylacetylene (XI; R = Fc) into *cis*-1,2-diferrocenylethylene (II; R = H) which is isomerised to the more stable *trans*-isomer in presence of acid and can be further reduced to 1,2-diferrocenylethane (III; R = H). The ultraviolet absorption spectra of these stereoisomers (see Experimental section) bear close analogy to those of the *cis*- and *trans*-stilbenes.[8] The structure (II; R = H) has been tentatively assigned by Hauser *et al.*[9] to a by-product isolated from the Stevens rearrangement of (ferrocenylmethyl)trimethylammonium iodide, but the wide discrepancy between the melting points of their product and the above stereoisomers disproves their formulation.

The acylphosphonium salts (IX) were smoothly reduced[5] to the ferrocenylmethyl ketones (XII; R = Ph or Fc) with zinc and acetic acid. We have also reduced both the phosphonium salt (V) and the corresponding phosphorane (VI) with lithium aluminium hydride. As expected from analogy with published work[10] the former compound yielded methylferrocene and triphenylphosphine, whereas the latter gave the phosphine (XIII) by fission of a phenyl–phosphorus bond.

Finally, we include the preparation of an additional acetylenic derivative (XIV; R = Ph). This compound has independently been prepared by Schlögl,[11] but our method involving treatment of the quaternary ammonium salt (IV) with lithium phenylacetylide is more direct and should be applicable to a range of such derivatives (XIV). An excess of phenyl-lithium must be avoided in the preparation of the acetylide since it competes with the latter for the salt (IV), leading to Stevens rearrangement to (2-ferrocenylethyl)-dimethylamine together with formation of small amounts of benzylferrocene. Treatment of the methiodide of the last-mentioned amine with potassium t-butoxide in refluxing benzene gave an 81% yield of vinylferrocene (VII; R = R′ = H), a much improved conversion over those previously reported.[9,12]

EXPERIMENTAL

For general instructions see Part X.[13] Ultraviolet spectra were recorded for ethanol solutions unless stated otherwise.

(*Ferrocenylmethyl*)*triphenylphosphonium Iodide* (V).—(Ferrocenylmethyl)trimethylammonium iodide (20·5 g., 0·052 mole) was refluxed in ethanol (600 ml.) for 16 hr. with triphenylphosphine (26·2 g., 0·01 mole). The solution was then cooled and poured slowly into ether (800 ml.) with stirring. The precipitated (*ferrocenylmethyl*)*triphenylphosphonium iodide* (29·0 g., 97%) was filtered off and washed with ether. The salt crystallised from ethanol in dark

[6] Bestmann and Arnason, *Chem. Ber.*, 1962, **95**, 1513.

[7] Gough and Trippett, *J.*, 1962, 2333.

[8] Gillam and Stern, " An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold, London, 1957.

[9] Hauser, Lindsay, and Lednicer, *J. Org. Chem.*, 1958, **23**, 358.

[10] Bailey and Buckler, *J. Amer. Chem. Soc.*, 1959, **79**, 3567; Bailey, Buckler, and Marktscheffel, *J. Org. Chem.*, 1960, **25**, 1996; Saunders and Burchman, *Tetrahedron Letters*, 1959, No. 1, 8; Gough and Trippett, *J.*, 1961, 4263.

[11] Schlögl and Mohar, *Monatsh.*, 1962, **93**, 861.

[12] Lednicer, Lindsay, and Hauser, *J. Org. Chem.*, 1958, **23**, 653.

[13] Knox and Pauson, *J.*, 1961, 4610.

yellow leaflets, m. p. 254—256° (decomp.) (Found: C, 59·1; H, 5·0. $C_{29}H_{26}FeIP$ requires C, 59·2; H, 4·5%).

1,2-*Diferrocenyl*-1,2-*diphenylethylene* (II; R = Ph).—A mixture of triphenylphosphine oxide (10·30 g., 0·038 mole) and sodium hydride (0·90 g., 0·038 mole; as 50% dispersion in oil) were stirred for 1 hr. at 200°. Benzene vapour was evolved and a dark brown residue produced. Benzoylferrocene (8·70 g., 0·03 mole) was then added and the mixture stirred at 200° for a further 3 hr. The mixture was cooled and the deep red residue leached with hot methanol. The resulting solution was diluted with much water and extracted with benzene, the extract was washed with water, dried (Na_2SO_4), and evaporated to small bulk, and the residue was chromatographed on alumina. Benzene eluted 1,2-*diferrocenyl*-1,2-*diphenylethylene* (2·72 g., 47%) which crystallised from benzene in deep orange prisms, m. p. 278—280°, $\lambda_{max.}$ (in $CHCl_3$) 277 (log ε 4·13) and 322 mμ (log ε 4·21) (Found: C, 74·8; H, 5·4. $C_{34}H_{28}Fe_2$ requires C, 74·5; H, 5·15%). Benzene eluted an unidentified compound (0·94 g.), crystallising from benzene in red prisms, m. p. 248—250°, $\nu_{max.}$ (in KCl) 1669 cm.[1] (Found: C, 73·75, 73·8; H, 5·6, 5·5%). Benzene also eluted unchanged benzoylferrocene (2·3 g., 26%).

trans-1,2-*Diferrocenylethylene* (II; R = H).—(*a*) Reaction as above of ferrocenecarboxyaldehyde (2·14 g., 0·01 mole) with sodium diphenylphosphinite [prepared from triphenylphosphine oxide (5·56 g., 0·02 mole) and sodium hydride (0·60 g., 0·025 mole)] afforded trans-1,2-*diferrocenylethylene* (1·44 g., 73%), which crystallised from benzene as an orange powder, m. p. 265—267°, $\lambda_{max.}$ 210 (log ε 4·60), 246 (log ε 4·08), and 314 mμ (log ε 4·05) (Found: C, 67·1; H, 5·3. $C_{22}H_{20}Fe_2$ requires C, 66·7; H, 5·1%).

(*b*) (Ferrocenylmethyl)triphenylphosphonium iodide (5·88 g., 0·01 mole) was added to a stirred solution of phenyl-lithium prepared in ether (100 ml.) from lithium (0·02 g., 0·03 g.-atom) and bromobenzene (1·71 g., 0·011 mole). The mixture was stirred for 3 hr., whereafter formation of (ferrocenylmethylene)triphenylphosphorane was complete. A solution of ferrocenecarboxyaldehyde (2·50 g., 0·011 mole) in ether (50 ml.) was then added, giving immediately an orange precipitate. The mixture was stirred for 10 hr., then the ether distilled off and replaced by tetrahydrofuran, and the mixture refluxed for 2 hr. The solution was filtered and evaporated. The residue was dissolved in ligroin–benzene (1 : 4) and chromatographed on alumina. Benzene eluted *trans*-1,2-diferrocenylethylene (1·01 g., 26%) which, after crystallisation from benzene, had m. p. 265—267° and was identical with the compound described under (*a*).

1-*Ferrocenyl*-2-*phenylethylene* (VII; R = H, R′ = Ph).—A reaction of benzaldehyde (2·70 g., 0·025 mole) with (ferrocenylmethylene)triphenylphosphorane [prepared from (ferrocenylmethyl)triphenylphosphonium iodide (8·82 g., 0·015 mole) and phenyl-lithium (0·020 mole)] was carried out like the preceding experiment. Chromatography on alumina in ligroin gave 1-ferrocenyl-2-phenylethylene (2·50 g., 48%) which crystallised from ligroin in scarlet needles, m. p. 120—122° (lit.,[14] 119—120°), $\nu_{max.}$ (in CCl_4) 1637 cm.$^{-1}$ (C=C) (Found: C, 75·3; H, 5·7. Calc. for $C_{18}H_{16}Fe$: C, 75·0; H, 5·6%).

1-*Ferrocenyl*-2,2-*diphenylethylene* (VII; R = R′ = Ph). A solution of benzophenone (4·60 g., 0·025 mole) in ether (50 ml.) was added to an ether solution (150 ml.) of (ferrocenylmethylene)triphenylphosphorane (0·015 mole), prepared as previously described. The mixture was stirred for 48 hr. by which time a flocculent orange precipitate had been formed. The ether was distilled off and the residue heated in refluxing benzene (150 ml.) for 3 hr. The mixture was filtered, evaporated to small bulk, and chromatographed on alumina. Ligroin slowly eluted 1-*ferrocenyl*-2,2-*diphenylethylene* (3·65 g., 67%) which crystallised from ligroin in orange-yellow leaflets, m. p. 77—79°, $\nu_{max.}$ (in KCl) 1613 cm.$^{-1}$ (C=C) (Found: C, 78·6; H, 5·8. $C_{24}H_{20}Fe$ requires C, 79·1; H, 5·5%).

1-*Ferrocenylbut*-1-*en*-3-*yne* (VII; R = H, R′ = C≡H). Propynal (2·70 g., 0·05 mole) was added to a solution of (ferrocenylmethylene)triphenylphosphorane (0·01 mole) prepared in ether (150 ml.) as previously described. The brick red precipitate was stirred for 2 hr., then the ether was distilled off and the residue heated for 3 hr. in refluxing benzene (200 ml.). The mixture was filtered and extracted exhaustively with dilute aqueous ferric chloride. The combined aqueous extracts were washed with benzene and then the ferricinium salts present were reduced by addition of an excess of aqueous titanous chloride. The resulting solution was extracted with benzene, and the extract was washed with water, dried (Na_2SO_4), evaporated

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[14] Guan-Li, Sokolova, Leites, and Petrov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1962, 887.

to small bulk, and chromatographed on alumina. Ligroin slowly eluted 1-*ferrocenylbut*-1-*en*-3-*yne* (1·66 g., 71%) which sublimed at 80°/0·1 mm. as an orange powder, m. p. 61—63°, $\nu_{max.}$ (in CCl_4) 3289 (≡C–H), 2105 (C≡C), and 1610 cm.$^{-1}$ (C=C) (Found: C, 71·9, 71·2; H, 5·35, 4·8. $C_{14}H_{12}Fe$ requires C, 71·2; H, 5·1%).

1,8-*Diferrocenylocta*-1,7-*diene*-3,5-*diyne* (VIII).—1-Ferrocenylbut-1-en-3-yne (1·78 g., 7·5 mmoles) was dissolved in pyridine–ethanol–ether (1 : 1 : 4; 600 ml.), and the solution refluxed in air for 2 hr. with anhydrous cupric acetate (14 g.). The mixture was then cooled, filtered free from green cuprous salt, acidified with dilute sulphuric acid, and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated, and the residual crimson gum was chromatographed in benzene on alumina. Benzene eluted 1,8-*diferrocenylocta*-1,7-*diene*-3,5-*diyne* (0·76 g., 43%) which was deposited from ligroin–benzene solution as an orange-red powder m. p. 216—218° (decomp.; on a preheated block), $\nu_{max.}$ (in KCl) 2128 (C≡C) and 1587 cm.$^{-1}$ (C=C) (Found: C, 71·0; H, 4·8. $C_{28}H_{22}Fe_2$ requires C, 71·5; H, 4·7%).

1-*Ferrocenyl*-2-*phenylethane*.—1-Ferrocenyl-2-phenylethylene (0·20 g., 0·7 mmole) was dissolved in ethanol (50 ml.) and reduced with sodium (5 g.), the solvent being allowed to reflux gently, until the solution became yellow. The solution was poured into water (200 ml.) and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated and the residual yellow gum was chromatographed in ligroin on alumina. Ligroin eluted 1-ferrocenyl-2-phenylethane (0·163 g., 86%) which crystallised from ligroin in stout yellow needles, m. p. 59—61° (lit.,[15] 57—58°) (Found: C, 75·0, 75·1; H, 6·6. 6·3. Calc. for $C_{18}H_{18}Fe$: C, 74·5; H, 6·3%).

1,2-*Diferrocenylethane*.—(*a*) *trans*-1,2-Diferrocenylethylene (0·20 g., 0·7 mmole) was dissolved in benzene–ethanol (1 : 1; 200 ml.), reduced with sodium (5 g.), and worked up as described in the previous experiment. On chromatography, the product could not be separated completely from starting material. The first ligroin eluate yielded 1,2-diferrocenylethane which crystallised from ligroin in pale yellow needles, m. p. 193—195° (lit.,[16] 193—195°). The total yield of pure material was 0·12 g. (60%). Elution of the orange band with ligroin yielded a mixture of product and starting material.

(*b*) Diferrocenylacetylene (0·13 g., 3·3 mmoles) was stirred with a suspension of prereduced 10% palladium–charcoal (20 mg.) in tetrahydrofuran (15 ml.) in hydrogen until 15 ml. had been absorbed. The mixture was filtered and the pale yellow filtrate evaporated, leaving 1,2-diferrocenylethane (0·123 g., 93%), identical with the compound described under (*a*).

1,2-*Diferrocenyl*-1,2-*diphenylethane*.—1,2-Diferrocenyl-1,2-diphenylethylene (0·55 g., 1 mmole) was reduced in benzene–ethanol (1 : 1; 200 ml.) with sodium (10 g.) as previously described. Working up as before gave the powdery yellow diastereoisomers of 1,2-diferrocenyl-1,2-diphenylethane (0·47 g., 84%). Fractional crystallisation of the mixture from acetone separated the more soluble form, m. p. 217—220° (lit.,[17] 218—220°) from the less soluble, m. p. 278—280° (lit.,[17] 280°).

1-*Ferrocenyl*-2,2-*diphenylethane*.—1-Ferrocenyl-2,2-diphenylethylene (1·82 g., 5 mmoles) was reduced in ethanol (250 ml.) with sodium (15 g.) as described above. The gummy yellow product was chromatographed in ligroin on alumina. Ligroin eluted 1-*ferrocenyl*-2,2-*diphenylethane* (1·72 g., 94%), a viscous yellow oil which slowly crystallised to a waxy solid, m. p. 52—55° (Found: C, 79·3, 78·0; H, 6·3, 5·9. $C_{24}H_{22}Fe$ requires C, 78·7; H, 6·1%).

n-Butylferrocene.—1-Ferrocenylbut-1-en-3-yne was reduced in ethanol (100 ml.) with sodium (10 g.) as above. The product was chromatographed in ligroin on alumina. Ligroin eluted n-butylferrocene (0·46 g., 95%), n_D^{20} 1·5791 (lit.,[18] 1·5795).

1,8-*Diferrocenyloctane*.—1,8-Diferrocenylocta-1,7-diene-3,5-diyne (0·24 g., 0·5 mmole) was reduced in ethanol (100 ml.) with sodium (10 g.) as in previous experiments. The product was chromatographed in ligroin on alumina. Ligroin slowly eluted 1,8-*diferrocenyloctane* (0·19 g., 79%) which slowly sublimed at 180° (bath)/0·1 mm. as a gummy solid, m. p. ~40° (Found: C, 70·5; H, 6·6. $C_{28}H_{34}Fe_2$ requires C, 69·7; H, 7·1%).

(α-*Ferrocenylphenacyl*)*triphenylphosphonium Iodide* (IX; R = Ph).—Benzoyl chloride

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[15] Nesmeyanov, Perevalova, and Shilovtseva, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1961, 1982.

[16] Rinehart, Michejda, and Kittle, *J. Amer. Chem. Soc.*, 1959, **81**, 3162.

[17] Berger, McEwen, and Kleinberg, *J. Amer. Chem. Soc.*, 1961, **83**, 2274; cf. Nesmeyanov and Kritskaya, *Izvest. Akad. Nauk. S.S.S.R., Otdel khim. Nauk*, 1962, 352.

[18] Schlögl, Mohar, and Peterlik, *Monatsh.*, 1961, **92**, 921.

(4·22 g., 0·03 mole) was added to a solution of (ferrocenylmethylene)triphenylphosphorane (0·01 mole) prepared in ether (100 ml.) as previously described. A red precipitate was immediately formed and the solution was stirred for 2 hr. and then filtered. Crystallisation of the product from aqueous acetone afforded pure (*α-ferrocenylphenacyl*)*triphenylphosphonium iodide* (3·14 g., 46%) as deep red granules, m. p. 176—179° (with softening from 160°), $\nu_{max.}$ (in KCl) 1672 cm.$^{-1}$ (C=O) (Found: C, 62·3, 62·1; H, 4·7, 4·4. $C_{36}H_{30}FeIOP$ requires C, 62·45; H, 4·4%).

Ferrocenoyl Chloride.—To a solution of ferrocenecarboxylic acid (7·36 g., 0·032 mole) in benzene (250 ml.) under nitrogen, phosphorus pentachloride (6·65 g., 0·032 mole) was added in small portions in 3 hr. After rapid washing with dilute sodium hydroxide solution (twice) and water (six times) the dried (Na_2SO_4) solution was evaporated under reduced pressure. The oily residue was redissolved in pentane, filtered, and evaporated at 0°, to afford deep red crystals, m. p. 50—51° (lit.,[19] 49°), of the acid chloride (7·21 g., 91%).

(*α-Ferrocenoylferrocenylmethyl*)*triphenylphosphonium Iodide* (IX; R = Fc).—The compound was prepared in a similar manner to the benzoyl analogue described above, with ferrocenoyl chloride (7·21 g., 0·029 mole) in place of benzoyl chloride; it was obtained as a brick red precipitate (5·9 g.), m. p. 200—203° (decomp.), which was not purified.

Phenacylferrocene (XII; R = Ph).—(α-Ferrocenylphenacyl)triphenylphosphonium iodide (0·9 g., 1·3 mmoles) was dissolved in chloroform (20 ml.), and zinc dust (10 g.) was added. The mixture was heated to the b. p. and glacial acetic acid (30 ml.) added dropwise. After 1 hr. the mixture was poured into water and the organic layer separated and combined with chloroform extracts of the aqueous phase. The total extract was washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed in pentane on alumina. Pentane eluted triphenylphosphine (0·34 g., 100%), m. p. and mixed m. p. 80°. Pentane–ether (4 : 1) eluted *phenacylferrocene* (0·38 g., 95%) which sublimed at 120° (bath)/0·02 mm. as a pale yellow powder, m. p. 80—82°, $\nu_{max.}$ (in CCl_4) 1692 cm.$^{-1}$ (C=O) (Found: C, 71·3; H, 5·6. $C_{18}H_{16}FeO$ requires C, 71·1; H, 5·3%). The compound slowly decomposed in air to a brown amorphous solid.

"*Deoxyferrocoin*" (1,2-*Diferrocenylethanone*) (XII; R = Fc).—Crude (α-ferrocenoylferrocenylmethyl)triphenylphosphonium iodide (0·5 g., 0·62 mmole) was dissolved in chloroform (100 ml.) and reduced with zinc and acetic acid as in the preceding experiment. The mixture was worked up as above and the product chromatographed in ligroin–benzene (1 : 1). Ligroin–benzene (1 : 1) eluted triphenylphosphine (0·13 g., 80%), and benzene eluted deoxyferrocoin (0·19 g., 74%) which sublimed at 160° (bath)/0·02 mm. as a red powder, m. p. 158—160° (lit.,[16] 159—161°).

(*α-Ferrocenylphenacylidene*)*triphenylphosphorane* (X; R = Ph).—(α-Ferrocenylphenacyl)triphenylphosphonium iodide (3·46 g., 5 mmoles) was stirred gently in a two-phase system comprising 8% aqueous sodium hydroxide (250 ml.) and benzene (250 ml.), the organic layer becoming gradually yellow. After 6 hr. the benzene layer was separated, washed with water, dried (Na_2SO_4), and evaporated. The residual gum was chromatographed in benzene on alumina. Benzene eluted several minor bands which were not investigated and 19 : 1 ether–acetone eluted (*α-ferrocenylphenacylidene*)*triphenylphosphorane* (2·32 g., 82%) which crystallised from ligroin–benzene in red-brown needles, m. p. 193—196° $\nu_{max.}$ (in KCl) 1492 cm.$^{-1}$ (O=C–C=P) (Found: C, 76·4; H, 5·3. $C_{36}H_{29}FeOP$ requires C, 76·6; H, 5·2%).

(*α-Ferrocenoylferrocenylmethylene*)*triphenylphosphorane* (X; R = Fc).—The phosphorane was prepared from crude (α-ferrocenoylferrocenylmethyl)triphenylphosphonium iodide (8·0 g., 0·01 mole) as described in the preceding paragraph. On chromatography 19 : 1 ether–acetone eluted (*α-ferrocenoylferrocenylmethylene*)*triphenylphosphorane* (2·89 g.) which crystallised from benzene as an orange powder, m. p. 201—203° (decomp.). $\nu_{max.}$ (in KCl) 1479 cm.$^{-1}$ (O=C–C=P) (Found: C, 71·05; H, 5·05. $C_{40}H_{33}Fe_2OP$ requires C, 71·4; H, 4·95%).

(*Phenylethynyl*)*ferrocene* (XI; R = Ph).—(α-Ferrocenylphenacylidene)triphenylphosphorane (1·5 g.) was heated at 200—210°/0·02 mm. It melted and a red solid sublimed on a water-cooled probe. After 30 min. the apparatus was cooled, the products were dissolved in benzene, and the solution was chromatographed. Benzene eluted (*phenylethynyl*)*ferrocene* (0·65 g., 85%) which sublimed at 120° (bath)/0·02 mm. as an orange-yellow powder, m. p. 121—123°, $\nu_{max.}$ (in CCl_4) 2237 cm.$^{-1}$ (C≡C) (Found: C, 75·2; H, 5·1. $C_{18}H_{14}Fe$ requires C, 75·55; H, 4·9%).

1,2-*Diferrocenylacetylene* (XI; R = Fc).—(α-Ferrocenoylferrocenylmethylene)triphenylphosphorane (0·57 g.) was pyrolysed at 210°/0·02 mm. as described for the preceding experiment.

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[19] Lau and Hart, *J. Org. Chem.*, 1959, **24**, 280.

On chromatography benzene eluted 1,2-*diferrocenylacetylene* (0·365 g., 93%) which sublimed at 180° (bath)/0·02 mm. as a bronze-coloured solid, m. p. 244—246° (Found: C, 67·4; H, 5·0. $C_{22}H_{18}Fe_2$ requires C, 67·05; H, 4·6%).

cis-1,2-*Diferrocenylethylene* (cf. II; R = H).—Diferrocenylacetylene (0·197 g., 0·5 mmole) was added to a suspension of prereduced Lindlar catalyst [20] (0·20 g., 5%) in tetrahydrofuran (15 ml.) and the mixture stirred in hydrogen. Uptake began after 10 min. and ceased after 45 min. when *ca.* 10 ml. had been adsorbed. The mixture was filtered and evaporated at 0°. The residue was chromatographed in benzene on neutralised alumina. Benzene eluted cis-1,2-*diferrocenylethylene* (0·186 g., 94%) which sublimed at 160° (bath)/0·5 mm. as an orange powder, m. p. 195—198° (with softening from 140°), $\lambda_{max.}$ 240 (log ε 4·23), 271 (log ε 3·98), and 305 mμ (log ε 3·94) (Found: C, 66·9; H, 5·2. $C_{22}H_{20}Fe_2$ requires C, 66·7; H, 5·1%). The compound was completely isomerised to the *trans*-isomer in benzene solution in presence of toluene-*p*-sulphonic acid.

Reduction of (Ferrocenylmethyl)triphenylphosphonium Iodide with Lithium Aluminium Hydride.—The iodide (5·88 g., 0·01 mole) was added during 15 min. to a stirred refluxing suspension of lithium aluminium hydride (0·57 g., 0·015 mole) in tetrahydrofuran (100 ml.), and the mixture was refluxed for 6 hr. The excess of hydride was decomposed with ethyl acetate, and the mixture poured into water (200 ml.) and extracted with ether. The extracts were dried (Na_2SO_4) and evaporated, and the residue was chromatographed in ligroin. Ligroin eluted methylferrocene (1·64 g., 82%) which sublimed at 100° (bath)/0·02 mm. in yellow leaflets, m. p. 34—36° (lit.,[21] 35·5—36·5°). Ligroin eluted triphenylphosphine (1·78 g., 68%). Benzene eluted several minor bands which were not examined further.

(*Ferrocenylmethyl*)*diphenylphosphine* (XIII).—Lithium aluminium hydride (1·2 g., 0·03 mole) was added to a solution of (ferrocenylmethylene)triphenylphosphorane (0·02 mole) in ether (100 ml.) prepared as described in previous experiments. The ether was distilled off under nitrogen and replaced with tetrahydrofuran (150 ml.). The mixture was refluxed with stirring for 76 hr. and worked up as in the preceding experiment. On chromatography ligroin eluted methylferrocene (0·23 g., 6%) followed by triphenylphosphine (0·36 g., 7%), both identical with authentic specimens, and ligroin–ether (10 : 1) eluted (*ferrocenylmethyl*)*diphenylphosphine* (5·14 g., 67%), a viscous yellow oil which slowly crystallised to a waxy solid, m. p. 85—87° (Found: C, 73·0; H, 5·7. $C_{23}H_{21}FeP$ requires C, 71·9; H, 5·5%). With methyl iodide, the phosphine gave a *methiodide* which crystallised from acetone in golden needles, m. p. 201—202° (Found: C, 54·5; H, 5·0. $C_{24}H_{24}FeIP$ requires C, 54·8; H, 4·6%).

3-*Ferrocenyl*-1-*phenylprop*-1-*yne* (XIV; R = Ph).—Phenylacetylene (10·2 g., 0·1 mole) was added to a solution of phenyl-lithium prepared in ether (100 ml.) from lithium (0·56 g., 0·08 g.-atom) and bromobenzene (4·71 g., 0·03 mole). The mixture was stirred for 30 min. (Ferrocenylmethyl)trimethylammonium iodide (3·85 g., 0·01 mole) was then added and the ether distilled off under nitrogen and replaced with tetrahydrofuran (100 ml.). The mixture was then refluxed with stirring for 48 hr. Methanol (10 ml.) was added, and the solution was filtered and diluted with water (500 ml.) and extracted with ether. The extract was dried (Na_2SO_4) and evaporated, and the residue chromatographed in ligroin. Ligroin slowly eluted 3-ferrocenyl-1-phenylprop-1-yne (1·29 g., 43%) which crystallised from ligroin in yellow needles, m. p. 77—79° (lit.,[11] m. p. 79—82°) (its identity with an authentic sample was kindly confirmed by Dr. K. Schlögl), $\nu_{max.}$ (in CCl_4) 2262 cm.$^{-1}$ (C≡C) (Found: C, 74·5, 76·8, 76·8; H, 5·3, 5·8, 5·6. Calc. for $C_{19}H_{16}Fe$: C, 75·9; H, 5·4%).

In a similar experiment with 0·03 mole of phenyl-lithium, 0·025 mole of phenylacetylene, and 0·02 mole of quarternary salt in which the reaction mixture was refluxed for only 6½ hr., the products were benzylferrocene (2%) and (2-ferrocenylethyl)dimethylamine [22] (62%), separated by chromatography on alumina.

Vinylferrocene (VII; R = R′ = H).—(2-Ferrocenylethyl)trimethylammonium iodide (1·0 g., 2·5 mmoles) was refluxed for 1 hr. with a solution of freshly sublimed potassium t-butoxide (2·24 g., 0·02 mole) in benzene (50 ml.). Trimethylamine was evolved. The orange solution was poured into water (100 ml.), and the organic layer was separated, washed with water, dried (Na_2SO_4), and evaporated. The residual gum was chromatographed in ligroin. Ligroin

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[20] Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446.

[21] Nesmeyanov, Perevalova, Shilovtseva, and Beinoravichute, *Doklady Akad. Nauk S.S.S.R.*, 1958, **121**, 117.

[22] Osgerby and Pauson, *J.*, 1961, 4600.

eluted vinylferrocene (0·43 g., 81%) which sublimed at 60° (bath)/0·02 mm. as yellow crystals, m. p. 48—50° (lit.,[12] m. p. 56°), $\lambda_{max.}$ 211 (log ε 4·36), 228 (log ε 4·30), and 276 mμ (log ε 3·86).

This work was assisted by the Air Force Office of Scientific Research of the Air Research and Development Command, U.S.A.F. We thank Mr. T. Boyle for technical assistance, Dr. A. C. Syme and his staff for microanalyses, and the Ethyl Corporation for supplies of ferrocene.

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[*Received, November 26th,* 1962.]