Journal of Organometallic Chemistry, 187 (1980) 361—373

QUANTUM YIELDS IN PHOTOLYSIS OF (DIENE)TRICARBONYLIRON AND BIS(DIENE)CARBONYLIRON COMPLEXES

O. JAENICKE, R.C. KERBER *, P. KIRSCH, E.A. KOERNER VON GUSTORF ** and R. RUMIN

Institut für Strahlenchemie im Max-Planck Institut für Kohlenforschung, D-4330 Mülheim Ruhr, Stiftstrasse 34—36 (B.R.D.)

(Received July 2nd, 1979)

Summary

Photolysis of diene carbonyliron complexes in the presence of excess trimethylphosphite results in both carbonyl replacement (Φ_{CO} typically 0.01—0.5) and diene replacement (Φ_D typically 0.001—0.07). All quantum yields are higher at shorter wavelengths, as is the ratio Φ_{CO}/Φ_D. A variety of evidence indicates the photolytic formation of transient (η^2-diene)iron intermediates, which are ineffectively trapped by trimethylphosphite due to rapid reversion to the starting (η^4-diene)carbonyliron complexes.

Introduction

Photochemical methods have come to be widely used in syntheses of organometallic compounds [1—4], including (diene)tricarbonyliron [2], bis(diene)-carbonyliron [3], and (diene)carbonylphosphineiron [4] complexes. In order to optimize the conditions for such syntheses, we undertook a study of quantum yields in photolysis of a number of (diene)carbonyliron complexes [5,6]. We were also interested in the mechanistic features of such photoreactions, especially in the question of relative ease of loss of diene and carbon monoxide upon photolysis at various wavelengths.

Our method was to photolyze solutions of the complexes (ca. 10 mM) in cyclohexane containing excess (0.2 M) trimethyl phosphite. The rates of loss of starting material and formation of products were determined from the rates

(Continuned on p. 364)

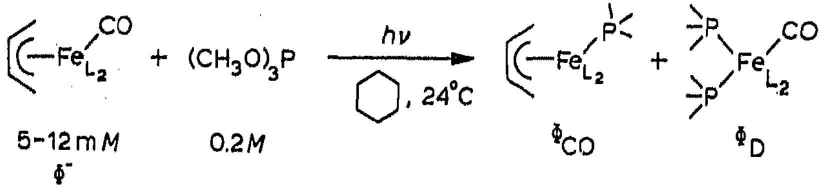
---

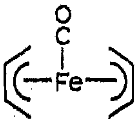
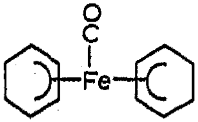
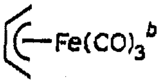
* To whom inquiries should be directed, at the Department of Chemistry, State University of New York, Stony Brook, New York 11794 (U.S.A.).

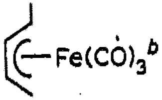
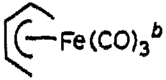
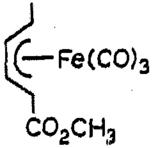
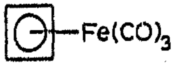
** Deceased September 18, 1975.

TABLE 1

QUANTUM YIELDS



	254 nm			313 nm			366 nm			405 nm		
	Φ^-	Φ_{CO}	Φ_D	Φ^-	Φ_{CO}	Φ_D	Φ^-	Φ_{CO}	Φ_D	Φ^-	Φ_{CO}	Φ_D
 , I	0.15	(0.12) [a]	0.03	0.12	(0.10) [a]	0.02	0.05	(0.04) [a]	0.007	0.019	(0.01) [a]	0.010
 , II	0.15	(0.11) [a]	0.04	0.10	(0.09) [a]	0.01	0.05	(0.05) [a]	0.004	0.01	(0.01) [a]	0.003
 [b], III	0.35	0.31	0.04	0.18	0.16	0.015	0.07	0.07	0.014	0.05	0.05	0.04

 $Fe(CO)_3$[b], IV	0.28	0.23	0.02	0.15	0.12	0.030	0.04	0.04	0.01	0.04	0.03	0.00
 $Fe(CO)_3$[b], V	0.51	0.46	0.07	0.27	0.24	0.04	0.20	0.15	0.05	0.14	0.05	0.09
 $Fe(CO)_3$, VI	0.19	0.19	0.016	0.12	0.11	0.007	0.06	0.053	0.003	0.04	0.032	0.00
 $Fe(CO)_3$, VII		—		0.69	>0.46	<0.01	0.88	>0.71	<0.01		—	

---

[a] By difference - not directly measurable. [b] Phosphite conc. 0.1 *M*.

of change of the corresponding infrared peaks. Ferrioxalate actinometry was used to determine the light intensity [7]. All solutions were stable in the absence of light, and concentrations were such as to assure complete absorption of light by the complexes at all wavelengths studied. Photoreactions were run to at most 15% completion to minimize secondary photolysis reactions. Effects of wavelength were studied in all cases, and effects of light intensity, reagent concentrations, and CO concentration were also studied using bis(butadiene)carbonyliron (I).

Results

Photolysis of (diene)tricarbonyliron compounds in the presence of trimethylphosphite leads to formation of two products: carbonyl displacement leads to a (diene)dicarbonyl(trimethyl phosphite)iron, and diene displacement leads to bis(trimethyl phosphite)tricarbonyliron. Analogous products result from the bis(diene)carbonyliron complexes. The measured quantum yields for loss of starting material (Φ^-) and formation of products (Φ_{CO} and Φ_D) are presented in Table 1. The values shown are the averages of two or more determinations in most cases; the reproducibility of quantum yields was generally within ±15%.

Several generalizations may be drawn from the data of Table 1: (a) the net quantum yields are considerably less than 1.00; (b) the quantum yields increase with decreasing wavelength at least down to 313 nm; (c) Φ_{CO} is greater than Φ_D; (d) the ratio Φ_{CO}/Φ_D increases with decreasing wavelength, and is particularly large for the methyl sorbate complex, VI, which has particularly small Φ_D's. Synthetic attempts to replace a CO by a phosphite or phosphine should therefore be run using light of short wavelength [6]'

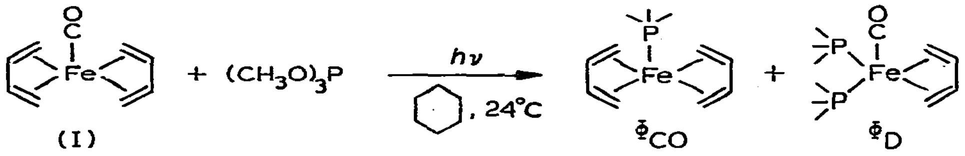
A number of studies of concentration effects have been carried out on complex I. As shown in Table 2, the observed quantum yields are unaffected by changes in the concentration of complex I or in light intensity. The observed quantum yields decrease noticeably at phosphite concentrations below 0.1 *M*, and when the solution is initially saturated with CO. The runs of Table 1 were performed at 0.1—0.2 *M* phosphite concentration because the use of 2 *M* phosphite decreases the sensitivity and reliability of the infrared analysis due to infrared band broadening, and thus degrades the quantum yield determinations. The Φ_{CO} values obtained using 2 *M* phosphite are, however, within experimental error of those measured at 0.2 *M*, indicating that at both these high concentrations, we are effectively trapping essentially all of the intermediate capable of reaction with excess phosphite. The absorption spectra of the complexes (see Fig. 1 for typical spectra) show a very intense absorption below 250 nm with one or more shoulders at longer wavelengths due to weaker absorption peaks. The weak longer wavelength peaks presumably correspond to ligand field absorption and the intense high-energy peaks to $M \rightarrow \pi^*_{CO}$ absorption [1a]. The results of Table 1 suggest that the $M \rightarrow \pi^*_{CO}$ excited state predominantly leads to CO substitution, perhaps via crossing to an upper *d-d* state, whereas the directly populated lower energy *d-d* state(s) has a greater tendency toward diene displacement *.

---

* Calculations by Dr. Franz Mark which explore the wavelength effect in detail will be published independently.

TABLE 2

EFFECTS OF CONDITIONS ON QUANTUM YIELDS



λ (nm)	[I], m*M*	[(CH$_3$O)$_3$P],	10^8 I, E/min	Φ^-	Φ_{CO} [a]	Φ_D
254	6.9	0.02	3.0	0.05	(0.05)	<0.002
254	6.4	0.2	2.9	0.15	(0.12)	0.03
254	6.8	2.0	3.0	0.20 [c]	(0.13)	0.07 [c]
313	5.6	0.02	18.0	0.05	(0.05)	0.003
313	6.2	0.04	18.2	0.07	(0.07)	<0.01
313	5.3	0.2	23.4	0.11	(0.09)	0.02
313	6.7	2.0	18.2	0.14 [c]	(0.11)	0.03 [c]
313	4.7	0.2	8.35	0.11	(0.09)	0.015
313	2.6	0.2	19.1	0.12	(0.10)	0.02
313	9.5	0.2	19.9	0.12	(0.10)	0.02
313 [b]	5.2	0.2	19.7	0.059	(0.04)	0.02
405	6.7	0.2	80.0	0.019	(0.01)	0.01
405	6.0	0.2	38.5	0.019	(0.01)	0.01
405	6.8	2.0	80.0	0.046 [c]	(0.03)	0.02 [c]

[a] Values by difference-not directly measurable. [b] Photolysis done under 1 atm. CO. [c] Quantum yields with 2 *M* phosphite ± 25%.

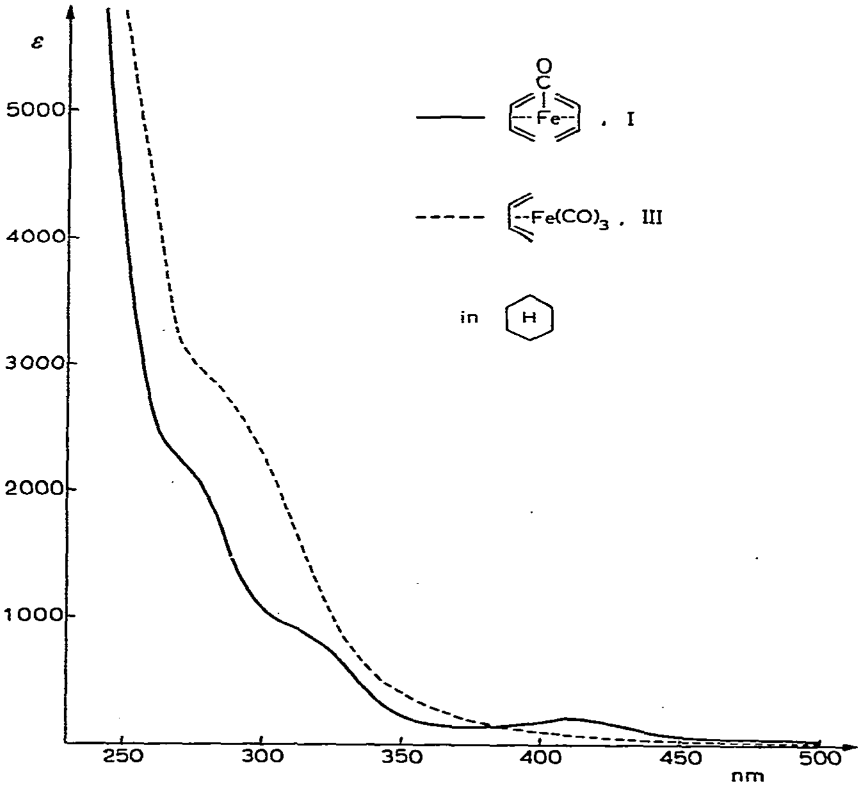
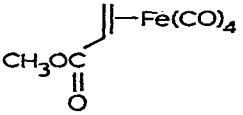
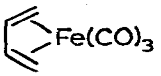
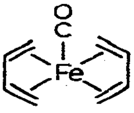


Fig. 1. UV-visible absorption spectra.

Discussion

Mechanisms of photochemical conversions

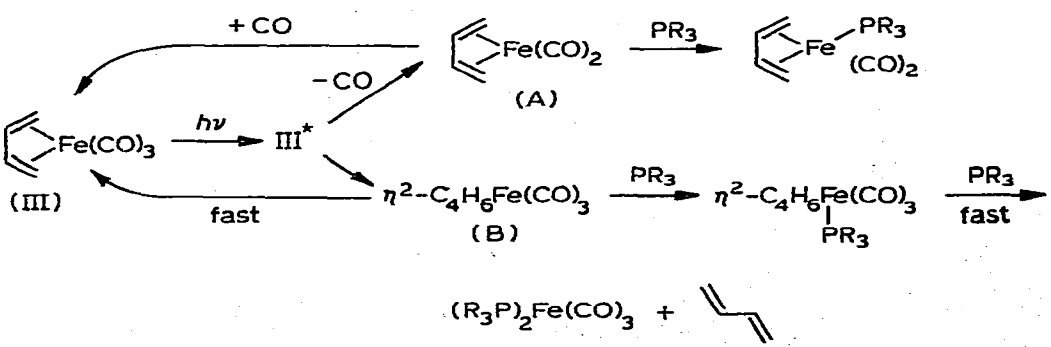
The quantum yield for CO evolution from $Fe(CO)_5$ upon photolysis was reported to be 0.99 at 254 nm, 0.98 at 300 nm, 0.88 at 366 nm, and 0.83 at 436 nm [8]. These values are much higher than those found for our diene complexes, and indeed the values depend directly on the number of CO ligands present. At 366 nm, for example, Φ_{CO} values are as given below:

	Φ_{CO}
$Fe(CO)_5$	0.88, 1.0[8]
	0.6[9]
 (III)	0.07
 (I)	0.04

Why does Φ_{CO} decrease so dramatically in the presence of the diene ligands? A clue may lie in the bond strengths in the complexes: the Fe—CO bond strength in $Fe(CO)_5$ is about 29 kcal/mol [10] whereas the Fe—C_2H_4 bond strength in ethylenetetracarbonyliron is about 23 kcal/mol, as is half the butadiene—iron bond strength in III [11]. Thus, excitation of III with photons of at least 70 kcal/mol might eventuate in dissociation of either CO or of part of the diene (Scheme 1). Partial dissociation of the diene is in fact the step

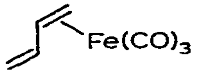
SCHEME 1

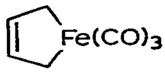
MECHANISM FOR PHOTOCHEMICAL CONVERSIONS



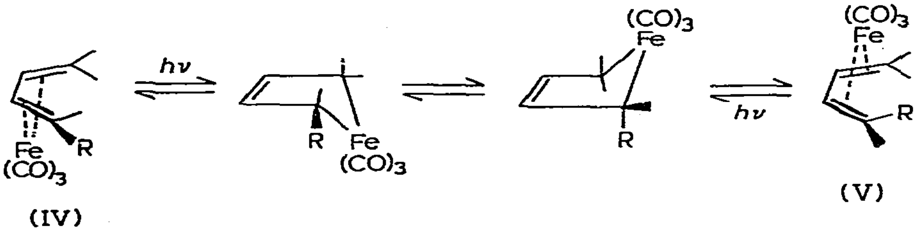
presumed to be responsible for the Φ_D process. Reversion of either unsaturated intermediate, A or B, to III provides a chemical mechanism for lowering the overall quantum yields Φ_{CO} and Φ_D. Scheme 1 is fully consistent with the observed effects of phosphite and CO concentrations on overall quantum yields. The effect of CO concentration allows an estimate that the ratio of second-order rate constants for reaction of A with CO and phosphite is about 50. Nonetheless, at phosphite concentrations above 0.1 *M*, at least 90% of the A formed is trapped by phosphite; thus the observed Φ_{CO} accurately reflects the quantum yield for formation of A.

The intermediate B, however, is destroyed in an intramolecular reversion to III, in competition with phosphite attack. One cannot be sure that B is effectively trapped by phosphite even with the large excess used. A major question pertaining to B is, of course, its structure. The most likely possibilities would be a 1,2-η^2 structure or a 1,4-η^2 structure:



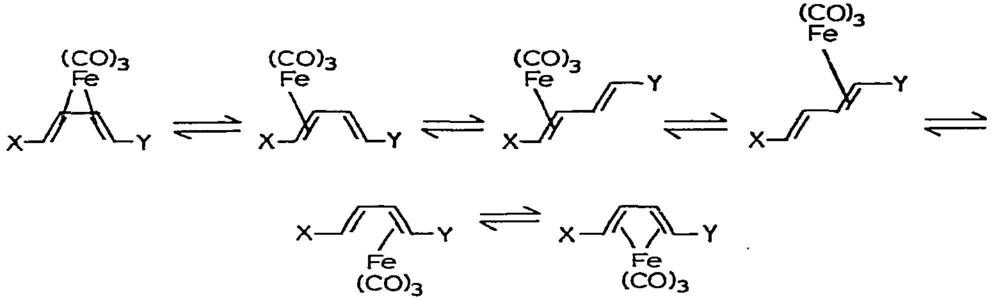


The 1,4-η^2 structure, if formed, should provide a mechanism for transfer of the Fe(CO)$_3$ group from one side of the diene unit to the other. In the process, any groups at the termini of the diene should undergo $E \rightleftharpoons Z$ interconversion:



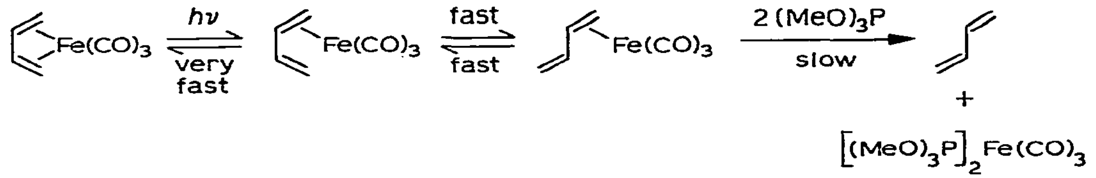
In fact, irradiation of the *Z*-pentadiene complex V for 13.5 h at room temperature with the wavelengths above 350 nm from a 125-W mercury lamp resulted in 18% conversion to the *E*-pentadiene complex IV. (The more stable IV did not photoisomerize detectably under these conditions.) However, the quantum yield for the process V → IV, at 366 nm, was less than 0.005. Since V → IV is an exothermic process, this very low quantum yield provides little support for reversible formation of the 1,4-η^2 intermediate as the principal reason for the low quantum yields Φ_{CO} and Φ_D. It is interesting to note, however, that the quantum yields observed for V (Table 1) are significantly higher than those of the other diene complexes, presumably as a consequence of relief of ground-state strain upon ligand dissociation.

A 1,2-η^2 structure for B remains a viable possibility. Whitlock and Markezich have shown that such intermediates are important in thermal isomerizations of polyene-Fe(CO)$_3$ complexes, although they are ineffectively trapped by phosphines [12]. In particular, thermal racemization of such a complex at 119°C apparently proceeded by the route:



Formation of a 1,2-η^2 intermediate through photoactivation should allow racemization to occur with much less activation energy than the 32 kcal required in Whitlock's thermal isomerizations [13]. The complex VI was therefore prepared in optically active form from resolved (sorbic acid)tricarbonyliron [14]. Several days' irradiation at 366 nm and 24°C (using the same cell and lamp as used in quantum yield measurements) caused a very small decrease in optical rotation of a cyclohexane solution of (—) — VI, allowing an estimate of the quantum yield for racemization at 24°C as 0.003. A similar run with the cuvette thermostatted at 60°C indicated a quantum yield for racemization of 0.03. (No detectible racemization occurred thermally at 60°C.) Thus, racemization does result from photochemical excitation of VI and does require a step with a thermal activation energy of about 13 kcal, presumably the shift of the $Fe(CO)_3$ unit across the *s-trans* diene.

This result on photoracemization of VI provides some support for the idea that much of the initially absorbed light energy is dissipated through partial photodissociation of the diene to η^2-coordinated intermediates, which can readily return to starting material by reclosure. This intramolecular process competes very effectively with attack of phosphite on the unsaturated η^2-coordinated intermediate.



In the case of the cyclobutadiene complex, VII, the quantum yield Φ_{CO} is much greater than for the butadiene complexes. The value at 366 nm is in fact identical to that of $Fe(CO)_5$. This may reflect unusual instability of the η^2-cyclobutadiene complex, consistent with results of Giering on related species [15]. Whatever the reason, exclusive loss of CO from VII on photolysis is consistent with results from matrix studies [16] and with the extensive reported photochemistry of VII and derivatives [17].

Conclusions

The observable quantum yields for photolysis of dienecarbonyliron complexes are small due to hidden formation of (η^2-diene)carbonyliron intermediates which predominantly revert to starting materials even in the presence of a large excess of trimethyl phosphite. Cyclobutadienetricarbonyliron does not detectibly form such an intermediate, however.

The conclusions described here, based on solution photochemical results, have recently been fully substantiated by matrix photolysis studies on III and (butadiene)tetracarbonyliron [18].

Experimental section

All reactions and manipulations were carried out under argon and in argon-saturated solvents. Compounds I and II [19] were prepared as previously reported [3]. The (diene)tricarbonyliron compounds III—VI were prepared by photochemical reaction of the dienes with pentacarbonyliron [2]. VII was prepared by the method of Emerson, Watts, and Pettit [20]. The (diene)dicarbonyl(trimethyl phosphite)iron compounds were prepared by preparative-scale irradiation of III—VII in the presence of trimethyl phosphite; a typical procedure appears below. Characterization data are given in Table 3.

(Methyl sorbate)dicarbonyl(trimethyl phosphite)iron

A solution of 2.55 g (9.58 mmol) of VI and 10.0 ml of trimethyl phosphite (12.5 g, 0.10 mol) in 150 ml of cyclohexane was placed in an immersion photoapparatus equipped with a filter of GWV glass ($\lambda > 350$ nm). After 30 min degassing by passing an argon stream through the solution, the apparatus was attached to a gas buret, and the 125 W medium pressure mercury lamp was turned on. After 5.5 h, 170 ml of gas (7.6 mmol) had been evolved, and photolysis was stopped. The solution was stripped of solvent and the residue chromatographed on silica gel, yielding: (1) a mixture of VI (0.95 g, 37% recovery) and bis(trimethyl phosphite)tricarbonyliron * (0.38 g, 10% yield), which eluted with benzene. The materials were identified by IR and NMR and the composition of the mixture was assayed by NMR; (2) the desired phosphite adduct, (1.67 g, 48%), eluted with 15% ether in benzene. The adduct was purified by recrystallization from pentane at —78°C but was a golden-yellow oil at room temperature. NMR spectrum (C_6D_6): δ 5.7 (1 H, m), 4.7 (1 H,

TABLE 3

CHARACTERIZATION OF (DIENE)DICARBONYL(TRIMETHYL PHOSPHITE)IRON COMPLEXES

Diene	ν_{CO} (cm^{-1})	Found (calc.) (%)			
		C	H	Fe	P
Butadiene [21]	1989, 1934	37.3 (37.2)	5.25 (5.17)	19.2 (19.3)	10.7 (10.7)
E-Pentadiene [22]	1989, 1931	40.0 (39.5)	5.86 (5.63)	18.6 (18.4)	10.1 (10.2)
Methyl sorbate	2003, 1946	39.8 (39.8)	5.59 (5.29)	15.3 (15.4)	8.6 (8.6)
Cyclobutadiene [23]	1988, 1932	37.4 (37.5)	4.48 (4.55)	19.0 (19.4)	10.6 (10.8)

---

* Previously reported by Reckziegel and Birgorgne [21].

m), 3.44 (3 H, s), 3.42 (9 H, d, $J = 11$ Hz), ca. 1.25 (4 H, m), and 0.7 ppm (1 H, m). Mass spectrum: *m/e* 362, 334, 306 ($P - O, 1, 2$ CO); 274 ($P - 2$ CO $-$ CH_3O); 124 ($(MeO)_3P$).

(E-Pentadiene)dicarbonyl(trimethyl phosphite) iron [22]

A solution of 2.70 g (13 mmol) of IV and 1.61 g (13 mmol) of trimethyl phosphite in 250 ml hexane was irradiated as above for 6.2 h. The residue after stripping the solvent (3.66 g yellow oil) was chromatographed on silica gel. Hexane eluted a yellow band which contained 1.48 g (55%) of recovered IV. Benzene eluted a second yellow band, which yielded 0.75 g (19%) of the phosphite adduct. This was recrystallized from 5 ml hexane at —78° to give 0.27 g of yellow solid with mp <20°C. Ether eluted a third yellow band from the column, which yielded 0.03 g (0.6%) of bis(trimethyl phosphite)tricarbonyliron. NMR spectrum of the product (C_6D_6) showed resonances at δ ca. 4.8 (2 H), 3.35 (9 H, $(CH_3O)_3$ P, $J_{PH} = 12$ Hz), 1.49 (1 H), 1.41 (3 H), 0.76 (1 H), —0.09 ppm (1 H). Mass spectrum: *m/e* 304, 276, 248 ($P - 0, 1, 2$ CO); 180 ($P - P(OMe)_3$); 165, 135; 119; 93; 56.

(Cyclohexadiene)bis(trimethyl phosphite)carbonyliron [22]

A solution of 1.00 g (4.1 mmol) of II and 5.00 ml of trimethyl phosphite (49 mmol) in 100 ml of cyclohexane was heated at 120°C in an autoclave for 53 hours. The solution was transferred to an argon-filled flask and the solvent pumped off, leaving 1.80 g of honey-like residue. Chromatography on silica gave: (1) unreacted phosphite, eluted with 300 ml pentane; (2) the product, eluted with 500 ml ether, 1.12 g yellow oil. Recrystallization from pentane at —78°C gave 1.08 g yellow crystals (64%) which melted on hand-warming. IR: 1916 cm^{-1}. NMR (Acetone-d_6): δ 4.9 (2 H, m), 3.65 (18 H, m), 2.65 (2 H, m), 1.5 ppm (4 H, m). Mass spectrum: *m/e* 412 (P), 384 ($P - CO$), 353 ($P - CO - OCH_3$), 304 ($P - CO - C_6H_8$), 258 ($C_6H_6FeP(OCH_3)_3$), 211 ($FeP(OCH_3)_4$), 93 ($P(OCH_3)_2$). Anal. Found: C, 37.90; H, 6.06; Fe, 13.51; P, 15.15. $C_{13}H_{26}FeP_2O_7$ calcd.: C, 37.88; H, 6.35; Fe, 13.55; P, 15.04%.

(Butadiene)bis(trimethyl phosphite)carbonyliron

A solution of 3.5 g (18 mmol) of III and 2.2 g of trimethyl phosphite in 80 ml benzene was irradiated as above through a Solidex filter (>300 nm) for 6 hours, during which 16 mmol of gas evolved. The resulting solution was stripped of solvent under vacuum and the residue chromatographed on silica, giving: (1) 0.36 g, primarily unreacted III; (2) a mixture of (butadiene)dicarbonyl(trimethyl phosphite)iron (1.28 g, 25%) and bis(trimethyl phosphite)tricarbonyliron (3.0 g, 43%); (3) 0.48 g (7%) of the bis(phosphite) product, mp 75—76°C. IR: 1916 cm^{-1}. NMR (C_6D_6, 10°C): δ 5.18 (2 H, m); 3.57 (18 H, m); 1.87 (2 H, m); —0.14 ppm (2 H, m). Mass spectrum: *m/e* 386 (P), 358 ($P - CO$), 355 ($P - OCH_3$), 304 ($P - C_4H_6$), 234 ($P - P(OCH_3)_3$). Anal. Found: C, 34.23; H, 6.34; Fe, 14.41; P, 16.31. $C_{11}H_{24}FeO_7P_2$ calcd.: C, 34.19; H, 6.22; Fe, 14.50; P, 16.06%.

Quantum yield measurements

All measurements were made using cylindrical quartz cells 5.00 cm in length and 2.00 cm in diameter (ca. 1.8 cm inner diameter), and having two narrow glass-stoppered necks affixed. Light from the appropriate lamp was focussed by quartz lenses through one circular end of the cell while a small magnetic stirrer bar provided stirring at the other end. Runs at 254 nm used a 4 W low-pressure mercury lamp, (Quarzlampengesellschaft Hanau NK-4-4). Runs at the other wavelengths used a Philips HBO 200-W lamp with a stabilized power supply and appropriate filters: Schott-Mainz interference filters (31% T and 313 nm, half-width 10 nm; 35% T at 366 nm, half-width 6 nm) and a Balzers filter for 405 nm. All runs were done at 24°C in a dark room. The lamp was run for at least an hour before each run, and ferrioxalate actinometry [7] was done immediately before or after each run using the same cell as the run.

An argon-flushed stock solution of 0.2 *M* (or 0.1 *M* in some cases) trimethyl phosphite in cyclohexane was used for preparing all solutions. Solutions 5—12 m*M* in organoiron complex were prepared by weighing appropriate amounts of complex into a 50 ml volumetric flask with a stopcock-sidearm above the fill mark to allow maintenance of an argon atmosphere. The flask was then filled to the mark with stock solution, in the dark room, while flushing with argon. After thorough mixing, a 13—14 ml portion was pipetted into the argon-flushed cell while argon flow was maintained. The cell was then stoppered and irradiation was begun. At appropriate intervals, samples (ca. 0.5 ml) were removed by pipette under argon flow and wrapped in aluminum foil. At the end of the run they were assayed for reactants and products using infrared analysis. All solutions were stable indefinitely in the dark.

Infrared analyses were performed on a Perkin-Elmer 621 Spectrometer using an expanded wavelength scale and the %T ordinate. Matched NaCl cells of 98.3 μm path length were used. Calibration curves were constructed for all carbonyl-containing reactants and products; the solutions were made as above using stock solution, and with the same solution in the reference IR cell. The carbonyl peaks broaden as the concentration of phosphite increases, requiring separate calibration curves for runs at different phosphite concentrations. The calibration curves for starting materials I—VII covered the concentration range 1—15 m*M*, and used the highest frequency carbonyl peak, at ca. 2050 cm^{-1} for the tricarbonyls III—VII. For the mono-phosphite substitution products, the peak used for IR analysis was at ca. 1985 cm^{-1} for the derivatives of III, IV and V, at 1946 cm^{-1} for the derivative of VI, and at 1928 cm^{-1} for the derivative of VII. Bis(trimethyl-phosphite)tricarbonyliron was determined at 1919 cm^{-1}. Calibration curves for the products were made using 0.1—5 m*M* solutions. Beer's law was accurately followed for all calibration solutions over the concentration ranges used; some 5—10 points were determined for each calibration curve, which was plotted using log (% T) vs. concentration.

The concentrations of each carbonyl-containing species were then determined for the samples taken during photolysis, and thus the rate of change of concentration of each species with time. Ferrioxalate actinometry provided the light flux in Einsteins per unit time, and hence the quantum yields could be calculated.

Photoisomerization of V to IV

a) A solution of 0.690 g of V (3.13 mmol) in 150 ml pentane was photolyzed (125 W lamp, GWV filter) as described above, for 13.5 h. Evaporation of the solvent and chromatography of the residue on silica gave 0.53 g of material which was shown by NMR to be a 82 : 18 mixture of V and IV. No conversion of IV to V could be detected under the same conditions.

b) An 11 m*M* solution of V in hexane was irradiated at 366 nm in the 5 cm cell for 16 hours. NMR as above showed no IV under conditions where 2% could be detected. Since the light intensity was found to be 5.7 × 10^{-7} E/min by ferrioxalate actinometry, the quantum yield for the isomerization is less than 0.005.

Photoracemization of VI

A sample of (sorbic acid)tricarbonyliron [24] was resolved by the method of Musco, Palumbo, and Palaro [14], using α(+)-phenylethylamine, Fluka purum, $[\alpha]_D^{20}$ + 37.1, to form diastereomeric salts. It was necessary to maintain an excess of amine during recrystallization to avoid formation of a solid containing acid: amine in a 2 : 1 ratio. A sample of 1 : 1 salt, 0.419 g, 1.12 mmol, $[\alpha]_{578}^{20}$ −100°C, was converted to the free acid by treatment with aq. HCl, and thence to the methyl ester using diazomethane. The ester was purified by chron tography on silica gel, yielding 0.291 g (1.09 mmol, 97%), $[\alpha]_{578}^{20}$ −149.5°. The material was identical by TLC and NMR to the racemic material. The optical purity was assessed by use of tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III) [25] (Willow Brook Laboratories), which fully resolved the multiplets for H-2 (δ 0.85) and H-3 (δ 5.52) of the enantiomers, the minor (+) enantiomer being shifted farther downfield in both cases. Integration of the spectra indicated a 6.50 ratio of (−) : (+) enantiomers, and thus 73% optical purity. The extrapolated $[\alpha]_{578}^{20}$ of optically pure (methyl sorbate)tricarbonyliron is thus 205°.

A 0.198 g sample of resolved ester was dissolved in 30.0 ml of cyclohexane. A 14.5 ml portion of this solution was transferred to a 5.000 cm quartz cell, argon briefly passed through, and the necks stoppered and sealed with Atmosit The observed rotation was −0.447°. During 9250 minutes' irradiation at 313 nm (1.60 × 10^{-7} E/min) no change in optical rotation was observed. Thus the quantum yield of racemization at 313 nm is less then 0.004.

The same cell and solution was then irradiated at 24°C with 366 nm light of 3.41 × 10^{-7} E/min intensity. The rotation fell to −0.434° after 14,075 min. Thus the quantum yield for racemization is 0.003 ± 0.001.

Likewise, during 2900 min. of irradiation at 60°C and 366 nm with light of intensity 2.29 × 10^{-7} E/min, the rotation of a solution of 0.149 mmol of ester in 14.5 ml cyclohexane fell from −0.186° to −0.168°. Stirring at 60° for an additional 2800 minutes with the lamp off resulted in no further decrea in rotation; thus the quantum yield for racemization at 60° and 366 nm is 0.0 0.01.

Acknowledgment

R.C. Kerber and P. Kirsch express their grateful appreciation to the Alexander-von-Humboldt-Stiftung, B.R.D., for award of Humboldt Fellowships during whose tenure this work was completed. R. Rumin gratefully acknowledges support from the Institut für Strahlenchemie.

References

1 (a) M. Wrighton, Chem. Rev., 74 (1974) 401; (b) E. Koerner von Gustorf and F.-W. Grevels, Fortschr. Chem. Forsch., 13 (1969) 366.

2 E. Koerner von Gustorf, Z. Pfajfer and F.-W. Grevels, Z. Naturforsch. 26b (1971) 66.

3 E. Koerner von Gustorf, J. Buchkremer, Z. Pfajfer, and F.-W. Grevels, Angew. Chem., 83 (1971) 249.

4 F.M. Chaudhuri and P.L. Pauson, J. Organometal. Chem., 5 (1966) 73; J.D. Warren and R.J. Clark, Inorg. Chem., 9 (1970) 373; J.D. Warren, M.A. Busch and R.J. Clark, Inorg. Chem., 11 (1972) 452; M.A. Busch and R.J. Clark, Inorg. Chem., 14 (1975) 219, 226; T.H. Whitesides and R.A. Budnik, Inorg. Chem., 14 (1975) 664; C.B. Ungermann and K.G. Caulton, J. Organometal. Chem., 94 (1975) C9.

5 A preliminary report of some of this work has appeared: J. Buchkremer, F.-W. Grevels, O. Jaenicke, P. Kirsch, R. Knoesel, E.A. Koerner von Gustorf, and J. Shields, Abstracts of 7th Internat. Conf. Photochem. Jerusalem, Israel, Sept. 1973, p. 61; see also C.R. Bock and E.A. Koerner von Gustorf, Adv. Photochem., 10 (1977) 221.

6 A paper by J. Buchkremer, F.-W. Grevels, E.A. Koerner von Gustorf and Z. Pfajfer, fully describing such photochemical syntheses, is in preparation by Dr. Grevels.

7 C.G. Hatchard and C.A. Parker, Proc. Roy. Soc. (London), A235 (1956) 518.

8 O. Warburg and E. Negelein, Biochem. Z., 204 (1929) 495; see also J.L. Graff, R.D. Sanner and M.S. Wrighton, J. Amer. Chem. Soc., 101 (1979) 273.

9 F.-W. Grevels and D. Schulz, unpublished results.

10 A. Cartner, B. Robinson, and P.J. Gardner, J. Chem. Soc. Chem. Commun., (1973) 317.

11 D.L.S. Brown, J.A. Connor, M.L. Leung, M.I. Paz-Andrade, and H.A. Skinner, J. Organometal. Chem., 110 (1976) 79.

12 H.W. Whitlock, Jr. and R.L. Markezich, J. Amer. Chem. Soc., 93 (1971) 5290.

13 H.W. Whitlock, Jr. and Y.N. Chuah, J. Amer. Chem. Soc., 87 (1965) 3605; H.W. Whitlock, Jr., C. Reich, and W.D. Woessner, ibid., 93 (1971) 2483.

14 A. Musco, R. Palumbo, and G. Palaro, Inorg. Chem., 5 (1971) 157.

15 A. Sanders and W.P. Giering, J. Amer. Chem. Soc., 97 (1975) 919; J. Organometal. Chem., 104 (1976) 49.

16 O.L. Chapman, J. Pacansky and P.W. Wojtkowski, J. Chem. Soc. Chem. Commun., (1973) 681; A.J. Rest, J.R. Sodeau, and D.J. Taylor, J. Chem. Soc. Dalton, (1978) 651.

17 Some recent examples: A. Bond and M. Green, J. Chem. Soc., Dalton, (1974) 763; P. Reeves, J. Henery and R. Pettit, J. Amer. Chem. Soc., 91 (1969) 5888; J.S. Ward and R. Pettit, ibid., 93 (1971) 262; R.H. Grubbs, T.A. Pancoast, and R.A. Grey, Tetrahedron Lett., (1974) 2425; P.L. Pruitt, E.R. Biehl, and P.C. Reeves, J. Organometal. Chem., 134 (1977) 37; I. Fischler, K. Hildenbrand, and E. Koerner von Gustorf, Angew. Chem., 87 (1975) 35.

18 G. Ellerhorst, W. Gerhartz, and F.-W. Grevels, Inorg. Chem., (1979) in press.

19 C. Krüger and Y.-H. Tsay, Angew. Chem., 83 (1971) 250.

20 G.F. Emerson, L. Watts and R. Pettit, J. Amer. Chem. Soc., 87 (1965) 132.

21 A. Reckziegel and M. Bigorgne, J. Organometal. Chem., 3 (1965) 341.

22 We thank Mr. Konrad Schneider for these results.

23 Data from the doctoral thesis of I. Fischler, Ruhr-Universität Bochum, 1974, pp. 134—135.

24 M. Cais and N. Maoz, J. Organometal. Chem., 5 (1966) 370.

25 H.L. Goering, J.N. Eikenberry, G.S. Koermer and C.J. Lattimer, J. Amer. Chem. Soc., 96 (1974) 1493.