

triphenylmethyl radical. Only a short illumination (10 min at  $\leq 50^\circ\text{C}$ ) with a more powerful light source, a 2500-W xenon lamp (operated at 1600-W), filtered through Pyrex, brought about a dramatic intensification of the signals. Again signals from two species were found; one (of stationary intensity) could be assigned to  $\text{Ph}_3\text{C}^\cdot$ , while the other (which decayed in the dark at room temperature) showed the typical six-line pattern of a spin adduct on the nitron (PBN).<sup>18</sup> Irradiation of a sample that did not contain  $\text{TiO}_2$  and PBN using both the 2500 and 450-W xenon lamps produced no ESR spectrum. The photo- and thermal decomposition of triphenylacetate<sup>19-21</sup> does not occur under the given experimental conditions.

These experimental results clearly establish the existence of methyl and triphenylmethyl radicals as heterogeneously (on  $\text{TiO}_2$ ) photogenerated radical intermediates in the photo-Kolbe reaction. As expected,<sup>5,6</sup> there is a close mechanistic parallel between the oxidation step in the photo- and electrochemical-Kolbe reactions. However, the generally high current densities and oxidation potentials in the latter reactions, as well as the possible strong adsorption of the radicals on the solid electrodes, have not allowed their detection by ESR up until now.<sup>3</sup> On the other hand, the low surface density of the photogenerated radicals on the  $\text{TiO}_2$  powder, together with the unimportance of follow-up oxidations in these reactions (because two-hole oxidations are improbable), permits the detection of the intermediate radicals here. Since many photoinduced oxidation reactions are known on n-type semiconductor materials, such as n- $\text{TiO}_2$ , the study by ESR of photogenerated intermediate radicals on partially platinized semiconductor powders should provide a useful tool in the investigation of photoredox processes on these materials.<sup>22-23</sup> Moreover, heterogeneous photocatalysis could provide a generally useful method for generating reactive radicals for study by ESR.<sup>24</sup>

## References and Notes

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- See, e.g., L. Ebersson in "The Chemistry of Carboxylic Acids & Esters", S. Patai, Ed., Interscience Publishers, London, 1969, p. 53, and references therein.
- (a) N. B. Kondrikov, V. V. Orlov, V. I. Ermakov, and M. Ya Fioshin, *Elektrokhimiya*, **8**, 920 (1972), reported the electrochemical generation and observation by ESR of the triphenylacetoxo radical. This has been disputed by (b) R. D. Goodin, J. C. Gilbert, and A. J. Bard, *J. Electroanal. Chem.*, **59**, 163 (1975).
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- The observable deviations of this spectrum from centrosymmetry point to the existence of yet another nitroxide radical. Its estimated coupling constants ( $a_N \approx 14.3$  G,  $a_H < 3.0$  G) leave open the possibility of a trapped acetoxy radical (by comparison with reported values in ref 10), but exclude a significant contribution of a trapped H atom (ref 7). A direct (photo-) reaction between the nitron and acetate is highly improbable, as a control experiment with photoinactive white anatase powder yielded no photoinduced ESR signal.
- Produced by mixing equimolar amounts of triphenylacetic acid (Aldrich Chemical Co.) in methanol and tetra-*n*-butylammonium hydroxide (Southwestern Analytical Chemicals), evaporation of solvents at room temperature, and drying at room temperature for 1 week under high vacuum.
- When this dark background signal attributed to the  $\text{TiO}_2$  powder was not observed, the catalyst was not effective in generating the radicals.
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- This nitroxide spectrum, with  $a_N = 14.88 \pm 0.1$  G and  $a_H = 2.75 \pm 0.1$  G, resembles the reported spectrum for the acetoxy adduct ( $a_N = 13.88$  G,  $a_H = 1.99$  G).<sup>10</sup> Trapping of the triphenylacetoxo radical is thus possible

as the alternative, trapping of trityl radical by PBN, has been shown not to occur.<sup>7</sup>

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- The support of this research by the Schweizerische Nationalfonds zur Foerderung der wissenschaftlichen Forschung (to B.K.) and by the National Science Foundation and the Robert A. Welch Foundation is gratefully acknowledged.

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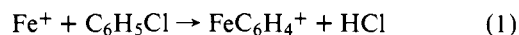
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Received January 16, 1978

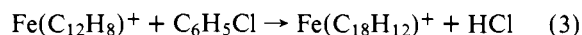
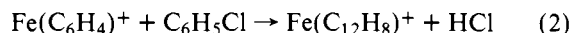
## $\text{Fe}^+$ Induced Dehydrohalogenation and Polymerization of Phenyl Halides in the Gas Phase

Sir:

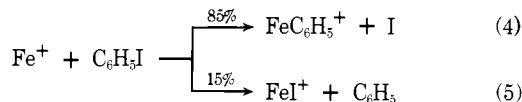
In the gas phase atomic transition metal ions react with a number of alkyl halides by insertion into the carbon-halogen bond.<sup>1,2</sup> If the alkyl group has  $\beta$ -hydrogen atoms, the metal insertion complex loses HX to form a metal ion-olefin complex. In the case of methyl halides, however,  $\text{M}^+$  reacts to form  $\text{MCH}_3^+$  and  $\text{MX}^+$ .<sup>1,2</sup> It might be expected that aryl halides would react as the methyl halides do since elimination of HX from an aryl halide is a very high energy process. We wish to report, however, the following reaction between  $\text{Fe}^+$  and chlorobenzene:



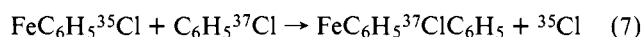
The  $\text{Fe}^+$  is formed by electron impact on  $\text{Fe}(\text{CO})_5$  and the reactions observed at low pressures ( $\sim 10^{-6}$  Torr) in an ion cyclotron resonance spectrometer.<sup>3</sup> Double-resonance techniques establish<sup>3</sup> that reaction 1 is a bimolecular process between the indicated reactants. The mass of the product of the analogous reaction of  $\text{C}_6\text{D}_5\text{Cl}$  verified the hydrogen content of the product. The rate constants for the reaction are within an order of magnitude of the reactant collision frequencies ( $\sim 10^{-9}$   $\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>). Furthermore, the following reactions succeed reaction 1.



Reactions of fluorobenzene and bromobenzene are analogous to reaction 1. Iodobenzene, however, reacts according to



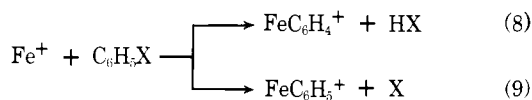
The products of reactions 4 and 5 are most readily rationalized in terms of a metal insertion followed by cleavage of either the metal-carbon bond or metal-iodine atom bond. The possibility that metal insertion plays a role in the mechanism of reaction 1 is suggested by the following series of reactions:



Double resonance establishes that the indicated isotopic variants of the reactants of reaction 7 give only the indicated isotopic variants of the products. If the product of reaction 6 is envisioned as  $\text{C}_6\text{H}_5\text{-Fe-Cl}^+$ , then elimination of a Cl atom

from the ionic reactant rather than from the neutral reactant in reaction 7 is easily understood.

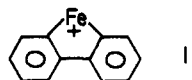
Perhaps the most dramatic examples of the importance of metal insertion in transition metal chemistry are the reactions of transition metal vapors with aryl halides.<sup>4,5</sup> The yields of products of the type RMX in reactions of transition metal vapors with aryl halides decreases with decreasing R-X bond strength, i.e., in the order aryl iodide > aryl bromide > aryl chloride.<sup>4,5</sup> The reactivity of Fe<sup>+</sup> toward aryl halides may also be determined by R-X bond strengths. Suppose we consider the following competing reactions:



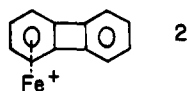
It is evident from Table I that  $\Delta H$  for reaction 8 changes very little as X changes.  $\Delta H$  for reaction 9, however, parallels the C<sub>6</sub>H<sub>5</sub>-X bond strengths becoming more negative for the heavier halides. It is thus possible that reaction 8 is exothermic for all the halides, but that reaction 9 is exothermic only for the iodide. The simpler process, reaction 9, is then predominant when it is exothermic; otherwise only reaction 8 occurs.

A mechanistic picture consistent with the observed reactions and these energetic considerations begins with the metal inserting into the C<sub>6</sub>H<sub>5</sub>-X bond. If sufficient energy is available, the complex immediately falls apart to form FeC<sub>6</sub>H<sub>5</sub><sup>+</sup> and X. Otherwise, more energy is released by shifting a hydrogen atom from the phenyl group to the metal and ultimately eliminating HX. The absence of reactions analogous to reaction 8 in the chemistry of metal vapors is intriguing. It may be that, under some as yet unexamined set of circumstances, products of such reactions would be observed.

Although there are few examples of metal-benzynes complexes in the literature, no other structure suggests itself for the product of reaction 1. Reported structures for metal-biphenylene complexes suggest structure **1** for the product of reaction 2.<sup>6,7</sup> The mechanism of reaction 2 probably resembles



that described above for reaction 1 except that addition of the two benzyne units accompanies the elimination of HCl. In any case, the mechanism does not involve scrambling of hydrogen atoms between the rings, since only FeC<sub>12</sub>H<sub>4</sub>D<sub>4</sub><sup>+</sup> appears as the product of reaction between FeC<sub>6</sub>H<sub>4</sub><sup>+</sup> and C<sub>6</sub>D<sub>5</sub>Cl. It is possible, of course, that the product of reaction 2 assumes the metal-biphenylene structure **2** or that rapid interconversion back and forth between **1** and **2** occurs. The reduced metal in



**2** would be available for insertion into another C-X bond and hence **2** may be the intermediate for subsequent reaction 3.

Our observation of reactions 1, 2, and 3 may be the first observation in the gas phase of the initial elementary steps in a metal catalyzed polymerization process. A search for the product of a fourth step was unsuccessful, but high mass products of multistep processes are difficult to detect with our instrumentation.<sup>8</sup> Wittig and co-workers have described the preparation of polyphenylenes using transition metal reagents.<sup>6</sup> Structures characterized in their work suggest **3** for the product

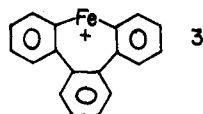


Table I.  $\Delta H^\circ_{298}$  for Reactions of Fe<sup>+</sup> with C<sub>6</sub>H<sub>5</sub>X<sup>a</sup>

X	kcal/mol	
	reaction 8	reaction 9
F	-317.3 + A <sup>b</sup>	-233.6 + B <sup>c</sup>
Cl	-314.9 + A <sup>b</sup>	-263.7 + B <sup>c</sup>
Br	-314.2 + A <sup>b</sup>	-278.8 + B <sup>c</sup>
I	-312.9 + A <sup>b</sup>	-293.8 + B <sup>c</sup>

<sup>a</sup> Calculated using  $\Delta H^\circ_{f298}$  values for C<sub>6</sub>H<sub>5</sub>X, HX, X, and Fe<sup>+</sup> from citation in ref 9. <sup>b</sup> A =  $\Delta H^\circ_{f298}(\text{FeC}_6\text{H}_4^+)$ . <sup>c</sup> B =  $\Delta H^\circ_{f298}(\text{FeC}_6\text{H}_5^+)$ .

Table II

reaction	$\Delta H^\circ_{298}$ , kcal/mol
C <sub>6</sub> H <sub>5</sub> Cl →  + HCl	66 <sup>a,b</sup>
2C <sub>6</sub> H <sub>5</sub> Cl →  + 2HCl	46 <sup>a,c</sup>
3C <sub>6</sub> H <sub>5</sub> Cl →  + 3HCl	-38 <sup>a,d</sup>

<sup>a</sup> Using  $\Delta H^\circ_{f298}(\text{HCl}) = -22.06$  kcal/mol and  $\Delta H^\circ_{f298}(\text{C}_6\text{H}_5\text{Cl}) = 12.39$  kcal/mol from ref 9. <sup>b</sup> Using  $\Delta H^\circ_{f298}(\text{C}_6\text{H}_4) \approx 100$  kcal/mol from ref 11. <sup>c</sup> Using  $\Delta H^\circ_{f298}(\text{C}_{12}\text{H}_8) = 115$  kcal/mol from A. F. Bedford, J. G. Carey, J. T. Millar, C. T. Mortimer, H. D. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 3895 (1962). <sup>d</sup> Using  $\Delta H^\circ_{f298}(\text{C}_{18}\text{H}_{12}) = 65$  kcal/mol from A. Magnus, H. Hartmann, and F. Becker, *Z. Phys. Chem.*, **197**, 75 (1951).

of reaction 3. If the benzyne units are linking up in this manner, then we are, in fact, observing elementary steps in a metal catalyzed polymerization in the gas phase. It is also possible that the product of reaction 3 assumes the structure of a metal-triphenylene complex analogous to **2**.

The results imply two conclusions of thermodynamic significance. As noted above, the observed reactions go at rates approaching collision rates. This implies that the reactions are thermoneutral or exothermic. Thus we conclude from the C<sub>6</sub>H<sub>5</sub>Br analogue of reaction 1 that  $\Delta H^\circ_{f298}(\text{Fe}(\text{C}_6\text{H}_4)^+) < 314$  kcal/mol,<sup>9</sup> and from reaction 4 that  $\Delta H^\circ_{f298}(\text{Fe}(\text{C}_6\text{H}_5)^+) < 294$  kcal/mol.<sup>9</sup> From these limits and analyses of available data which suggest that  $\Delta H(\text{C}_6\text{H}_5) = 78$  kcal/mol<sup>10</sup> and  $\Delta H(\text{C}_6\text{H}_4) \approx 100$  kcal/mol,<sup>11</sup> we deduce that  $D(\text{Fe}^+-\text{C}_6\text{H}_4) > 66$  kcal and  $D(\text{Fe}^+-\text{C}_6\text{H}_5) > 64$  kcal/mol. Both bond strength limits appear reasonable in view of the limited data on such bond strengths in the literature. Results in the literature suggest, for example, that  $D(\text{Fe}^+-\text{C}_2\text{H}_4) > 63$  kcal/mol<sup>12</sup> and  $D(\text{Fe}^+-\text{CH}_3) > 56$  kcal/mol.<sup>1</sup>

We may also consider the accessibility of structures **1** and **3** as products of the observed reactions from a thermodynamic point of view. Our observations suggest the overall processes forming **1** and **3** must be exothermic. As may be seen in Table II, the overall process forming **1** will be exothermic if introducing Fe<sup>+</sup> into biphenylene lowers its energy by 46 kcal/mol. If we assume that opening the four-membered ring requires ~55 kcal/mol (the energy required to open a cyclobutane ring<sup>13</sup>) and that the Fe-carbon bond strengths in **1** average 51 kcal/mol or more, then the condition will be met and the formation of **1** will be exothermic. Given the above limit on  $D(\text{Fe}^+-\text{C}_6\text{H}_5)$  it seems reasonable that the Fe-carbon bonds in **1** average at least 51 kcal/mol. Similarly we see from Table II that the overall process forming **3** will be exothermic if introducing Fe<sup>+</sup> into triphenylene does not raise its energy by more than 38 kcal/mol. If we assume breaking a carbon-carbon bond between the external rings in triphenylene requires ~112 kcal/mol ( $D(\text{C}_6\text{H}_5-\text{C}_6\text{H}_5) = 112$  kcal/mol<sup>14</sup>)

and that the Fe-carbon bonds in **3** average 37 kcal/mol or more, then the condition will be met and the overall process forming **3** will be exothermic. The Fe-carbon bonds in **3** certainly average at least 37 kcal/mol. Hence the proposed structures are reasonable from a thermodynamic viewpoint.

It has been reported that  $D(\text{Cr}^+-\text{C}_6\text{H}_6) \approx 50$  kcal/mol.<sup>15</sup> If this is indicative of the strength of the  $\text{Fe}^+$ -arene interaction in **2** and the analogous triphenylene complex, then formation of those structures as products of the observed reactions would also be exothermic.

**Acknowledgments** are made to Professors G. R. Brubaker and J. D. Roberts for helpful discussions, to donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work, and to the NSF for partial support of this work under Grant No. CHE77-09952.

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- Note also the following report that benzyne precursor benzo[1,2-d]oxazole 1,1-dioxide reacts in the presence of zero-valent platinum species to form triphenylene in good yield: T. L. Gilchrist, F. J. Graveling, and C. W. Rees, *Chem. Commun.*, 821 (1968).
- A referee properly points out that a structure analogous to **3** but with four phenyl groups would be quite strained even with phenyl group rotation. A metal capable of higher oxidation states might form  $\text{M}(\text{C}_{18}\text{H}_{12})_2^+$ .
- Determined using the following values of  $\Delta H_{1298}^\circ$  in kilocalories/mole from H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data*, **6**, Suppl. 1 (1977):  $\text{Fe}^+ = 280.4$ ,  $\text{C}_6\text{H}_5\text{Br} = 25.1$ ,  $\text{HBr} = -8.7$ ,  $\text{C}_6\text{H}_5\text{I} = 38.9$ , and  $\text{I} = 25.5$ .
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- NSF Undergraduate Research Participant.

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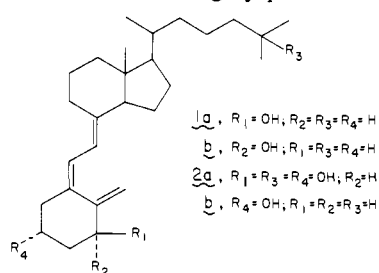
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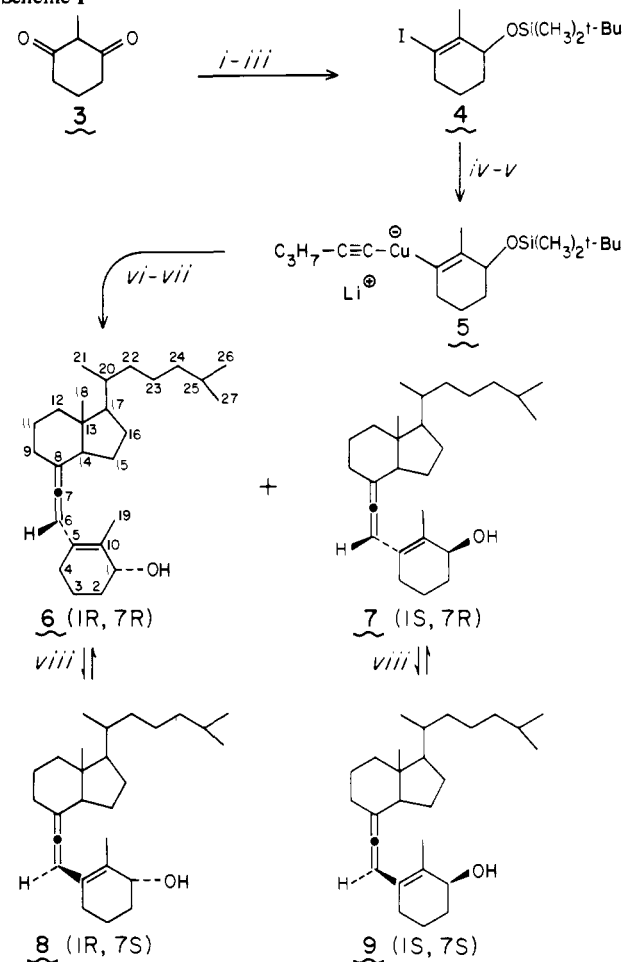
## Sigmatropic Rearrangement of Vinylallenes: A Novel Route to the 1-Hydroxyvitamin D System<sup>1</sup>

Sir:

We wish to describe our initial results on the preparation and sigmatropic rearrangement of vinylallene intermediates for synthesizing the physiologically important 1-hydroxyvitamin D system.<sup>2-4</sup> As the first example of this approach, we describe a synthesis of 3-deoxy-1-hydroxyvitamin D<sub>3</sub>, whose 1 $\alpha$  or 1S epimer<sup>5</sup> **1a** is known to be a highly potent analogue of the



Scheme I



Reagents: *i*,  $\text{Ph}_3\text{PI}_2$ ,  $\text{Et}_3\text{N}$ ,  $\text{CH}_3\text{CN}$ , reflux 3 hrs. (76%); *ii*,  $\text{NOBH}_4$ ,  $\text{EtOH}$ , RT, 3 hrs. (88%); *iii*,  $t\text{-Bu}(\text{CH}_3)_2\text{SiCl}$ , imidazole, DMF, RT, 3 hrs. (97%); *iv*,  $t\text{-BuLi}$ ,  $-78^\circ$  (2 hrs.),  $-30^\circ$  (1 hr.); *v*,  $\text{C}_3\text{H}_7\text{C}\equiv\text{C}-\text{Cu}\cdot 2\text{P}(\text{N}(\text{CH}_3)_2)_3$ ,  $-78^\circ$ , 1 hr.; *vi*,  $\underline{10b}$ ,  $-78^\circ$ , 5 hrs.; *vii*,  $\text{Bu}_4\text{N}^+\text{F}^-$ , THF, RT, 4 hrs. (37% based on  $\underline{10b}$ ); *viii*, hv, hexone, RT, 1 hr. (33%).

naturally occurring steroid hormone 1 $\alpha$ ,25-dihydroxyvitamin D<sub>3</sub> (**2a**).<sup>6</sup>

Scheme I summarizes the synthesis of the vinylallenes where the key step is the coupling of cuprate **5** with the ethynyl acetate **10b**.<sup>7</sup> The latter was prepared from Grundmann's ketone **11a**<sup>8</sup> (**2b**,  $\text{O}_3/\text{CH}_3\text{CH}_2\text{CHO}$ , 75-92%)<sup>9</sup> by treatment with

