relative concentrations of the two monomers.[11,12]

The first three entries in Table I are in good agreement with rate constant ratio of 24 reported by Giese[13] for competitive addition of these monomers to cyclohexyl radical. The final two entries show that *the rate constant ratio is indeed sensitive to the nature of the* γ-*substituent*; 3-cyanopropyl retains a preference for addition of acrylonitrile, but this preference is reduced 3.5-fold in comparison with that shown by 3-phenylpropyl. The most likely explanation for the reduction in the relative rate of acrylonitrile addition to 3-cyanopropyl is the development in the transition state of dipolar repulsion between cyano groups on the monomer and radical. The remarkable correspondence of the γ-substituent effect measured directly in this simple model system with that calculated by application of the penultimate model to the copolymerization of styrene and acrylonitrile (vide supra) lends strong support to the use of the penultimate model as a physically meaningful description of this copolymerization.

(11) In a typical experiment, the radical precursor in deoxygenated DMF was reduced with NaBH$_4$ in the presence of precisely known, excess quantities of styrene and acrylonitrile. After 1 h at room temperature the reaction mixture was filtered (all operations in closed vessels) and the relative yields of **2** and **3** were determined by gas chromatography (for *n*-butylmercuric bromide on a 20-ft glass column, 10% Supelco SP-1000, Supelcoport support; for the other precursors on a 9-ft stainless steel column, 3% SE-30, Supelcoport support; flame ionization detection). Peak areas were determined by electronic integration (Hewlett-Packard 3380A integrator), and relative response factors were determined by injection of authentic samples of each of the monomer adducts. Identification of adducts was confirmed by combined gas chromatography–mass spectrometry, through comparison of fragmentation patterns of the nominal adducts with those of authentic samples.

(12) k_A/k_S was found to be independent of relative monomer concentrations and independent of total monomer concentration if large (≥25-fold) excesses of monomer (with respect to organomercurial) were used.

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Flash Vacuum Pyrolysis of Organomanganese Pentacarbonyl Compounds

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Received March 20, 1985

Flash vacuum pyrolysis (fvp)[1,2] has proved to be a useful technique in both synthetic organic chemistry[3] and as a means of generating detectable concentrations of a variety of organic intermediates.[4] Considering the scale of recent interest in organometallic compounds, it is surprising that the fvp method has not been exploited for organomanganese pentacarbonyls (R–Mn(CO)$_5$), especially in view of the reactivity implied by estimates
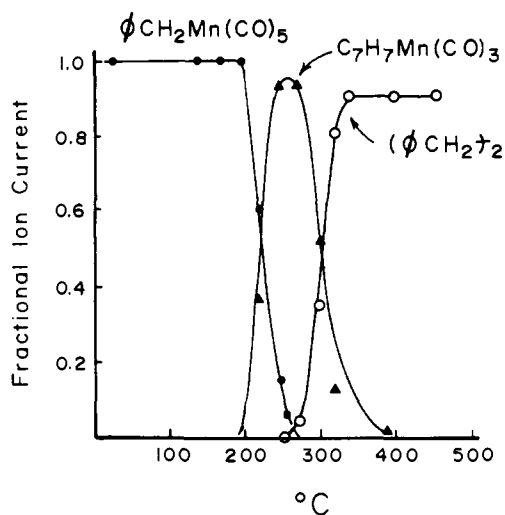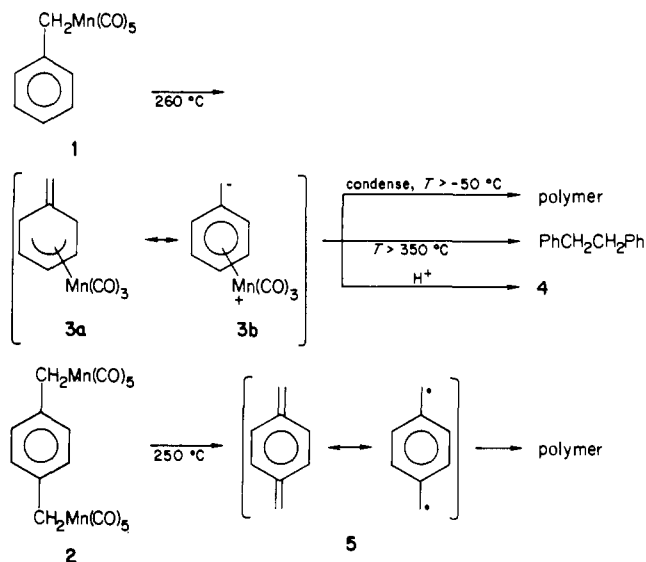
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Figure 1.

Scheme I

of the bond energies for R–Mn homolysis[5] and ligand dissociation[6] (DE ≤ 40 kcal/mol). We presently wish to report the results of our investigation of the reactivities of two such compounds (**1** and **2**, Scheme I) by fvp as monitored by mass spectrometry and product isolation. The results show that pentacarbonyl(phenylmethyl)manganese[7] (**1**) gives the previously unknown tricarbonyl(2-6-η⁵-1-methylenecyclohexadienyl)manganese (**3**) as an intermediate which is kinetically unstable although it can be characterized at low temperature by NMR and chemical reactivity. Also, we show that the previously unknown bis(manganese) compound **2**[8] is a reasonably efficient, low temperature (260 °C) gas-phase source of *p*-xylylene (**5**).

Preliminary work showed that the benzyl compound **1** cleanly gives bibenzyl (67% yield, isolated) and metallic manganese (98% yield, titration) in our fvp system at 350 °C. Figure 1 shows the temperature profile for fvp of **1**, which was obtained at ca. 0.1

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(8) The bis(manganese) compound **2** is readily obtained from α,α′-dibromo-*p*-xylene and the sodium manganese pentacarbonyl salt in THF (68% yield, mp 140 °C dec, appropriate ¹H NMR, IR, mass spectral, and microanalytical results).
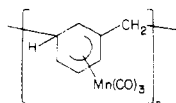
torr through a 17 cm × 1.2 cm quartz pyrolysis tube fitted with a 0.06-mm capillary leak between the reaction zone and the source of a Hewlett-Packard HP 5930 A quadrupole mass spectrometer. The mass spectral fragmentation pattern (electron impact, 5-eV nominal bombarding voltage) of the flow material below 160 °C showed fragments at m/z 286, 258, 230, 202, and 174 in ratios that were insensitive to temperature change. The intensities of the fragments of **1**, in ratio to the parent, were summed and divided by total ion current to give the fractional ion current (Fi) of the starting material which begins to decrease at oven temperatures above 160 °C. At 260 °C, ions indicative of starting material **1** have disappeared almost entirely and those of bibenzyl are not yet present. A metastable manganese tricarbonyl intermediate (m/z 230) is clearly suggested.

In experiments where the furnace temperature was held at 260 °C a yellow substance collected in a cold (liquid N_2) trap located between the furnace and pumping system. This material polymerized[9] on warming but could be dissolved in cold (−78 °C) acetone or methylene chloride. The ^{1}H and ^{13}C NMR spectral data[10] (−78 °C, deuterioacetone) are consistent with the $(\eta^5 \rightleftarrows \eta^6$-benzyl)-manganese tricarbonyl structure shown (**3**). This structure is also indicated by the isolation (35% yield) of the known[11] (η^6-toluene)tricarbonylmanganese(+1) cation (**4**) after treatment of an acetone solution of **3** with trifluoroacetic acid at −78 °C followed by metathesis with PF_6^-.

Finally, when a second pyrolysis oven was placed immediately downstream from a first oeven set at 260 °C, the m/z 230 (**3**) ions were replaced by those of bibenzyl (m/z 182) as the temperature of the second oven was raised to 350 °C. These observations suggest **3** is an intermediate in the formation of bibenzyl from **1** and not the product of an unconnected separate reaction. A CO dissociative σ–π rearrangement[12] to **3** is faster than the simpler C–Mn homolysis route to bibenzyl.

The mass spectral temperature profile for bis(manganese) compound **2** showed that the decrease in fractional ion current for starting material (m/z 494, 354, 299, 214, 159), beginning above 190 °C, is compensated principally by the appearance of a C_8H_8 compound (m/z 104) and dimanganese decacarbonyl (m/z 390). The latter compound was found, in independent experiments, to be unstable with respect to metallic manganese and CO in the present fvp system above 250 °C. The identity of the C_8H_8 species as p-xylylene was confirmed by the polymeric film that was isolated (40% yield based on Mn)[13] after warming the cold trap. This isolated hydrocarbon polymer showed infrared bands

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identical with those of poly(p-xylylene).[14] The results for **2** are consistent with a single C–Mn bond homolysis if the second $CH_2Mn(CO)_5$ group stabilizes the corresponding transition state relative to that for the unsubstituted case (**1**). Concerted possibilities also can explain the low-temperature formation of **5**.

In summary, our results show that the bis(manganese) compound **2** undergoes a relatively rapid cleavage of the C–Mn bonds providing a low-temperature gas-phase source of p-xylylene **5**. Reduced temperatures for generating reactive intermediates can be an important requirement for their direct observation, as has recently been demonstrated by Schweig's recent success[4b] in the case of the o-xylylene. The fvp route has provided an entry into the new $[(\eta^5 \rightleftarrows \eta^6)$-benzyl]tricarbonylmanganese (**3**) which is shown to undergo a fairly clean self-initiated polymerization and to be reactive with electrophiles. This species appears to be on the reaction surface between **1** and bibenzyl, indicating that a CO dissociative rearrangement is faster than the simpler C–Mn homolysis which could rationalize the ultimate bibenzyl product. The present results are suggestive as to a means (fvp) of characterizing the related $CpFeC_7H_7$ complexes which are not kinetically stabilized[15] by methylation[10] or delocalization.[16] The self-initiated polymerization of **3** suggests a new type of organometallic polymer which could be expected to show a number of interesting properties. Fvp studies of other examples of this type of compound are currently in progress.

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(9) The infrared spectrum of this insoluble polymer (ν_{CO} 2018, 1940 cm^{-1}) strongly suggests an interesting (η^5-cyclohexadienyl)manganese tricarbonyl system though the details of the structure are not available.

(10) ^{1}H NMR spectrum

(360 MHz (CD$_3$)$_2$CO, −60 °C) δ 366 (s, 2 = H, H$_1$), 4.43 (d, J = 7.4 Hz, 2 H, H$_3$), 5.50 (d, d, J = 7.4, 5.6 Hz, 2 H, H$_4$), 6.01 (t, J = 5.6 Hz, 1 H, H$_5$); ^{13}C NMR (90.8 MHz (CD$_3$)$_2$CO, −60 °C) 86.24 (C$_1$, J_{CH} = 158.5 Hz), 137.15 (C$_2$), 73.65 (C$_3$, J_{CH} = 167.6 Hz), 100.57 (C$_4$, J_{CH} = 170.3 Hz), 76.29 ppm (C, J_{CH} = 179.15 Hz). A closely related iron analogue is described by: Astruc, D.; Hamon, J.-R.; Román, E.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 7502–7514; **1979**, *101*, 2240. Astruc, D.; Enrique, R. E.; Hamon, J. R.; Batail, P. *Ibid.* **1979**, *101*, 2240.

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(13) The volatility of **2** is such that some solid-phase decomposition competes with sublimation so that the titrated amount of Mn, depositing in the reaction zone, is used as a basis of yield.

Farnesylpyrophosphate Synthetase. A Case for Common Electrophilic Mechanisms for Prenyltransferases and Terpene Cyclases

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Received March 25, 1985

The isoprene biosynthetic pathway is truly unique in the diversity of metabolites it produces. Carbon–carbon bonds are formed in the major building steps by intermolecular prenyl transfer reactions or by intramolecular cyclizations,[1,2] and there is evidence the reactions occur by attack of electrophilic carbocations on neighboring π-electron functional groups.[1-11] Farnesyl-PP[12]

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