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REACTIONS OF IRON CARBONYLS WITH YLIDES

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SUMMARY

Phosphoranes having the structure p-$XC_6H_4CH{=}P(C_6H_5)_3$ [where $X{=}H$, CH_3, OCH_3] react with iron carbonyls in dry tetrahydrofuran to give low-reasonable yields of stilbenes as well as unstable purple-red organometallic complexes, triphenylphosphineiron tetracarbonyl, and triphenylphosphine oxide. Most phosphoranes of type $RCH{=}P(C_6H_5)_3$ [$R{=}$alkyl] also formed unstable organometallics and $(C_6H_5)_3PFe(CO)_4$, but only in two instances were the substituted ethylenes isolated in low yields. Substantial variation in the *cis–trans* alkene distribution and in the overall yield of alkene was observed in the reaction of $Fe(CO)_5$ with p-$CH_3C_6H_4CH{=}P(R')_3$, where $R'{=}p$-FC_6H_4, C_6H_5, n-C_4H_9, and $(CH_3)_2N$. The reaction of $Fe(CO)_5$ with $C_6H_5COCH^-M^+$, where $M^+ = P^+(C_6H_5)_3$, $P^+(p\text{-}FC_6H_4)_3$, $N^+C_5H_5$, and $S^+(CH_3)_2$, and several other stable ylides was also investigated.

Iron pentacarbonyl [$Fe(CO)_5$] is finding increased usage as a reagent for the synthesis of organic compounds*. The reactions of $Fe(CO)_5$ with nucleophiles, such as amines and organolithium compounds, have been investigated in considerable detail.

Ylides, particularly phosphoranes, are versatile reagents, exhibiting nucleophilic character in many of their reactions (*e.g.* Wittig reaction)[2]. This paper is concerned with the reaction of iron carbonyls with ylides. The purpose of this investigation was to determine: (a) what products are obtained in these reactions; (b) the effect of changing from a phosphorus to a sulfur or nitrogen ylide; and (c) the effect of varying R in $R_3P{=}CR'R''$ on the course of the reaction.

RESULTS AND DISCUSSION

Several phenyl and alkyl substituted methylenetriphenylphosphoranes were refluxed with $Fe(CO)_5$ in dry tetrahydrofuran (THF) for 20–48 hours. The results of these reactions are listed in Table 1.

The benzylic ylides (I, $X{=}H$, CH_3, and OCH_3) react with $Fe(CO)_5$ to give, on work-up, stilbenes, $(C_6H_5)_3PFe(CO)_4$, $(C_6H_5)_3PO$, and a dark purple organometallic complex. The stilbenes formed were, in several instances, mixtures of *cis* and

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* For reviews dealing in whole, or in part, with $Fe(CO)_5$ as a stoichiometric reagent, see ref. 1.

TABLE 1

PRODUCTS OBTAINED FROM THE REACTION OF $RCH=P(C_6H_5)_3$ WITH $Fe(CO)_5$ IN THF[a]

R	*Reflux time (h)*	*Organic products*	*Yield (%)*	*$(C_6H_5)_3PFe(CO)_4$ Yield(%)*	*IR carbonyl stretching frequencies for organometallic complexes formed (cm^{-1}) [solvent]*
I C_6H_5	24	$C_6H_5CH=CHC_6H_5$	14	60	2094 vw, 2067 vw, 2051 m, 2022 m, 1998 vs, 1973 s, 1943 s [CH_2Cl_2]
I p-$CH_3C_6H_4$	20	p-$CH_3C_6H_4CH=CHC_6H_4CH_3$-$p$	43	36	2056 w-m, 2010 w-m, 1932 vs [neat]
I p-$CH_3OC_6H_4$	20	p-$CH_3OC_6H_4CH=CHC_6H_4OCH_3$-$p$	47	43	2063 w, 2048 w-m, 1996 s, 1951(sh) [CH_2Cl_2]
II H	24	None isolated		[b]	2018 m, 1940 vs [CH_2Cl_2]
II CH_3CH_2	20	None isolated		[b]	2048 w-m, 2019 m, 1990 m(sh), 1937 s [CH_2Cl_2]
II $CH_3CH_2CH_2$	30	None isolated		[b]	2038 m, 1965 s, 1939 s [neat]
II $(CH_3)_2CHCH_2$	20	None isolated		[b]	2038 m, 1968 s [neat]
II $CH_3(CH_2)_3CH_2$	25	$CH_3(CH_2)_4CH=CH(CH_2)_4CH_3$	trace	[b]	2068 w, 2048 m, 2000 s, 1971 s [CH_2Cl_2]
II $C_6H_5CH_2CH_2$	48	$C_6H_5CH_2CH_2CH=CHCH_2CH_2C_6H_5$	7.3	11.6	2030 w, 1980 s, 1945 m [CH_2Cl_2]

[a] Yields are based on moles of the phosphonium salt reacted.

[b] Formed in undetermined yield.

$p\text{-}XC_6H_4CH{=}P(C_6H_5)_3$
(I) $X{=}H, CH_3, OCH_3$

trans isomers which could be separated by column chromatography and/or by their solubility differences. Ylide I ($X{=}H$), gave only *trans*-stilbene but the *cis* compound was obtained as the major isomer from I ($X{=}CH_3$, OCH_3). For the reaction of I ($X{=}OCH_3$) with iron carbonyls, substantial yields of *p*-methylanisole were sometimes found. Analogous products were not obtained from I ($X{=}H$, CH_3). Ketenes and/or allenes were not formed in these reactions.

Stilbene derivatives are products derived from the reaction and not from secondary reactions involving the starting halides[2a] or from air oxidation[3]. Stilbenes can be prepared by treating a phosphorane with organic halides. When the halide is the same as that used to prepare the phosphonium salt, symmetrical olefins result. Care was taken in this work to purify the starting salt before the ylide was prepared. Bestmann and Kratzer[3] reported that stilbenes, having a higher percent of the *trans* isomer, could be obtained by air oxidation of solutions of phosphorus ylides. The isomer distribution contrasts with some of the above results. The possibility of ylide oxidation in the $Fe(CO)_5$ reaction was eliminated by deoxygenating the tetrahydrofuran solvent prior to use and by conducting the reaction under a dry nitrogen atmosphere. The procedure of Köster, Simic, and Grassberger[4] was used for generating solutions of phosphoranes free from phosphonium salts, excess base and sodium halide.

$RCH{=}P(C_6H_5)_3$
(II)

The alkylmethylenetriphenylphosphoranes (II) did react to form purple organometallic complexes, $(C_6H_5)_3PFe(CO)_4$ and $(C_6H_5)_3PO$, but in most cases failed to give isolable organic products. These products may have been low boiling alkanes which were removed by gentle nitrogen flush. Unsuccessful attempts were made to trap these products. n-Pentylmethylenetriphenylphosphorane (II, $R{=}n\text{-}C_5H_{11}$) reacted with $Fe(CO)_5$ to give a trace amount of 6-dodecene. 1,6-Diphenyl-3-hexene was isolated in 7.3% yield from the reaction of ylide II ($R{=}C_6H_5CH_2CH_2$) with $Fe(CO)_5$.

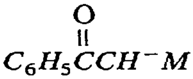
The infrared carbonyl stretching frequencies for the organometallic complexes formed in the reaction of I and II with $Fe(CO)_5$ are listed in Table 1. Most of the IR spectra of these complexes were taken in methylene chloride solution in which the sample was contaminated by triphenylphosphine oxide, but the latter does not show significant absorptions in the region 1800–2100 cm^{-1}. These complexes are unstable to air and light and could not be isolated without some contamination from triphenylphosphine oxide. Attempts to purify the complexes by column chromatography failed to separate $(C_6H_5)_3PO$ and in most instances, decomposition occurred using Florisil, neutral alumina or silica gel as adsorbents. These complexes decompose rapidly when stripped of any solvent using a flash evaporator. They are also very unstable in chloroform and carbon tetrachloride, but decompose more slowly in benzene, acetone, and ether solvents. The complexes decompose even when refrigerated under a nitrogen atmosphere. Satisfactory NMR spectra could not be obtained due to the formation of iron oxide in solution (one of the decomposition products).

Unsuccessful attempts were made to obtain a mass spectrum. The same unstable complexes could also be prepared by reaction of $Fe_2(CO)_9$ with phosphoranes.

Variation of R′ in $p\text{-}CH_3C_6H_4CH{=}P(R')_3$ (III)

A series of phosphoranes were prepared and reacted, as above, with $Fe(CO)_5$ to learn what effect a change in the phosphorus ligand (R′) has on product formation and distribution. The results are recorded in Table 2. 4,4′-Dimethylstilbene was formed in all instances although the *cis–trans* ratio varied considerably with $R' = n\text{-}C_4H_9$ giving solely the *trans* isomer, while *cis*-alkene was obtained for $R' = C_6H_5$. The purple organometallic complexes analogous to those listed in Table 1 were also formed and their terminal metal carbonyl stretching frequencies are noted in Table 2. Small quantities of substituted phosphine iron tetracarbonyls were also obtained in these reactions. Little or no IR data for $(p\text{-}FC_6H_4)_3PFe(CO)_4$ and $(n\text{-}C_4H_9)_3PFe(CO)_4$ is available in the literature[5,6] and thus the terminal metal carbonyl stretching frequencies for these compounds are noted in the experimental section.

The results indicate that the nature of R′ does not generally affect the organic and organometallic products formed although there are substantial variations in the *cis–trans* alkene distribution and in the overall yield of alkene. It is noteworthy that very rapid formation of the purple complex was observed using III, $R' = N(CH_3)_2$, as the phosphorane.



The reaction of $Fe(CO)_5$ with the "stable" ylides, $C_6H_5\overset{\overset{O}{\|}}{C}CH^-M^+$ (IV), where $M^+ = P^+(C_6H_5)_3$, $P^+(p\text{-}FC_6H_4)_3$, $N^+C_5H_5$, $S^+(CH_3)_2$

In the introduction, it was noted that sulfur and nitrogen ylides are known, and hence it was of interest to see what effect a change in the heteratom from phosphorus to nitrogen or sulfur would have on the course of the reaction. The air-stable ylides IV [$M^+ = {}^+P(C_6H_5)_3$, ${}^+P(p\text{-}FC_6H_4)_3$, ${}^+NC_5H_5$, $S^+(CH_3)_2$] prepared from α-bromoacetophenone[7–9], were each reacted with $Fe(CO)_5$ under similar conditions and the results are listed in Table 3. Using similar work-up procedures, the two phosphoranes and the nitrogen ylide gave 1,4-diphenylbutane-1,4-dione in 8.5–16% yield. Only 1.0% of the 1,4-diketone was formed in the reaction of IV, $M^+ = S^+(CH_3)_2$,

TABLE 2

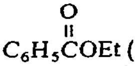
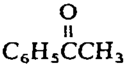
THE RESULTS OF THE REACTION OF $p\text{-}CH_3C_6H_4CH{=}P(R')_3$ (III) AND $Fe(CO)_5$ IN THF SOLUTION

R′	*Yield of 4,4′-dimethylstilbene (%)*	*Carbonyl stretching frequencies for organometallic complexes formed (cm^{-1}) [solvent]*
III $p\text{-}FC_6H_4$[a]	15 (1/1 *cis/trans*)	2046 w-m, 2022 m(sh), 1944 vs [CH_2Cl_2][b]
I[c] C_6H_5	43 (*cis*)	2056 w-m, 2010 w-m, 1932 vs [neat]
III $n\text{-}C_4H_9$	23 (*trans*)	2047 w-m, 2021 w-m, 1946 vs [CH_2Cl_2]
III $(CH_3)_2N$[d]	26 (>97 *trans*)	2043 w-m, 2020 w-m, 1945 vs [CH_2Cl_2]

[a] p-Xylene was also obtained in 12% yield.
[b] A band at 1996 cm^{-1} was also observed which may be due to unreacted $Fe(CO)_5$.
[c] $R = p\text{-}CH_3C_6H_4$.
[d] 1,2-Bis(4-methylphenyl)ethane was also obtained as a low yield (7%) by-product.

TABLE 3

PRODUCTS OBTAINED FROM REACTION OF $C_6H_5(CO)C^-H$–M^+ (IV) WITH $Fe(CO)_5$ IN THF SOLUTION

M^+	*Reflux time (h)*	*Yield of 1,4-diphenylbutane-1,4-dione (%)*	*Other reflux products obtained, Yield (%)*
$(C_6H_5)_3P^+$	26	16	$(C_6H_5)_3P$–$Fe(CO)_4$ (4)
$(p\text{-}FC_6H_4)_3P^+$	28	8.5	$(p\text{-}FC_6H_4)_3PFe(CO)_4$ (2) $[(p\text{-}FC_6H_4)_3P]_2Fe(CO)_3$ (trace)
$C_5H_5N^+$	25	13–15	 $C_6H_5\overset{O}{\overset{\|}{C}}OEt$ (3.7) C_5H_5N–$Fe(CO)_4$
$(CH_3)_2S^+$	20	1.0	 $C_6H_5\overset{O}{\overset{\|}{C}}CH_3$ (9) 1,2,3-tribenzoylcyclopropane (20) Unknown (*m/e* 347)

with $Fe(CO)_5$; however, acetophenone (9%) and two organic solids were obtained. The first, m.p. 218–219°, was identified as 1,2,3,-tribenzoylcyclopropane (20% yield; mass spectrum gave a parent ion at *m/e* 354), a product reported by Johnson and Amel[10] to be derived from the thermal decomposition of the sulfur ylide in refluxing THF. The mass spectrum of the second solid, m.p. 232–234°, showed a parent ion at *m/e* 347 and abundant fragments at *m/e* 312, 250, 222, 207, 105, 77 and 51. The structure for this compound could not be identified on the basis of this and other spectral results. A surprising product, ethyl benzoate, was formed in 3.7% yield from the reaction of IV, $M^+ = C_5H_5N^+$ with $Fe(CO)_5$. This yield was reproducible but it is unknown how the ester is formed. Depending on the reactant, $(C_6H_5)_3PFe(CO)_4$, $(p\text{-}FC_6H_4)_3PFe(CO)_4$[5], and pyridine iron tetracarbonyl[11] were formed as by-products but dimethyl sulfide iron tetracarbonyl[12,*] was not formed from reaction of IV, $M^+ = S^+(CH_3)_2$, and $Fe(CO)_5$. 1,2-Dibenzoylethene was not isolated in any of these reactions and neither were the purple-red organometallic complexes formed as in the other ylide reactions.

Reaction of $Fe(CO)_5$ with other "stable" ylides

Carbomethoxymethylenetriphenylphosphorane (V), diphenylmethylenetriphenylphosphorane (VI), vinylmethylenetriphenylphosphorane (VII), triphenylphosphonium cyclopentadienylide (VIII), and fluorenylidenetriphenylphosphorane (IX) were subjected to iron carbonyl treatment. Unstable purple-red organometallic complexes (except IX), $(C_6H_5)_3PFe(CO)_4$, $(C_6H_5)_3PO$, and recovered ylide resulted on work-up of these reactions.

Olefins were isolated from ylides VI [tetraphenylethylene–$Fe(CO)_5$ (3% yield); $Fe_2(CO)_9$ (22%)] and IX [bis(fluorenylidine)–$Fe_2(CO)_9$ (10%)]. The IR metal carbonyl stretching bands for methylene chloride solutions of the unstable organometallic complexes are listed in Table 4.

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[*] Strohmeier *et al.* reported a carbonyl stretching frequency for the related tetramethylene sulfide iron tetracarbonyl at 2053 cm^{-1}. There must, of course, be other bands present[12].

TABLE 4

IR CARBONYL STRETCHING FREQUENCIES (CH_2Cl_2) FOR THE ORGANOMETALLIC COMPLEXES FORMED FROM REACTION OF STABLE PHOSPHORANES WITH IRON CARBONYLS

Phosphorane	*Iron carbonyl*	*Terminal metal carbonyl stretching frequencies [bridging]* (cm^{-1})
V	$Fe(CO)_5$ $Fe_3(CO)_{12}$	2020 w-m, 1958 s, 1940 s
VI	$Fe(CO)_5$ $Fe_2(CO)_9$ $Fe_3(CO)_{12}$	2048 vs, 2020 w, 1945 s
VII	$Fe(CO)_5$	2092 w, 2066 w, 1982 s(br), [1812 s]
	$Fe_2(CO)_9$	2050 w, 2021 m, 1998 s, 1955 m(sh), 1940 m
VIII[a]	$Fe_2(CO)_9$	2049 m, 1993 m, 1970 m, 1934 s
IX	$Fe(CO)_5$ $Fe_2(CO)_9$ $Fe_3(CO)_{12}$	No organometallic product

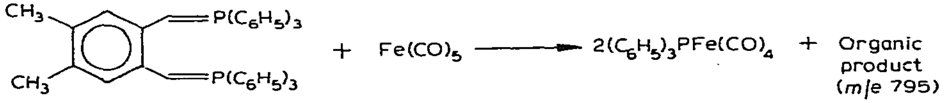
[a] Cashman and Lalor recently reported that a complex showing four carbonyl stretching bands in the 2100–1900 cm^{-1} region, was obtained by reaction of VIII with $Fe(CO)_5$ in refluxing 1,2-dimethoxyethane. The band positions were not given[13].

Mechanism of the reaction

The mechanism of formation of alkenes (or 1,4-diketones) in the ylide–iron carbonyl reactions is unknown. It was anticipated that nucleophilic attack on a carbonyl carbon by the ylide carbanion would occur to give a dipolar species. Collapse of the latter, via a concerted or stepwise process, to a ketene and monophosphineiron tetracarbonyl did not take place as ketenes (and/or allenes) were not formed in these reactions. Conversion of the dipolar intermediate to an alkylidenylcarbeneiron tetracarbonyl complex and a phosphine oxide is also possible. In fact, such a deoxygenation process does occur in the reaction of $Fe(CO)_5$ and other metal carbonyls with phosphineimines[14] as well as by treatment of hexaphenylcarbodiphosphorane with manganese pentacarbonyl bromide[15]. Cumulene formation (not observed) is a likely product of collapse of the alkylidenylcarbeneiron tetracarbonyl. It is not apparent how substituted ethylenes and monophosphineiron tetracarbonyls would arise from the alkylidenylcarbeneiron tetracarbonyl. However, there is evidence in the literature to support the collapse of carbene–metal complexes to alkenes[16] and consequently it is possible that carbene–iron carbonyl complexes may be involved in most of the reactions discussed above.

Phosphine iron tetracarbonyls

Thermal reaction of $Fe(CO)_5$ and an organophosphine usually gives mixtures of mono- and disubstituted phosphineiron carbonyls[17–20]. All five carbonyl groups can be replaced by heating $Fe(CO)_5$ and PF_3 at elevated temperatures and pressures[21]. Monosubstitued phosphineiron tetracarbonyls can now be prepared in reasonable yields by the reaction of $RCH{=}PR'_3$ and $Fe(CO)_5$. Virtually any combination of halide and phosphine that will form a phosphonium salt can be utilized to prepare the substituted phosphineiron tetracarbonyl, with little, if any, contamination from the diphosphineiron tricarbonyl. Larger quantities of product were obtained when the phosphonium salt was prepared from a benzyl type halide. Ease of separation of $R'_3PFe(CO)_4$ from any formed organic by-product can be markedly enhanced if the organic product is of high molecular weight. For example, reaction of X (obtained from commercially available diphosphonium salt) with $Fe(CO)_5$ readily gave pure triphenylphosphineiron tetracarbonyl in 57% yield. The organic product gave a molecular ion peak at *m/e* 795. The structure of this compound is unknown.



(X)

EXPERIMENTAL SECTION

General information

Infrared (IR) spectra were recorded on Perkin–Elmer 457 and/or 521 grating infrared spectrophotometers and the spectra were calibrated against polystyrene film. Nuclear magnetic resonance (NMR) spectra were measured with Varian A60 or HA-100 spectrometers using tetramethylsilane as an internal standard. The mass spectra were recorded on an Atlas CH-4 or Varian 902 mass spectrometer. Elemental analyses were determined by: A. Bernhardt, Fritz-Pregl-Strasse, Elbach-über-Engelskirchen, Germany; Meade Microanalytical Laboratory, Amherst, Massachusetts; Galbraith Laboratories, Knoxville, Tennessee; and PCR, Inc., Gainesville, Florida. Melting points (m.p.) were determined on a Fisher–John melting point apparatus or on a Thomas Hoover capillary melting point apparatus and are uncorrected. All reaction solvents and initial work-up solvents were dried in the usual manner. THF was distilled from sodium metal and a small amount of benzophenone. Benzene, hexane, petroleum ether, and ether were dried and distilled from lithium aluminum hydride or anhydrous calcium chloride. Pyridine was dried and distilled from barium oxide. Other solvents were of spectral grade and used as received.

Starting materials

Iron pentacarbonyl [$Fe(CO)_5$], diiron enneacarbonyl [$Fe_2(CO)_9$] and triiron dodecacarbonyl [$Fe_3(CO)_{12}$] were obtained from Pressure Chemical Company, Pittsburgh, Pennsylvania and used without further purification. The following known phosphonium salts were prepared according to standard procedures: phenacyltriphenylphosphonium bromide[1], benzyltriphenylphosphonium bromide[22], alkyltriphenylphosphonium bromide[23], 3-phenylpropyltriphenylphosphonium bromide[24], diphenylmethyltriphenylphosphonium bromide[25], *p*-methylbenzyltriphenylphosphonium bromide[26], fluorenyl-9-triphenylphosphonium bromide[27], and phenacylpyridinium bromide[8]. Also prepared by standard procedures were: *p*-methylbenzyltris(4-fluorophenyl)phosphonium bromide [100% yield, m.p. 268–269°. Found: C, 62.46; H, 4.34. $C_{26}H_{21}BrF_3P$ calcd.: C, 62.27; H, 4.19%.]; phenacyl(4-fluorophenyl)phosphonium bromide [85% yield, m.p. 260–261°. Found: C, 60.31; H, 3.73. $C_{26}H_{19}BrF_3OP$ calcd.: C, 60.60; H, 3.71%]; *p*-methylbenzyltri-n-butylphosphonium bromide [52% yield, m.p. 120–121°. Found: C, 62.15; H, 9.02. $C_{20}H_{36}$-

BrP calcd.: C, 62.16; H, 9.30%.]; *p*-methylbenzyltris(dimethylamine)phosphonium bromide [90% yield, m.p. 194.5–196.5°. Found: C, 48.52; H, 7.60. $C_{14}H_{27}BrN_3P$ calcd.: C, 48.28; H, 7.76%.]

Preparation of sodamide

Freshly prepared sodamide was usually obtained by the procedure of Vaughn, Vogt, and Nieuwland[28]. Small pieces of sodium metal were added slowly to a stirred solution of liquid ammonia, while cooling the reaction vessel in a dry ice/acetone bath. Several small pieces of ferric nitrate were added to catalyze the reaction. The deep blue color slowly disappeared leaving the insoluble grey sodamide. Cold THF (−30°) was added to the grey solution and the temperature of the bath allowed to come to room temperature causing the excess ammonia to evaporate.

The tetrahydrofuran–sodamide slurry is used immediately without isolation. *Note.* The sodamide purchased from Fisher Scientific was found to be inferior to freshly prepared sodamide in converting phosphonium salts to the corresponding phosphoranes.

Preparation of benzylidene and alkylidenetriarylphosphoranes

Phosphoranes. The general procedure of Köster and co-workers[4] was utilized for converting phosphonium salts to their respective phosphoranes. The following procedure is typical.

Preparation of benzylidenetriphenylphosphorane (I, X = H). Benzyltriphenylphosphonium chloride (12.5 g, 0.032 moles) was added slowly to a refluxing solution of freshly prepared sodamide (1.69 g, 0.043 moles) in dry degassed tetrahydrofuran (150 ml) under a nitrogen blanket. After refluxing for 4 h, the reaction vessel was cooled in an ice bath to 5–10° and transferred to a glove box (N_2 atmosphere) where the orange solution is filtered quickly through Celite into a 500 ml three-necked flask. The Celite is washed with 50 ml cold THF. The stoppered flask (under N_2) is transferred to the hood where a nitrogen inlet, reflux condenser, magnetic stirrer and an additional funnel is added while maintaining a brisk nitrogen flow. This orange solution is now ready for the addition of the iron carbonyl.

Reaction of benzylidenetriphenylphosphoranes (I) with iron pentacarbonyl in refluxing tetrahydrofuran

General procedure. (a) Iron pentacarbonyl in dry THF (10 ml) was added rapidly to a freshly prepared phosphorane in dry, degassed THF (200 ml). With rapid stirring the orange solution was refluxed for approximately 20 h under a gentle nitrogen flush. The dark purple solution was cooled, filtered through Celite and concentrated in vacuo. The residue was taken up in n-hexane or benzene (150 ml), refluxed for 20 h, cooled to room temperature, filtered and concentrated in vacuo to give a yellow-orange semi-solid. This extract was chromatographed on Florisil to give $(C_6H_5)_3P{-}Fe(CO)_4$, olefin and $(C_6H_5)_3P{=}O$.

The n-hexane insoluble material (above) was dissolved in THF, filtered and concentrated in vacuo. An infrared spectrum indicated it to be an organometallic complex and $(C_6H_5)_3P{=}O$.

(b) The reaction mixture, after concentrating in vacuo to approximately 15 ml was chromatographed on Florisil. Elution with n-hexane/benzene (5/1) gave a mixture of triphenylphosphineiron tetracarbonyl and the olefin. The mixture was taken up in a small amount of methanol and nearly all the $(C_6H_5)_2P\text{–}Fe(CO)_4$ was filtered off. Triphenylphosphineiron tetracarbonyl is sparingly soluble in cold methanol. The filtrate is concentrated and chromatographed, as above, to yield the substituted phosphineiron tetracarbonyl and the olefin.

Procedure (b) was followed if only the olefin was important because the organometallic complexes generally decompose on chromatographing.

The alkenes were identified by comparison of their melting points and IR and NMR spectra with literature data.

Reaction of 4,5-dimethyl-1,2-dimethylenetriphenylphosphorane (X) with $Fe(CO)_5$ in THF

Diphosphorane X (obtained from 43.5 mmoles of phosphonium salt) and $Fe(CO)_5$ (17.7 ml, 130 mmoles) gave a purple solution under the usual reaction conditions. n-Hexane/benzene (3/1) (200 ml) soluble material (room temperature) removed 18.4 g (49%) nearly analytically pure $(C_6H_5)_3PFe(CO)_4$. Refluxing the residue in n-hexane (150 ml) gave 4.2 g yellow solid. This material was taken up in a small amount of benzene and chromatographed on Florisil. Triphenylphosphineiron tetracarbonyl 2.9 g (8%) was eluted first with n-hexane/benzene (3/1), followed by 0.4 g of a white solid. Anal. data: C, 89.91; H, 9.20%, melting point 125–130°. A mass spectrum gave a parent ion at *m/e* 795 followed by abundant fragments at *m/e* 793, 530, 279, 277, 265, 263, 249, 148 (intense), 133 (intense). Total yield of $(C_6H_5)_3PFe(CO)_4$ was 31.2 g (57%).

Reaction of alkylidenetriphenylphosphoranes (II) with iron pentacarbonyl in refluxing tetrahydrofuran

General procedure. The freshly prepared alkylidenetriphenylphosphorane and $Fe(CO)_5$ in dry, degassed THF (200 ml) were refluxed with stirring in a nitrogen atmosphere for 20–48 h. The nitrogen flush was bubbled through benzene to trap any low boiling olefins formed in the reaction. (The benzene solution was distilled slowly. NMR spectra of the first few drops showed only benzene.) The purple solution, once cooled to room temperature, was filtered through Celite and concentrated by distillation. In several instances olefins were found (Table 1). In all cases triphenylphosphineiron tetracarbonyl, triphenylphosphine oxide and an organometallic complex were formed. The latter complexes are extremely unstable in solution or neat. Some reactions were carried out in 1,2-dimethoxyethane or di-n-butylether with similar results.

Reaction of p-methylbenzylidene-trisubstituted-phosphoranes (III) with iron pentacarbonyl in refluxing tetrahydrofuran

(i). Reaction of p-methylbenzylidenetris(4-fluorophenyl)phosphorane (III, R' = p-FC_6H_4) with $Fe(CO)_5$ in THF. Ylide III, R' = *p*-FC_6H_4 (obtained from 27.0 mmoles of phosphonium salt) and $Fe(CO)_5$ (4.40 ml, 32.4 mmoles) were reacted under the conditions described for *p*-methylbenzylidenetriphenylphosphorane. The n-hexane soluble material was chromatographed on Florisil. Elution with n-hexane/benzene gave 0.35 g (12%) of *p*-xylene, 0.45 g (15%) of 4,4'-dimethylstilbene [*cis/trans* (1/1)] and 0.14 g (1%) of $(p\text{-}FC_6H_4)_3P\text{–}Fe(CO)_4$ [IR (KBr) $\nu(C{\equiv}O)$: 2059 m, 1982 m, 1940 s

cm^{-1}]. A substantial amount of the substituted phosphineiron tetracarbonyl decomposed in solution and on the column.

The hexane insoluble material was shown by IR to be a mixture of the substituted phosphine oxide and an organometallic complex [IR (CH_2Cl_2) ν(C≡O): 2046 w-m, 2022 m(sh), 1996 s, 1944 vs cm^{-1}].

(ii) Reaction of p-methylbenzylidenetri-n-butylphosphorane (III. R'=n-C_4H_9) with $Fe(CO)_5$ in THF. The reaction of ylide III, R'=n-C_4H_9 (obtained from 25.0 mmoles) and $Fe(CO)_5$ (4.1 ml, 30.0 mmoles) was conducted in the usual manner. The reaction residue was extracted with benzene/n-hexane (3/1) and the soluble material was chromatographed on Florisil. Elution with petroleum ether/n-hexane (3/1) gave *trans*-4,4'-dimethylstilbene (0.6 g, 23 %). Further elution with n-hexane/benzene (1/1) gave tri-n-butylphosphineiron tetracarbonyl, 0.7 g (7.6%), m.p. 207–210°, which decomposed slowly on contact with air [IR (NaCl smear) ν(C≡O): 2045 m, 1963 m, 1928 s cm^{-1}] [lit.[6] IR (CS_2) 1945 cm^{-1}].

The n-hexane/benzene insoluble material was shown by IR to be a mixture of tri-n-butylphosphine oxide and an organometallic complex [IR (CH_2Cl_2) ν(C≡O): 2047 w-m, 2021 w-m, 1946 vs cm^{-1}].

(iii) Reaction of p-methylbenzylidenetris(dimethylamino)phosphorane (III) $R'=N(CH_3)_2$] with $Fe(CO)_5$ in THF. Reaction of ylide III, R'=$N(CH_3)_2$ (obtained from 27.0 mmoles of phosphonium salt) and $Fe(CO)_5$ (4.4 ml, 32.4 mmoles) in dry THF (200 ml) under the usual conditions gave a n-hexane soluble oily solid. Chromatography on Florisil with n-hexane gave 0.73 g (26 %) of 4,4'-dimethylstilbene (essentially pure *trans* isomer as shown by its NMR spectrum) and a trace of $[(CH_3)_2N]_3P\text{-}Fe(CO)_4$, a yellow oil, which decomposed rapidly in solution or on contact with air. [IR (Nujol) ν(C≡O): 2055 m, 1973 m, 1934 s cm^{-1}] [lit.[29] IR (halocarbon) ν(C≡O): 2041 s, 1969 s, 1930 vs cm^{-1}].

Further elution with benzene gave a yellow oil, 1,2-bis(4-methylphenyl)ethane, 0.21 g (7 %) as identified by comparing its NMR with that reported in the literature[30].

The hexane insoluble material was shown by IR to be a mixture of $[(CH_3)_2N]_3$-P=O and an organometallic complex. [IR (CH_2Cl_2) ν(C≡O): 2043 w-m, 2020 w-m, 1945 vs cm^{-1}].

Reactions of stable ylides

(i) Reaction of phenacylidenetriphenylphosphorane [IV, $M^+=(C_6H_5)_3P^+$] *with $Fe(CO)_5$ in THF.* Phosphorane IV, $M^+=(C_6H_5)_3P^+$ (7.00 g, 18.4 mmoles) and $Fe(CO)_5$ (2.70 ml, 20.0 mmoles) in THF (200 ml) were refluxed and stirred for 26 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature, filtered and the solvent concentrated in vacuo. The residue was chromatographed on Florisil. Elution with benzene gave 1.4 g of a green oil and 4.2 g (60 %) of starting ylide.

The green oil was chromatographed with hexane on Florisil to yield 0.3 g (4 %) of triphenylphosphineiron tetracarbonyl. Elution with benzene gave 0.42 g of a colorless oil. Rechromatography of the colorless oil on Florisil [benzene/chloroform (3/1)] gave 0.14 g (16 %) of 1,4-diphenylbutane-1,4-dione, m.p. 140–141° (lit.[31] m.p. 143–144°).

(ii) Reaction of phenacylidenetris(4-fluorophenyl)phosphorane [IV, $M^+=(p\text{-}FC_6H_4)_3P^+$] with $Fe(CO)_5$ in THF. Phosphorane IV, $M^+=(p\text{-}FC_6H_4)_3P^+$ (2.94 g,

6.77 mmoles) and $Fe(CO)_5$ (1.09 ml, 7.36 mmoles) in THF (50 ml) were refluxed with stirring for 28 h. After cooling the mixture to room temperature, filtering, and evaporating THF in vacuo, benzene was added to the resulting oil to precipitate out inorganic material. The latter was filtered and the solvent removed using a flash evaporator. Pentane (50 ml) was added to the residue and the solution allowed to stand overnight. A solid (mostly unreacted ylide) was filtered, the filtrate concentrated and then chromatographed on Florisil. Elution with pentane/benzene (3/1) gave 22 mg of tris(*p*-fluorophenyl)phosphineiron tetracarbonyl, m.p. 157–159° (dec.) [lit.[5] m.p. 152–155° (dec.); $\nu(C{\equiv}O)$ (KBr): 2059 m, 1982 m, 1940 s]. Elution with chloroform/benzene (3/1) gave 23 mg of 1,4-diphenylbutane-1,4-dione, m.p. 142–143° (lit.[31] m.p. 143–144°). The pentane insoluble solid was chromatographed on Florisil. Elution with benzene gave 10 mg of $(p\text{-}FC_6H_4)_3PFe(CO)_4$, followed by trace amounts of $[(p\text{-}FC_6H_4)_3P]_2Fe(CO)_3$, and recovered ylide (1.57 g). Elution with $CHCl_3$ gave 12 mg of $(C_6H_5COCH_2)_2$. Total yield of 1,4-diketone was 8.5% while that of $(p\text{-}FC_6H_4)_3PFe(CO)_4$ was 2.0%.

(*iii*) *Reaction of N-pyridinium phenacylid* [*IV*, $M^+ = C_5H_5N^+$] *with* $Fe(CO)_5$ *in refluxing tetrahydrofuran.* The freshly prepared *N*-pyridinium phenacylid (IV, $M^+ = C_5H_5N^+$] (3.52 g, 17.8 mmoles) and $Fe(CO)_5$ (2.5 ml, 18 mmoles) in THF (200 ml) were refluxed with stirring under nitrogen for 25 h. To the solution was added 40 g Celite, the solvent was removed by concentrating in vacuo and the residue extracted several times with benzene. The benzene extract was chromatographed on Florisil. Elution with benzene gave 0.4 g (15%) of 1,4-diphenylbutane-1,4-dione, m.p. 142–143.5° (lit.[31] m.p. 143–144°). Further elution with benzene gave 0.10 g (3.7%) of ethylbenzoate identified by comparing the IR and NMR spectra with those from an authentic sample.

A small yield of pyridine iron tetracarbonyl was isolated from the benzene insoluble material by chromatographing the residue with methylene chloride on Florisil [IR (CH_2Cl_2) $\nu(C{\equiv}O)$: 2040 m, 1968 m-s, 1939 m cm^{-1}] [lit.[11] IR (hexane) $\nu(C{\equiv}O)$: 2055 m, 1968 m, 1944 s cm^{-1}]. The IR agreement is reasonable if one considers the polairty differences between the two solvents.

(*iv*) *Reaction of phenacyldimethylsulfurane* [*IV*, $M^+ = (CH_3)_2S^+$] *with* $Fe(CO)_5$ *in refluxing tetrahydrofuran.* Freshly prepared IV, $M^+ = (CH_3)_2S^+$ (4.0 g, 22.2 mmoles) was stirred under a nitrogen atmosphere in dry THF (200 ml). To this was added dropwise over a 4 minute period a solution of $Fe(CO)_5$ (3.25 ml, 24 mmoles) in dry THF (10 ml). After refluxing for 12 h, the solution was cooled to room temperature, filtered through Celite and concentrated in vacuo. Under the usual work-up conditions the pentane soluble material was chromatographed with benzene on Florisil to yield 0.20 g (9%) of acetophenone.

The pentane insoluble material was chromatographed with benzene on Florisil to give dimethyl sulfoxide (6%), and a trace, 0.02 g (1.0%) of 1,4-diphenylbutane-1,4-dione. Further elution gave a tan solid m.p. 218–219° (IR $\nu(C{=}O)$ 1670 cm^{-1}). This material was identified as 1,2,3-tribenzoylcyclopropane (20%) (lit.[10] m.p. 218–219°) from its mass spectrum and other spectral features (molecular parent ion *m/e* 354).

Elution with chloroform yielded a second solid m.p. 232–234°C showing the following mass spectral fragmentation pattern: *m/e* 347 (parent ion), 312, 250, 222, 207, 105, 77 and 51. The infrared spectrum showed strong-medium absorptions at

1660–1670 (C=O), 1360, 1470, 1585 and 1545 cm^{-1} and NMR ($CDCl_3$) signals at 3.16 ppm (singlet) and 7.2–7.7 ppm (multiplet). Further elution with chloroform gave 0.83 g (20.8 %) of the starting ylide.

(*v*) *Reaction of V–IX with iron carbonyls.* Ylides V–IX were treated with $Fe(CO)_5$ as above. [Room temperature conditions were used with $Fe_2(CO)_9$ while refluxing benzene was employed when $Fe_3(CO)_{12}$ was the reagent.] The IR spectra of the organometallic complexes obtained in these reactions are listed in Table 4.

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