W. Jolly and R. Pettit, *J. Am. Chem. Soc.*, **88**, 5044 (1966).

(24) Nevertheless, characterization of optically active **7** has been reported by Davison and co-workers.[15b]

(25) Davison and Martinez have suggested sequencing rules for the assignment of the *R* or *S* designation to the absolute configurations of these molecules.[15c]

(26) Compound **8** has such a low specific rotation at 578 nm in benzene (ca. 50°) that we have been forced to use methylene chloride for this particular measurement. Solutions were used as soon as prepared and we have had no difficulty in obtaining reproducible numbers this way.

(27) This type of reactivity is precedented for the nonchiral analogue $CpFe(CO)_2CH_2Cl$.[23b]

(28) Davison and co-workers have found that treatment of (+)**4a** (same configuration as (+)**6a**) with $HBF_4$ also leads to cyclopropanation of this same olefin, but in this case the (−)-(1*R*,2*R*)-cyclopropane predominates.[15b]

(29) For examples of such lanthanide-shifted spectra, see ref 1.

(30) On rare but unpredictable occasions we have observed up to 30% racemization upon $SO_2$ insertion into iron alkyls when carried out in $CH_2Cl_2$ solution. These racemization components appear to be caused by impurities in the alkyl or by the presence of air, etc. While the use of DMF is much less convenient and gives very low yields of sulfinate product, this solvent does appear to render the reaction less sensitive to impurities.

(31) Trapping of intermediates by iodide ion has been carried out in nonchiral metal–alkyl insertion reactions: S. E. Jacobson, P. Reich-Rohrvig, and A. Wojcicki, *Inorg. Chem.*, **12**, 717 (1973).

(32) J. K. P. Ariyaratne and M. L. H. Green, *J. Chem. Soc.*, 1 (1964).

(33) (a) M. Rosenblum, *Acc. Chem. Res.*, 7, 122 (1974); (b) W. P. Giering and M. Rosenblum, *J. Am. Chem. Soc.*, **93**, 5299 (1971).

(34) Professor Davison and his co-workers independently reported the preparation of **4** by a slightly different route and its conversion to **5** and **7**.[15b]

(35) S. E. Jacobson and A. Wojcicki, *J. Am. Chem. Soc.*, **95**, 6962 (1973); A. Wojcicki, *Acc. Chem. Res.*, **4**, 344 (1971).

(36) V. W. Day and A. Davison, unpublished results. We thank Professors Day and Davison for communication of their results prior to publication.

(37) Details of these empirical correlations will be published.[20b]

(38) D. L. Miles and T. C. Flood, unpublished results.

(39) A. Saunders, L. Cohen, W. P. Giering, D. Kenedy, and C. V. Magatti, *J. Am. Chem. Soc.*, **95**, 5430 (1973).

(40) J. J. Eisch and R. B. King, "Organometallic Syntheses", Vol. I, Academic Press, New York, N.Y., 1965: (a) p 114; (b) p 151.

(41) K. A. Andrianov, A. A. Mamedov, L. M. Volkova, and E. I. Klabanovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2305 (1969).

(42) This compound has recently been prepared, but fully characterizing data have not been reported.[15b]

(43) H. E. Simmons and R. P. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(44) Optically pure (1*S*,2*S*)-1-methyl-2-phenylcyclopropane has been reported to have $[\alpha]_D$ +144.9° (H. Nozaki, H. Takaya, S. Moriuti, and R. Noyori, *Tetrahedron*, **24**, 3655 (1968)) and $[\alpha]_D$ +96° (J. E. Baldwin, J. Loliger, W. Rastetter, L. L. Huckstep, and N. De La Higuera, *J. Am. Chem. Soc.*, **95**, 3796 (1973)).

(45) The absolute configuration has been shown previously: T. Sugita and Y. Inouya, *Bull. Chem. Soc. Jpn.*, **39**, 1075 (1966).

(46) P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, **5**, 1177 (1966).

(47) D. L. Reger, *Inorg. Chem.*, **14**, 660 (1975).

(48) M. Graziani and A. Wojcicki, *Inorg. Chim. Acta*, **4**, 347 (1970).

---

Contribution from the Department of Chemistry,
California State University, Fullerton, Fullerton, California 92634

# Reactivity of the Radical and Anion of $C_3H_5Fe(CO)_2P(C_6H_5)_3$: The Debromination of Vicinal Organic Dibromides

P. A. WEGNER* and M. S. DELANEY

*Received February 3, 1976* AIC60089R

Tetrahydrofuran solutions of the $C_3H_5Fe(CO)_2P(C_6H_5)_3$ radical and the $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ anion were generated from $\eta^3$-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$ using zinc dust and sodium amalgam, respectively. The solutions of these species free from reducing agents were found to be effective debromination reagents for vicinal organic dibromides. The stereochemistry of the debromination reactions was studied using racemic (*R*,*R* and *S*,*S*) and (*R*,*S*)-3,4-dibromohexane. The radical does not react stereospecifically but the anion can react stereospecifically with anti elimination.

Since the synthesis[1-3] of the $\eta^3$-$C_3H_5Fe(CO)_3X$ (X = Cl, Br, I) system, principally structural[4] and spectral properties[5,6] of the allyliron derivatives have been investigated. The salient chemical feature of the system is the existence of both a stable radical[7] $C_3H_5Fe(CO)_3$ and anion[8] $C_3H_5Fe(CO)_3^-$. The iron atom in the monomeric radical has an effective atomic number of 17 while in the anion it has the inert gas configuration. The radical species was suggested[7] and recently unequivocally confirmed[9] to be in equilibrium with its dimer $[C_3H_5Fe(CO)_3]_2$. In the case of monophosphine substituted derivatives of the radical $C_3H_5Fe(CO)_2L$ (L = $P(C_6H_5)_3$, $P(C_4H_9)_3$), the equilibrium favors the monomeric radical.[7,9] Both the radical and anion exhibit an affinity toward halogen to regenerate the parent $\eta^3$-$C_3H_5Fe(CO)_3X$ (X = Cl, Br, I) system. This paper reports the ability of both the radical and the anion to debrominate vicinal organic dibromides and compares the reactivity to the two related species. The principal comparison involves the stereochemistry of the debromination reaction.

## Experimental Section

Chemicals were purchased from the following sources: triphenylphosphine, Pressure Chemical Co., iron pentacarbonyl, Alfa Inorganics; 3-bromopropene, Aldrich; *cis*- and *trans*-3-hexene, Chemical Samples Co. Tetrahydrofuran was purified by distillation under nitrogen from Vitride. The photochemical preparation of $\eta^3$-$C_3H_5Fe(CO)_3Br$ and the preparation of $\eta^3$-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$ from $\eta^3$-$C_3H_5Fe(CO)_3Br$ were by the method of Heck.[1] The racemic (*R*,*R* and *S*,*S*) and (*R*,*S*)-3,4-dibromohexanes were synthesized by the method of Stokr and Doskocilova.[10] Photochemical reactions were run under nitrogen in a Rayonet photochemical reactor equipped with a magnetic stirrer. Infrared spectra were obtained using a Perkin-Elmer 137 spectrophotometer while $^1H$ NMR spectra were obtained using a Varian A60A Spectrometer. Gas chromatographs were obtained on a Model 700 Hewlett-Packard Chromatograph.

**Preparation of the $C_3H_5Fe(CO)_2P(C_6H_5)_3$ Radical (I).** The radical was prepared under nitrogen either in a drybox or in a Schlenk flask. A 0.742-g (1.5 mmol) sample of $\eta^3$-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$ was mixed with an excess of zinc dust, 0.327 g (5.0 mmol), and 20 ml of tetrahydrofuran was added. The brown solution was stirred until a dark green color appeared. The mixture was filtered to remove excess Zn and the resulting solution was used to study the reaction of the radical, $\nu_{CO}$(THF) = 1960, 1897 $cm^{-1}$.

**Preparation of the $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ Anion (II).** The anion was prepared under nitrogen either in a drybox or using a Schlenk flask. A 0.742-g (1.5 mmol) sample of $\eta^3$-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$ in 20 ml of tetrahydrofuran was added to Na(Hg) containing 0.12 g of sodium (5 mmol). After about 3 min of stirring the green color of the radical appeared and within 15 min a deep red-brown color appeared. The mixture was then filtered through Celite to remove excess sodium amalgam and the filtrate used to study reactions of the anion $\nu_{CO}$(THF) = 1960, 1890 $cm^{-1}$.

**Reaction of 3,4-Dibromohexane with the Radical and the Anion of $C_3H_5Fe(CO)_2P(C_6H_5)_3$.** The procedure for the reaction of either $C_3H_5Fe(CO)_2P(C_6H_5)_3$ or $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ with the stereoisomers of 3,4-dibromohexane was the same. This procedure is illustrated for the radical. A solution of 1.5 mmol of the radical in tetrahydrofuran was prepared as described above. The solution was placed under nitrogen in a single necked flask modified with a side arm. The side arm contained a 1-mm stopcock which allowed a syringe needle to be inserted into the flask and was capped with an airtight septum. The flask was attached to a vacuum line and partially evacuated. A 5-ml tetrahydrofuran solution of 0.75 mmol of (*R*,*S*)-3,4-dibromohexane was added to the solution of the radical by syringe, and the reaction was allowed to proceed for 30 min at room temperature. The reaction solution was then distilled into a clean trap. During distillation the solution was kept at room temperature so only the tetrahydrofuran solvent and the hexene products distilled. Products containing iron and unreacted (*R*,*S*)-3,4-dibromohexane remained in the reaction vessel. The distillate was then removed and diluted to the mark in a 50-ml volumetric flask. The hexene products were analyzed by vapor phase chromatography using a 40 ft, $^1/_8$ in. $AgNO_3$ column (80% by weight Chromosorb (firebrick) 60–80 mesh:20% by weight saturated solution of $AgNO_3$ in propanediol) at a flow rate of 10 ml/min and at 30 °C. The iron-containing products were identified by infrared spectroscopy to be $\eta^3$-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$ and 1,5-$Fe(CO)_3[P(C_6H_5)_3]_2$. Unreacted 3,4-dibromohexane could be obtained by extracting the residue in the reaction vessel with hexane and diluting the filtered extracts to the mark in a 25-ml volumetric flask. The 3,4-dibromohexane was analyzed by vapor-phase chromatography using a commercial 6 ft × $^1/_8$ in. column of silicone gum rubber UCC-W-982 on acid washed chromosorb W (dimethyldichlorosilane treated).

**Reaction of 1,2-Dibromo-1,2-diphenylethane with the Radical and the Anion.** The reaction was run as with the 3,4-dibromohexane derivatives except that after the solvent was distilled the residue contained both the organic products and the derivatives containing iron. The residue was extracted with hexane to remove the organic products. The hexane was removed to yield *trans*-stilbene which was identified by melting point and infrared and $^1H$ NMR spectra.

## Results

The course of the reaction of the $C_3H_5Fe(CO)_2P(C_6H_5)_3$ radical and the $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ anion with vicinal organic dihalides was elucidated with (*R*,*S*)-stilbene dibromide. The *rac* and *R*,*S* isomers of 3,4-dibromohexane were used to examine the stereochemistry of the reaction of the radical and the anion with vicinal dibromides. In this paper *rac* is taken to indicate the racemic mixture of (*R*,*R*)- and (*S*,*S*)-3,4-dibromohexane.

The reaction of $C_3H_5Fe(CO)_2P(C_6H_5)_3$ radical with stilbene dibromide in a 2:1 mol ratio produced *trans*-stilbene in 51% yield as the sole organic product. No evidence for any isomer of bromostilbene was observed using thin-layer chromatography and the only other organic derivative was unreacted stilbene dibromide. The $C_3H_5Fe(CO)_2P(C_6H_5)_3$ radical was converted into two organometallic derivatives of iron: $\eta^3$-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$ and 1,5-$Fe(CO)_3[P(C_6H_5)_3]_2$. The principal product was $\eta^3$-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$ in a better than 3:2 mol ratio.

Reaction of $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ with stilbene dibromide in a 1:1 mol ratio also produced *trans*-stilbene in 59% yield as the sole organic product. The $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ anion was converted to either $\eta^3$-$C_3H_5Fe(CO)_2P(C_3H_5)_3Br$ or 1,5-$Fe(CO)_3[P(C_6H_5)_3]_2$ with the former predominating by a greater than 5:1 mol ratio.

The reaction of the isomeric 3,4-dibromohexanes with the $C_3H_5Fe(CO)_2P(C_6H_5)_3$ radical or the $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ anion produced the isomers of 3-hexene as the sole organic product except for unreacted 3,4-dibromohexane. No evidence for 1- or 2-hexene derivatives was obtained nor was there any indication of the formation of isomers of 3-bromohexene. Neither *cis*- nor *trans*-3-hexene are isomerized in the presence of either the radical or the anion. The relative amounts of *cis*- and *trans*-3-hexene formed are thus apparently a function of the debromination reaction and not of a subsequent isomerization.

The principal organometallic derivative formed in the reactions with the isomeric 3,4-dibromohexanes was $\eta^3$-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$. The other product 1,5-$Fe(CO)_3[P(C_6H_5)_3]_2$ usually was less than 20% of the amount of the $\eta^3$-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$ formed except when a large excess of $C_3H_5Fe(CO)_2P(C_6H_5)_3$ or $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ was present. Generally as was the case with stilbene dibromide more 1,5-$Fe(CO)_3[P(C_6H_5)_3]_2$ formed when the reactions involved the radical as opposed to the anion. The formation of 1,5-$Fe(CO)_3[P(C_6H_5)_3]_2$ requires the reaction of at minimum two allyl groups; however, the fate of the allyl ligand was not followed quantitatively. Nevertheless propylene was qualitatively identified in the reaction mixture during the gas chromatographic analysis although no biallyl was observed.

**Table I.** Reaction of *rac*- and (*R*,*S*)-3,4-Dibromohexane with the $C_3H_5Fe(CO)_2P(C_6H_5)_3$ Radical

| Organic substrate[a] | Dibromide: complex | mmol of dibromide | % yield of 3-hexene[b] | Trans/cis | % trans |
|---|---|---|---|---|---|
| *rac* | 3:1 | 4.50 | 53 | 2.07 | 67 |
| *rac* | 2:1 | 3.00 | 41 | 2.22 | 69 |
| *rac* | 1:1 | 1.50 | 48 | 2.27 | 69 |
| *rac* | 1:1.5 | 1.00 | 72 | 2.00 | 67 |
| *rac* | 1:2 | 0.75 | 82 | 1.95 | 66 |
| *rac* | 1:3 | 0.50 | 71 | 2.24 | 69 |
| *R,S* | 2:1 | 3.00 | 46 | 8.9 | 90 |
| *R,S* | 1:1 | 1.50 | 59 | 9.9 | 91 |
| *R,S* | 1:2 | 0.75 | 65 | 10.0 | 91 |
| *R,S* | 1:3 | 0.78 | 80 | 9.9 | 91 |

[a] *rac* represents the racemic mixture of (*R*,*R*)- and (*S*,*S*)-3,4-dibromohexane. [b] Yields are based on the limiting reagent assuming a stoichiometric ratio of 1 mol of dibromide to 2 mol of complex.

**Table II.** Reaction of *rac*- and (*R*,*S*)-3,4-Dibromohexane with the $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ Anion

| Organic substrate[a] | Dibromide: complex | mmole of dibromide | % yield of 3-hexene[b] | Trans/cis | % trans |
|---|---|---|---|---|---|
| *rac* | 3:1 | 4.50 | 28 | 1.10 | 52 |
| *rac* | 2:1 | 3.00 | 39 | 1.46 | 59 |
| *rac* | 1:1 | 1.50 | 74 | 1.74 | 64 |
| *rac* | 1:2 | 0.75 | 65 | 1.62 | 62 |
| *rac* | 1:3 | 0.50 | 91 | 0.40 | 29 |
| *rac* | 1:4 | 0.38 | 98 | 0.15 | 13 |
| *R,S* | 1:1 | 1.50 | 44 | 18.2 | 95 |
| *R,S* | 1:3 | 0.50 | 82 | 19.5 | 95 |
| *R,S* | 1:5 | 0.30 | 99 | No cis | 100 |

[a] *rac* represents the racemic mixture of (*R*,*R*)- and (*S*,*S*)-3,4-dibromohexane. [b] Yields are based on the limiting reagent assuming a stoichiometric ratio of 1/1.

Representative stereochemical results for the debromination of *rac*- and (*R*,*S*)-3,4-dibromohexane with the $C_3H_5Fe(CO)_2P(C_6H_5)_3$ radical are given in Table I. At equimolar ratios or with excess dibromohexane yields are in the 40–60% range. In reactions where the iron derivative is in excess the yields of hexene increase to 80% or greater. The trans/cis ratio for the reaction of the radical with *rac*-3,4-dibromohexane is constant and averages 2.1/1. The trans/cis ratio for the reaction with (*R*,*S*)-3,4-dibromohexane is also constant and averages 9.7/1.

Table II presents representative results for the reaction of $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ with *rac*- and (*R*,*S*)-3,4-dibromohexane. The yields for the reaction with the anion are slightly better than with the radical. Yields of hexene are below 50% in experiments with an excess of 3,4-dibromohexane. When the iron complex is in excess yields rise rapidly and approach 100%. In the case of (*R*,*S*)-3,4-dibromohexane the trans/cis ratio remains better than 18/1. In fact at large molar excesses of the iron complex essentially no *cis*-3-hexene is observed. Unlike the reaction of the anion with the *R*,*S* isomer or the reaction of the radical with either the *rac* or the *R*,*S* isomers, the reaction of the anion with *rac*-3,4-dibromohexane does not produce a constant trans/cis ratio of hexenes. When the dibromohexane is near equimolar or in molar excess more *trans*-3-hexene is produced than the cis isomer. But when significant excess $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ is present *cis*-3-hexene is the favored product. At a ratio of dibromide/anion of 1/4, the trans/cis ratio is 0.154 (i.e., cis/trans 6.5/1). It is at these ratios of reactants that essentially quantitative yields are obtained.

The formation of 1,5-$Fe(CO)_3[P(C_6H_5)_3]_2$ in the debromination reactions of both stilbene dibromide and the isomeric 3,4-dibromohexane led to an infrared examination of the thermal stability of $C_3H_5Fe(CO)_2P(C_6H_5)_3$ and $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$. Both derivatives decompose slowly at room temperature in tetrahydrofuran solution under nitrogen and in both cases 1,5-$Fe(CO)_3[P(C_6H_5)_3]_2$ is the major organometallic product formed. The fate of the allyl group was not determined in these experiments. The rate of decomposition of either the radical or the anion was not fast enough to account for any but small amounts of 1,5-$Fe(CO)_3[P(C_6H_5)_3]_2$ formed in the debromination reactions. The half-life of the radical or anion was conservatively estimated at 3 h while all reactions with these derivatives were carried out within 0.5 h of their preparation. The majority of 1,5-$Fe(CO)_3[P(C_6H_5)_3]_2$ is thus apparently formed during the course of the reaction of the anion or radical with the vicinal dibromide.

## Discussion

Equations 1 and 2 give the stoichiometry expected for the

$$2C_3H_5Fe(CO)_2P(C_6H_5)_3 + RCHBrCBrHR \rightarrow 2\eta^3\text{-}C_3H_5Fe(CO)_2P(C_6H_5)_3Br + RHC{=}CHR \qquad (1)$$

$$C_3H_5Fe(CO)_2P(C_6H_5)_3^- + RCHBrCBrHR \rightarrow \eta^3\text{-}C_3H_5Fe(CO)_2P(C_6H_5)_3Br + RHC{=}CHR + Br^- \qquad (2)$$

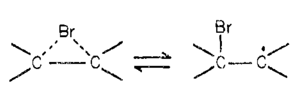
$$R = C_6H_5, C_2H_5$$

reaction of a vicinal organic dibromide with the $C_3H_5Fe(CO)_2P(C_6H_5)_3$ radical and the $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ anion, respectively. These equations probably best describe the stoichiometry of the debromination reactions (vide infra) although the results indicate that the overall reactions are somewhat more complex. For example, 1,5-$Fe(CO)_3[P(C_6H_5)_3]_2$ is observed as a minor product in all reactions and the optimum yields of olefin are not observed at the stoichiometric ratio of reagents.

The $C_3H_5Fe(CO)_2P(C_6H_5)_3$ radical and $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ anion have a great deal of similarity in their reaction with vicinal organic dibromides in spite of the electronic differences between the complexes. Both reagents strictly dehalogenate but do not dehydrohalogenate nor do they induce any other reaction of the organic dibromide. The relative stability of an iron–halide vs. an iron–hydride bond in the organometallic product may be the factor controlling this behavior. The $\eta^3$-$C_3H_5Fe(CO)_2P(C_6H_5)_3H$ derivative has not been isolated while the corresponding bromide derivative is stable. Both reagents react with 3,4-dibromohexane to yield the same organic product 3-hexene. Neither reagent isomerizes *cis*- or *trans*-3-hexene further. This agrees with recent work on the radical and its derivatives[9] which indicates 1-hexene is isomerized to 2-hexene but which also reports 3-hexene is not isomerized under comparable conditions. The trend in the yield of organic product is also similar for both reagents. The maximum yields are obtained when the complex is substantially in excess of the organic dibromide while the lowest yields occur when the organic reagent is in excess. The lower yield of product when the organic substrate is in excess to the complex restricts the catalytic utility of either reagent. Nevertheless enhanced rates of debromination and also enhanced rates of coupling of benzyl bromides have been observed[11] using zinc and catalytic amounts of $\eta^3$-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$. Presumably the radical is the catalytic species.

The observation of 1,5-$Fe(CO)_3[P(C_6H_5)]_2$ during the interaction of the anion and radical with organic dibromides was unexpected. The mode of formation of 1,5-$Fe(CO)_3[P(C_6H_5)_3]_2$ during the reaction is undoubtedly complex and our data do not completely illuminate it. The thermal decomposition studies on the anion and radical indicate the majority of 1,5-$Fe(CO)_3[P(C_6H_5)]_2$ must form as a consequence of the debromination reaction and not by thermolytic decomposition. However, the derivative does not form in a stoichiometric fashion during the debromination reaction. We feel that 1,5-$Fe(CO)_3[P(C_6H_5)_3]_2$ probably results from the reaction of an intermediate or product of the debromination reaction with unreacted iron reagent. Support for this view comes from an examination of the yield data. Low yields of olefin occur when the complex is the limiting reagent; however, the organic dibromide is not converted to other products but remains unreacted. The low yield consequently must result from the loss of unreacted anion or radical presumably through reaction with the intermediates or products of the debromination reaction.

The principal differences in the reactivity of the two iron complexes occur in the stereochemistry of the debromination of (*R,S*)- and *rac*-3,4-dibromohexane. The radical reacts with either the *R,S* or the *rac* isomer to yield predominately *trans*-3-hexene. The ratio of *trans/cis*-3-hexene in each case is invariant with regard to reagent ratio and averages about 90% trans for the *R,S* isomer and about 70% trans for the *rac* isomer. The constant trans/cis ratio of product from either isomer is indicative that the mechanism of debromination by the radical is not affected by reagent ratio. The observed product ratios are close to the equilibrium ratio of *trans/cis*-3-hexene at 25 °C (79% trans; trans/cis 3.86/1).[12] Mechanistically the debromination reaction of $C_3H_5Fe(CO)_2P(C_6H_5)_3$ radical may be similar to that of Cr(II), one of the best studied debromination reagents.[13-15] In debromination reactions with Cr(II) a bromine bridged radical intermediate was suggested to form initially.[13] This intermediate either reacted further with excess Cr(II) to form a chromium alkyl intermediate which ultimately formed olefin product or alternatively formed olefin product directly by expulsion of a bromine atom.[15] Stereochemical integrity was suggested to be lost if the bromine bridged radical had a sufficiently long lifetime to be in equilibrium with an open radical within which bond rotation could occur[15] (eq 3). Debromination of either



(3)

isomer of 3,4-dibromohexane with $C_3H_5Fe(CO)_2P(C_6H_5)_3$ radical may also yield the respective bromine bridged intermediate which could undergo the equilibrium indicated in eq 3. In such a case, each isomer would yield both *cis*- and *trans*-3-hexene but also each isomer likely would produce more of the thermodynamically favored product *trans*-3-hexene. It should be emphasized that although this may be the predominate mode of reactivity complete thermodynamic control does not obtain since the same product ratio is not observed for both the *rac* and *R,S* isomers.

The debromination reaction of the $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ anion with the isomers of 3,4-dibromohexane can be made to proceed in high yield (>98%) and stereoselectively by working at low dibromide/complex ratios. Overall anti removal of bromine atoms is observed under these conditions. Thus the *R,S* isomer generates product greater than 95% *trans*-3-hexene in all cases, while the *rac* isomer can yield product which is up to 87% *cis*-3-hexene. The $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ anion is apparently reacting similarly to iodide ion in a classical E2 mechanism.[16] The stereochemistry of the reaction of the anion with the *R,S* isomer does not change appreciably with change in reagent ratio and the trans/cis product ratio is essentially constant at >95% trans. In the case of the *rac* isomer a complex variation of product ratio with reagent ratio exists. High stereoselectivity is observed only at low dibromide/complex ratios. When the dibromide/complex ratio is greater than 1:2 (i.e., whenever the complex is not in substantial excess), the reaction is not selective and in fact *trans*-3-hexene can be 50–60% of the 3-hexene yield. The reason for the change in product ratio with reagent ratio is not clear but two possibilities are (1) a mechanistic change or (2) an alteration[17] of the iron reagent under the experimental conditions. We prefer the latter possibility since it might also explain the very low conversion to 3-hexene observed at these conditions.[17]

The data presented indicate both the $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ anion and the $C_3H_5Fe(CO)_2P(C_6H_5)$ radical are effective debromination agents for vicinal organic dibromides under mild, aprotic conditions. Both reagents debrominate but do not dehydrohalogenate. Under appropriate conditions the debromination reaction of the anion can be highly stereoselective and proceed in high yield.

**Acknowledgment**. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for the support of this research.

**Registry No.** I, 12098-67-8; II, 59388-96-4; $\eta^3$-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$, 59388-97-5; *rac*-3,4-dibromohexane, 16230-28-7; (*R,S*)-3,4-dibromohexane, 16230-27-6; *trans*-3-hexene, 13269-52-8; *cis*-3-hexene, 7642-09-3.

## References and Notes

(1) R. F. Heck and C. R. Boss, *J. Am. Chem. Soc.*, **86**, 2580 (1964).
(2) R. A. Plownam and F. G. A. Stone, *Z. Naturforsch, B*, **17**, 575 (1962).
(3) H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **45**, 1927 (1962).
(4) M. K. Minosyan, Y. T. Struchkov, I. I. Kvitskaya, and R. L. Avoyan, *Zh. Strukt. Khim.*, **7**, 903 (1966).
(5) A. N. Nesmeyanov, I. I. Kritskoya, and E. I. Fedin, *Dokl. Akad. Nauk. SSSR*, **164**, 1058 (1965).
(6) A. N. Nesmeyanov, Y. A. Ustynyuk, I. I. Kritskaya, and G. A. Shchembelov, *J. Organomet. Chem.*, **14**, 395 (1968).
(7) H. D. Murdoch and E. A. C. Kucken, *Helv. Chim. Acta*, **47**, 1517 (1964).
(8) S. P. Gubin and L. I. Denisovich, *J. Organomet. Chem.*, **15**, 471 (1968).
(9) E. L. Muetterties, B. A. Sosinsky, and I. I. Zamaraev, *J. Am. Chem. Soc.*, **97**, 5299 (1975).
(10) J. Stokr and D. Doskocilova, *Collect. Czech. Chem. Commun.*, **34**, 1875 (1969).
(11) P. A. Wegner and B. Mills, unpublished data. For example, during the same time period, the coupling of benzyl bromide by zinc to form bibenzyl in tetrahydrofuran at ambient conditions proceeds to 80% conversion when catalyzed by $\eta^3$-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$ (200/1 substrate/catalyst ratio) compared to 16% conversion for the uncatalyzed reaction.
(12) Calculated from data in "CRC Handbook of Chemistry and Physics", 50th ed, Chemical Rubber Publishing Co., Cleveland, Ohio.
(13) W. Kray and C. Castro, *J. Am. Chem. Soc.*, **86**, 4603 (1964).
(14) D. M. Singleton and J. K. Kochi, *J. Am. Chem. Soc.*, **89**, 6547 (1967).
(15) J. K. Kochi and D. M. Singleton, *J. Am. Chem. Soc.*, **90**, 1582 (1968).
(16) W. H. Saunders, Jr., and A. F. Cockerill, "Mechanisms of Elimination Reactions", Wiley, New York, N.Y., 1973, pp 333–353.
(17) A possible sequence of reactions of the anion which would be compatible with the data assumes a relatively slow reaction of $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ with the *rac*-3,4-dibromohexane. A reaction product would be $\eta$-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$ which could react rapidly with remaining anion to form the radical $C_3H_5Fe(CO)_2P(C_6H_5)_3$ and $Br^-$. The radical does not debrominate stereospecifically and also produces more 1,5-$Fe(CO)_3[P(C_6H_5)_3]_2$ during its reactions. The (*R,S*)-3,4-dibromohexane may not be susceptible to the same set of reactions since this isomer may react more rapidly with the $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$. Differences of this type in the rate of reactivity of *R,S* and *rac* isomers have been previously observed.[16]

---

Contribution from Chemistry Department 1, H. C. Ørsted Institute,
DK 2100 Copenhagen Ø, Denmark

# Oxidation of Some Tris(2,2′-bipyridyl)- and Tris(1,10-phenanthroline)osmium(II) Salts by Thallium(III) in Aqueous Acid

GWYNETH NORD[1]

*Received February 3, 1976* AIC60090Q

The oxidation rate of $Os(bpy)_3^{2+}$ and of $Os(phen)_3^{2+}$ by Tl(III) is first order in each of the reactants and increases with decrease in $H^+$ concentration. For $Os(bpy)_3^{2+}$ the rate constants at 25 °C are 16.6 $dm^3\ mol^{-1}\ s^{-1}$ in 1 M $HClO_4$ + 0.4 M $NaClO_4$, 0.26 $dm^3\ mol^{-1}\ s^{-1}$ in 1.05 M $HNO_3$ + 0.31 M $NaNO_3$, and 0.054 $dm^3\ mol^{-1}\ s^{-1}$ in 0.453 M $H_2SO_4$ + 0.535 M $Na_2SO_4$. The decrease in rate with change in medium is attributed to the formation of unreactive Tl(III) anion complexes. The $H^+$ dependence is attributed to the more rapid reaction of $TlOH^{2+}$. The oxidation of $Os(phen)_3^{2+}$ was measured in nitrate media only and is faster than that of $Os(bpy)_3^{2+}$. $k$ at 25 °C in 1.05 M $HNO_3$ + 0.31 M $NaNO_3$ is 2.68 $dm^3\ mol^{-1}\ s^{-1}$. Activation parameters are given for the reactions of both of the Os complexes, and the changes in these with change of ligand are discussed in terms of an intermediate formed by attack of $TlOH^{2+}$ on a carbon atom of the ligand.

Earlier work[2] on the oxidation of the tris(2,2′-bipyridyl)[3] complex of Os(II) by Tl(III) in 3 M[4] aqueous $HClO_4$–$NaClO_4$ purported to show that this reaction occurred by a mechanism which was analogous to that established[5] for the Tl(III)–Fe(II) reaction

$$\mathrm{Tl(III)} + \mathrm{Fe(II)} \underset{k_{-1\mathrm{H}}}{\overset{k_{1\mathrm{H}}}{\rightleftharpoons}} \mathrm{Tl(II)} + \mathrm{Fe(III)} \qquad (1)$$

$$\mathrm{Tl(II)} + \mathrm{Fe(II)} \xrightarrow{k_2} \mathrm{Tl(I)} + \mathrm{Fe(III)} \qquad (2)$$

However, in contrast to that found for the preceding mechanism, the oxidation rate of Os(II) was reported to increase with increasing $H^+$ concentration. Later[6] the same effect was reported for the Tl(III)–$Ru(bpy)_3^{2+}$ reaction. We find that this anomalous acid dependence arises from side reactions and present here data for what we believe to be the true thermal rates. In our interpretation of the new experimental results we use recent work[7,8] on Tl(II) and also the fact that for at least one other redox reaction[9,10] the relative rates of bpy and phen complexes are known to be determined by the type of ligand and not by the overall free energy change.

## Experimental Section

All chemicals were analytical grade or were prepared by published methods.[2,11] $Os(bpy)_3(ClO_4)_2$ and $Os(phen)_3(ClO_4)_2$ were repeatedly recrystallized from redistilled water until reproducible rates were observed. Stock solutions of the sulfate and nitrate were prepared from the perchlorates by repeated absorption and elution using columns of SP Sephadex Type C-25 from Pharmacia, Uppsala, Sweden.

Rates were followed by measuring the decrease of color at or near the maximum absorbance of the Os(II) complexes. Both conventional and stopped-flow spectrophotometries were used. Because of the high molar absorbances, measurements could be made only with very dilute solutions.