

REACTIONS OF SODIUM MANGANESE PENTACARBONYL WITH α,ω -DIACYL HALIDES

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SUMMARY

The reactions between $\text{ClCO}(\text{CH}_2)_n\text{COCl}$ ($n=2, 3, 4$ or 5) and sodium manganese pentacarbonyl have been studied and the major products isolated and characterized. Based upon infrared, proton magnetic resonance and molecular weight

measurements, an unusual ring structure, $(\text{CO})_5\text{Mn}-\overset{\text{O}}{\parallel}\text{C}=\text{CH}-(\text{CH}_2)_{n-1}$, is proposed for the products obtained from succinyl chloride ($n=2$) and glutaryl chloride ($n=3$). Acid hydrolysis of the ring system yields the acids $(\text{CO})_5\text{MnCO}(\text{CH}_2)_n\text{CO}_2\text{H}$ which were characterized as their methyl esters. Adipyl and pimelyl chlorides yield products whose physical properties and elemental composition are consistent with the formulation $(\text{CO})_5\text{MnCO}(\text{CH}_2)_n\text{COMn}(\text{CO})_5$, where $n=4$ and 5 , respectively.

INTRODUCTION

Even though many acylmanganese pentacarbonyl complexes are known¹, none of these complexes are derived from α,ω -diacyl halides. In 1963, King² reported that $\text{NaFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ reacts with glutaryl and adipyl chlorides to yield $(\pi\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeCO}(\text{CH}_2)_3\text{COFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ and $(\pi\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeCO}(\text{CH}_2)_4\text{COFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$, respectively. Only perfluoroglutaryl chloride was observed to react with both $\text{NaMn}(\text{CO})_5$ and $\text{NaFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ to yield the expected diacyl products $(\text{CO})_5\text{MnCO}(\text{CF}_2)_3\text{COMn}(\text{CO})_5$ ³ and $(\pi\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeCO}(\text{CF}_2)_3\text{COFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ ². As part of our investigation of alkyl and acyl transition metal complexes, we planned to prepare a series of $(\text{CO})_5\text{MnCO}(\text{CH}_2)_n\text{COMn}(\text{CO})_5$ complexes by reacting $\text{NaMn}(\text{CO})_5$ with α,ω -diacyl halides. We describe here the results of our study which has led to the discovery of a new and unusual reaction of the manganese pentacarbonyl anion with succinyl and glutaryl chlorides.

EXPERIMENTAL

General

Dimanganese decacarbonyl (Pressure Chemical Co.) was purified by sublimation prior to use. Tetrahydrofuran (Fisher Scientific Co.) was stored over and distilled from lithium aluminum hydride in a nitrogen atmosphere. Hexane for extraction

purposes was dried by distillation from phosphorus pentoxide. Other solvents mentioned in the following sections were normally used as received from various suppliers. The diacyl halides, obtained from Eastman Organic Chemicals, were purified by fractional distillation under vacuum and stored under nitrogen.

IR were recorded with a Perkin-Elmer Model 21 Spectrophotometer. PMR spectra were obtained with a Varian Associates A-60 Spectrometer. A Hitachi-Perkin-Elmer Mass Spectrometer was employed in the determination of mass spectra.

All melting points are of samples in tubes sealed under nitrogen. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Preparation of (I). Reaction between succinyl chloride and sodium manganese pentacarbonyl

A sodium amalgam was prepared under nitrogen by adding 2.2 g (95 mmol) of sodium metal to 10 ml of mercury in a 200-ml three-necked reaction flask. After the amalgam cooled to room temperature 100 ml of dry THF was distilled into the flask. Dimanganese decacarbonyl (10 g, 26 mmol) was added in one amount and the resulting mixture was mechanically stirred for two h at room temperature. The unused amalgam was removed with a hypodermic syringe equipped with a long, wide-bore needle. Amalgam clinging to the sides of the flask was removed by adding two separate 7 ml portions of clean mercury and stirring. Each time the added mercury was removed as completely as possible with the hypodermic syringe. During these operations, oxygen was prevented from entering the flask by maintaining a steady flow of nitrogen into the flask and out the open neck.

A solution of 4.3 g (3.1 ml, 27 mmol) of succinyl chloride in 10 ml of dry THF was added dropwise to the well-stirred solution of sodium manganese pentacarbonyl. There was no discernable heating or gas evolution during or after the addition. Within 4 h the reaction mixture had turned bright orange in color. The mixture was allowed to stand overnight without stirring. Removal of the THF from the reaction mixture under aspirator vacuum yielded a red, gummy residue (*A*) and a colorless distillate (*B*) which had been collected in a trap cooled with liquid nitrogen. Upon warming to room temperature, solution (*B*) became orange in color owing to the formation of $\text{Mn}_2(\text{CO})_{10}$ which was readily identified by its IR spectrum.

Two different procedures were employed to separate the materials present in *A*.

Procedure 1. Extraction of *A* with 50 ml of n-hexane at room temperature gave a yellow solution which upon concentration to dryness under aspirator vacuum yielded 0.93 g of yellow solid which was primarily $\text{Mn}_2(\text{CO})_{10}$. Residue *A* was then extracted with five successive 50-ml portions of hot n-hexane and each yellow extract was filtered while hot. After each filtrate had been allowed to cool to room temperature, a near white solid, (*I*), precipitated and this was collected by pressure filtration under nitrogen. The weight of (*I*) from the five fractions amounted to 2.55 g. Further extraction of *A* with two 50-ml portions of hot ether also gave a yellow solution from which 1.32 g of (*I*) precipitated upon cooling. The filtrates from these two extraction procedures were evaporated to dryness and yielded 1.04 g of impure solid which contained both (*I*) and some $\text{Mn}_2(\text{CO})_{10}$. The remaining portion of *A* was subjected to sublimation at $55^\circ/0.1$ mm and yielded an additional 0.72 g of a solid containing both (*I*) and $\text{Mn}_2(\text{CO})_{10}$. The minimum yield of (*I*) by this method is 50% based on the amount

of succinyl chloride employed, but can be improved by further recrystallization of the residues of the filtrates and the sublimate.

Procedure 2. Residue *A* was extracted with 100 ml of dichloromethane to yield an intense red solution which was filtered to remove suspended solids. Approximately 50 ml of *n*-hexane was then added to the filtrate after which the resulting mixture was heated to 40° in a stream of nitrogen to reduce the volume of the solution. A brown, gummy solid precipitated from the mixture and was removed by filtration when the volume of the solution was ~75 ml. The resulting yellow filtrate was concentrated to ~50 ml and after cooling yielded 4.0 g of (I) as slightly off-white needles which was collected by pressure filtration under nitrogen and washed with *n*-hexane. Concentration under vacuum of the filtrate from the collection of (I) yielded 2 g of yellow solid which was mostly $\text{Mn}_2(\text{CO})_{10}$. Although the yield of (I) is 65% in this simplified separation procedure, the filtration of the dichloromethane solution is tedious. Furthermore, the unidentified red material originally present in *A* undergoes decomposition during the separation procedure in a very uncertain fashion and frequently coats the crystals of (I). With time, however, this red gummy material decomposes to materials which may be removed in a simple recrystallization process.

The white solid (I) obtained from either procedure may be recrystallized from *n*-pentane or ether to yield pure (I), m.p. 80.5–81.5° and decomposing with gas evolution at 95°. Pure (I) is a white sublimable solid (55°/0.1 mm) and is soluble in most of the common polar and non-polar organic solvents. The substance reacts very slowly with atmospheric moisture to yield (III), but is stable when stored under nitrogen. [Found: C, 38.72; H, 1.08; Mn, 19.94; mol.wt., 278 (mass spectrometry), 288 (cryoscopic in benzene). $\text{C}_9\text{H}_3\text{MnO}_7$ calcd.: C, 38.87; H, 1.08; Mn, 19.75%; mol.wt., 278.] The spectral properties of (I) are discussed in the text.

Preparation of (II). Reaction between glutaryl chloride and sodium manganese pentacarbonyl

Sodium manganese pentacarbonyl was prepared in 100 ml of THF from 5.11 g (13 mmol) of $\text{Mn}_2(\text{CO})_{10}$ and an amalgam containing 0.74 g of sodium in 6 ml of mercury according to the previous procedure. Glutaryl chloride (2.12 g, 13 mmol) dissolved in 10 ml of THF was added to the mixture with good stirring. The reaction was rapid as evidenced by an immediate clouding of the mixture. Stirring of the mixture was continued for 3 h and yielded a red solution together with a large amount of insoluble salts. Removal of the THF under aspirator vacuum at room temperature left a red gummy residue. Extraction of this residue at room temperature with 50 ml of *n*-hexane yielded a yellow solution which upon concentration to dryness in vacuum left 1.5 g of a yellow solid consisting primarily of $\text{Mn}_2(\text{CO})_{10}$. Further extraction of the red residue with five successive 50-ml portions of warm *n*-hexane gave yellow solutions which were combined, filtered and evaporated to dryness under vacuum. The resulting mixture of white solid (II) and $\text{Mn}_2(\text{CO})_{10}$ was most easily separated by fractional sublimation. The $\text{Mn}_2(\text{CO})_{10}$ (0.5 g) sublimed first and was removed during 24 h at room temperature and 0.1 mm while (II) (1.5 g) was sublimed over a period of 48 h at 45°/0.1 mm. The sublimed (II) is very pure but may be recrystallized from *n*-pentane. Based on the glutaryl chloride taken the yield is 40%. The white, sublimable (II), which is soluble in many polar and non-polar organic solvents, melts sharply at 53–54° and decompose completely at 120°. Unlike (I), solid (II) does not

appear to react with atmospheric moisture. [Found: C, 41.32; H, 2.10; Mn, 18.86; mol. wt., 292 (mass spectrometry), 300 (cryoscopic in benzene). $C_{10}H_5MnO_7$ calcd.: C, 41.32; H, 1.72; Mn, 18.81%; mol. wt., 292.] The spectral properties of (II) are discussed in the text.

Acid hydrolysis of (I). Preparation of $(CO)_5MnCOCH_2CH_2COOH$, (III)

A suspension of 0.20 g (0.7 mmol) of (I) in a dilute hydrochloric acid solution, prepared from 20 ml of water and 0.5 ml of concentrated hydrochloric acid, was stirred with a magnetic stirrer under nitrogen for 48 h at room temperature. During this time the insoluble white solid was consumed and pale yellow plates were formed. The suspended yellow solid was removed by shaking the solution with three 10 ml portions of methylene chloride. The organic layers were combined, dried over anhydrous magnesium sulfate for 6 h and filtered. Evaporation of the filtrate afforded pale yellow plates which were recrystallized from ether to yield 0.17 g (80%) of (III), a white solid which does not melt but decomposes at 98°. The acid (III) is non-sublimable and has fair to poor solubility in polar organic solvents and is insoluble in water. Purification of (III) by solution in dilute base (HCO_3^-) and reprecipitation by acidification is possible but is not recommended as the acid anion is decomposed slowly and irreversibly in dilute base. More basic solutions lead to rapid decomposition. For this reason, a neutralization equivalent value for (III) could not be obtained. (Found: C, 36.33; H, 1.71; Mn, 18.75; $C_9H_5MnO_8$ calcd.: C, 36.47; H, 1.69; Mn, 18.55%.) Owing to the low solubility of the substance in commonly used solvents, a PMR spectrum was not obtainable.

Compound (III) was not successfully decarbonylated to an alkyl compound upon heating (i) in the solid state, (ii) in refluxing benzene, (iii) in refluxing THF, or (iv) in refluxing dichloromethane. With the last solvent no reaction was observed presumably because of its low boiling point. The higher boiling solvents led to red mixtures in which only $Mn_2(CO)_{10}$ was readily identified.

Acid hydrolysis of (II). Preparation of $(CO)_5MnCO(CH_2)_3COOH$, (IV)

The hydrolysis of 0.32 g of (II) and subsequent workup to obtain (IV) were effected in a manner similar to that of the previous preparation. The yield of (IV) was 0.26 g (79%). The acid melts with decomposition at 99–102°, is nonvolatile, soluble in polar organic solvents, insoluble in water and soluble in base with decomposition. (Found: C, 38.50; H, 2.34; Mn, 17.65. $C_{10}H_7MnO_8$ calcd.: C, 38.73; H, 2.27; Mn, 17.71%.)

Preparation of $(CO)_5MnCO(CH_2)_2COOCH_3$, (V)

Acid (III) (0.65 g, 2.2 mmol) was slurried in 15 ml of n-hexane. A solution of diazomethane in hexane⁴ was added dropwise until nitrogen evolution ceased and a persistent faint yellow color was noticeable. This solution was evaporated under vacuum to yield an impure product. Recrystallization of the residue from hot n-pentane gave 0.52 g (77%) of (V) in two crops, m.p. 57–58°. [Found: C, 38.93; H, 2.36; Mn, 17.93; mol. wt., 310 (mass spectrometry). $C_{10}H_7MnO_8$ calcd.: C, 38.73; H, 2.27; Mn, 17.71%; mol. wt., 310.]

The white solid methyl ester (V) is soluble in both polar and non-polar organic solvents. Compound (V) was prepared independently in a reaction between $NaMn-$

(CO)₅ and ClCOCH₂CH₂COOCH₃. As had been noted for the acid (III), this ester is unaffected by refluxing dichloromethane after 48 h, whereas in refluxing benzene and THF extensive decomposition is noted.

Preparation of (CO)₅MnCO(CH₂)₃COOCH₃, (VI)

When 0.61 g (2.0 mmol) of acid (IV) was methylated with diazomethane according to the previous procedure, 0.28 g (71%) of white solid, m.p. 49–50°, was obtained. This ester (VI) is soluble in both polar and non-polar organic solvents. (Found: C, 40.72; H, 2.88; Mn, 17.11; C₁₁H₉MnO₈ calcd.: C, 40.76; H, 2.79; Mn, 16.95%.)

Preparation of (VII). Reaction of adipyl chloride with sodium manganese pentacarbonyl

A solution of 3.28 g (17.9 mmol) of adipyl chloride in 10 ml of THF was added to an ice-cooled solution of sodium manganese pentacarbonyl prepared from 7.00 g (17.9 mmol) of Mn₂(CO)₁₀ and excess sodium amalgam. A rapid reaction ensued as indicated by an immediate colour change to a deep red brown. Mechanical stirring was continued for 4 h at 0° after which the mixture was allowed to stand at room temperature overnight. The THF was evaporated at room temperature under water aspirator vacuum to leave a yellow-brown solid residue. Extraction of the solid with 500 ml of n-hexane at room temperature produced a pale yellow solution which contained very little Mn₂(CO)₁₀. Further extraction of the residue at room temperature with 50 ml of dichloromethane gave a red solution from which nearly pure white crystals of (VII) precipitated upon concentration of the solution to 20 ml and cooling. This process was repeated ten times and the combined yield of good purity (VII) was 3.31 g (39%). Concentration of the combined filtrates from the collection of (VII) yielded 0.33 g of red, impure material. The product, which may be readily recrystallized from large volumes of dichloromethane, turns yellow upon heating to 115° and melts with decomposition at 119–122°. (Found: C, 38.16; H, 1.77; Mn, 22.11. C₁₆H₈Mn₂O₁₂ calcd.: C, 38.27; H, 1.65; Mn, 21.88%.)

The poor solubility of (VII) in all common organic solvents precluded the obtaining of a PMR spectrum.

Preparation of (VIII). Reaction of pimelyl chloride with sodium manganese pentacarbonyl

A solution of 2.56 g (13 mmol) of pimelyl chloride in 10 ml of THF was added to a THF solution of sodium manganese pentacarbonyl at 0° prepared from 5.07 g (13 mmol) of Mn₂(CO)₁₀ and a dilute sodium amalgam. After the addition was complete, the mixture was stirred vigorously at 0° for 1 h and then allowed to warm to room temperature. The THF was removed from the reaction mixture under vacuum at room temperature to leave a red-brown residue. The residue was extracted initially with two 100-ml portions of n-hexane to give a yellow solution which left a gummy residue upon evaporation to dryness. Sublimation of this residue yielded 0.8 g of impure Mn₂(CO)₁₀. All of the remaining organometallic products were extracted from the residue with 100 ml of methylene chloride. Evaporation of this methylene chloride extract to dryness left a gummy impure product which was extracted with ten separate 100 ml portions of ether. Concentration of each fraction to ~ 50 ml and subsequent cooling under nitrogen produced a precipitate of near-white solid crystals.

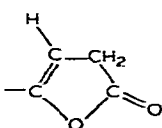
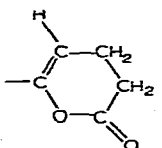
The solids were combined and recrystallized two times from ether to give 1.84 g of (VIII) as a nearly white solid, melting at 109–112°. All of the filtrates from the above collection procedures were combined and evaporated to dryness. This last residue was dissolved in methylene chloride and placed on an alumina column. Continuous elution with methylene chloride yielded only a trace amount of $\text{Mn}_2(\text{CO})_{10}$. Elution with 11% acetone in methylene chloride produced a pink band which passed down the column; the color disappeared as the band was eluted. Removal of the solvent from this particular fraction yielded a pale yellow solid which was recrystallized from ether to give 0.14 g of (VIII), m.p. 109–111°. The total yield of (VIII) is 1.98 g (30%). (Found: C, 39.37; H, 1.89; Mn, 21.00. $\text{C}_{17}\text{H}_{10}\text{Mn}_2\text{O}_{12}$ calcd.: C, 39.56; H, 1.95; Mn, 21.29%.) Compound (VIII) has poor solubility in most of the common organic solvents and a good PMR spectrum was not obtainable.

RESULTS

The reactions of several α,ω -diacyl halides, $\text{ClCO}(\text{CH}_2)_n\text{COCl}$, $n=2,3,4,5$, with the manganese pentacarbonyl anion, $\text{Mn}(\text{CO})_5^-$, were carried out in a manner analogous to the synthetic procedures used for preparing acylmanganese complexes from monofunctional acid halides¹. As shown in eqn. (1), the expected products $\text{ClCO}(\text{CH}_2)_n\text{COCl} + 2 \text{Mn}(\text{CO})_5^- \rightarrow (\text{CO})_5\text{MnCO}(\text{CH}_2)_n\text{COMn}(\text{CO})_5 + 2 \text{Cl}^-$ (1) of these reactions would be difunctional acylmanganese derivatives. Although both adipyl dichloride and pimelyl dichloride, $n=4$ and 5 respectively, appear to react

TABLE I

INFRARED SPECTRAL DATA OF $\text{RMn}(\text{CO})_5$ COMPOUNDS, cm^{-1}

No.	R	$\text{Mn}-^{12}\text{C}\equiv\text{O}$	$\begin{array}{c} \text{O} \\ \\ \text{Mn}-\text{C}- \\ \\ \text{C} \\ / \quad \backslash \\ \text{O} \quad \text{C}=\text{O} \end{array}$	C=C	Solvent
(I)		2134 m, 2068 w, 2034 s, 2012 s	1805 s	1578 m	n-Hexane
(II)		2131 m, 2060 w, 2031 s, 2006 s	1782 s	1609 m	n-Hexane
(III)	$-\text{CO}(\text{CH}_2)_2\text{COOH}$	2121 m, 2058 s, 2015 s	1643 s	1755 w(sh) 1716 m	CH_2Cl_2
(IV)	$-\text{CO}(\text{CH}_2)_3\text{COOH}$	2117 w, 2052 m, 2013 s	1645 s	1753 w(sh) 1716 s	CH_2Cl_2
(V)	$-\text{CO}(\text{CH}_2)_2\text{COOH}_3$	2122 w, 2058 m, 2015 s	1656 m	1750 m	n-Hexane
(VI)	$-\text{CO}(\text{CH}_2)_3\text{COOH}_3$	2119 w, 2058 m, 2013 s	1657 m	1752 m	n-Hexane
(VII)	$-\text{CO}(\text{CH}_2)_4\text{CO}-$	2119 m, 2056 m, 2015 s(doublet)	1648 m		CH_2Cl_2
(VIII)	$-\text{CO}(\text{CH}_2)_5\text{CO}-$	2119 m, 2054 m, 2013 s(broad)	1648 m		CH_2Cl_2

exclusively in the anticipated manner, the two shorter chain compounds, succinyl dichloride ($n=2$) and glutaryl chloride ($n=3$), yield completely unexpected products.

Compounds (I) and (II)

The reaction of succinyl chloride with $\text{Mn}(\text{CO})_5^-$ in THF yields (I) as a white, readily sublimable solid which has a good solubility in non-polar organic solvents.

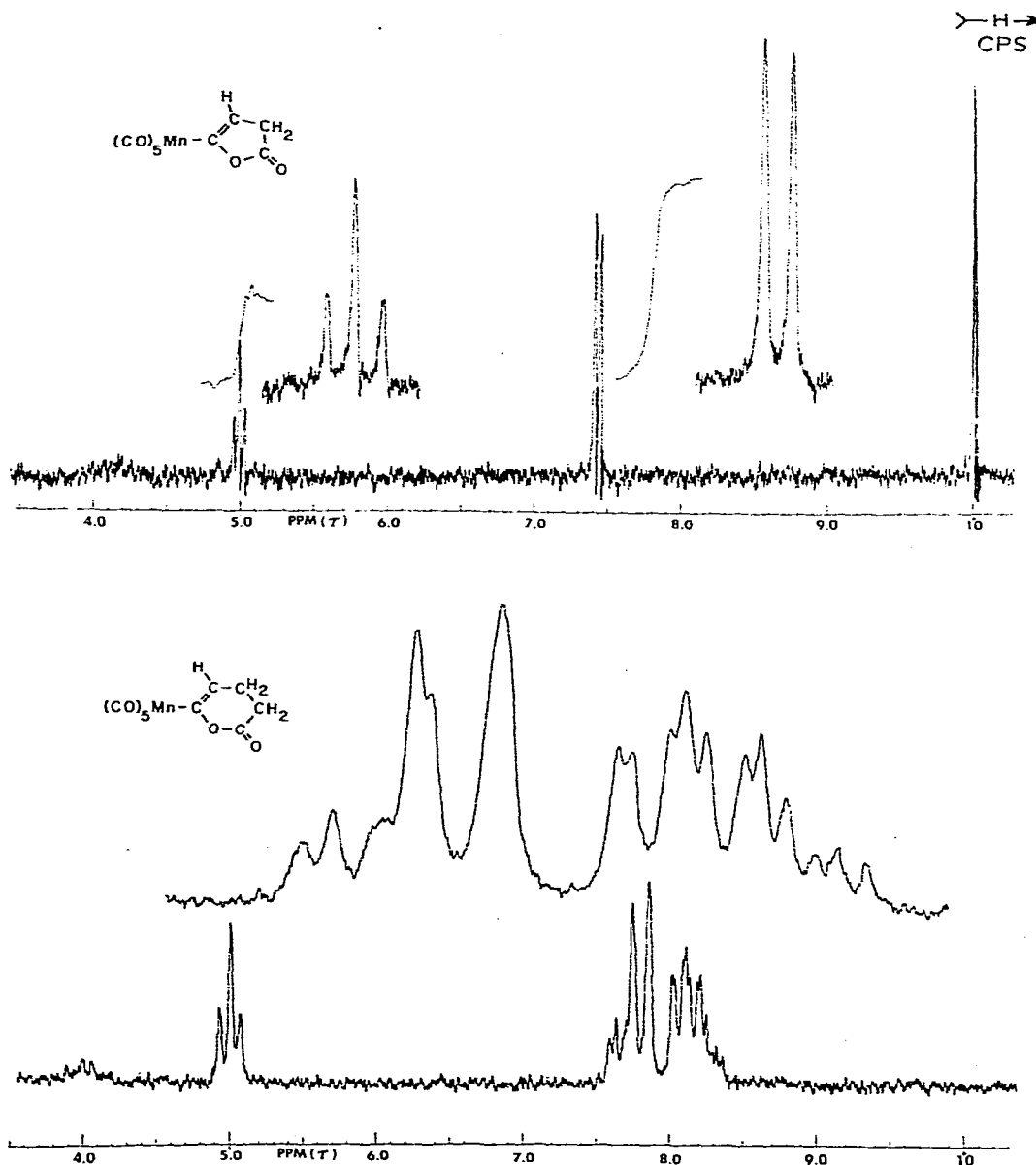
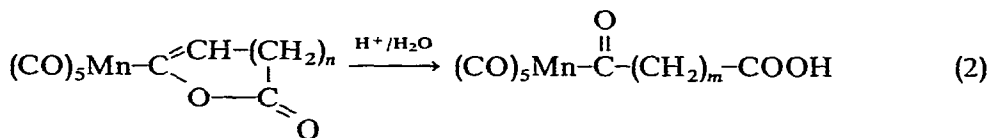


Fig. 1. PMR spectra of compounds (I) and (II) in benzene with tetramethylsilane as an internal standard at τ 10. Ordinate scales for inserts have been expanded five times that for the normal scale.

Elemental analysis and molecular weight values, both mass spectral and cryoscopic in benzene, indicate clearly that the molecular formula is $C_9H_3MnO_7$. The infrared spectrum of (I) in the $2200-2000\text{ cm}^{-1}$ region (Table 1) is typical of that of an $L-Mn(CO)_5$ compound⁵ which would require that $L=C_4H_3O_2$. Other IR spectral characteristics of (I) which aid in a structural assignment for L include the following:

- (i) the intense carbonyl stretching band at 1805 cm^{-1} is of considerably higher energy than is noted for normal esters, ketones and aldehydes and could correspond most likely to a vinyl ester grouping or a small ring lactone;
- (ii) a medium intensity band at 1578 cm^{-1} can only be reasonably assigned to the stretching of a carbon-carbon double bond.

These features have been incorporated into the suggested structure for (I) shown in eqn. (2). The PMR spectrum of (I) is reproduced in Fig. 1 and as expected for a simple AX_2 system consists of a sharp triplet in the vinyl proton region at τ 4.99 and a sharp doublet at τ 7.43 for the pair of equivalent aliphatic protons.

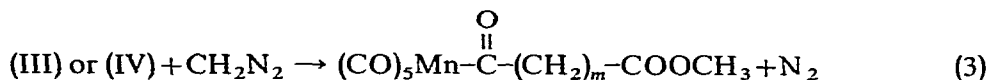


(I) $n=1$

(III) $m=2$

(II) $n=2$

(IV) $m=3$



(V) $m=2$

(VI) $m=3$

The spin-spin splitting value measured from each signal is 2.3 cps. Perhaps the most convincing evidence for this structure is the ease of acid hydrolysis of the lactone ring to give the carboxylic acid (III) as shown in eqn. (2). Although the poor solubility of (III) in common organic solvents prohibits the obtaining of its PMR spectrum directly, the compound has been characterized as the methyl ester (V) prepared according to eqn. (3). In the PMR spectrum of (V) as shown in Fig. 2, the more deshielded half of the A_2B_2 pattern can be ascribed to the pair of protons on the aliphatic carbon nearer the manganese in line with the previous spectral assignments for $(CO)_5MnCOCH_2CH_3$ and $(CO)_5MnCOCH(CH_3)_2$ (ref. 1). In this particular instance the methyl ester (V) has also been synthesized by the reaction of stoichiometric amounts of $Mn(CO)_5^-$ and $ClCO(CH_2)_2COOCH_3$.

The white, sublimable compound (II) has a molecular formula of $C_{10}H_5MnO_7$ and has been assigned a structure similar to that of (I) except that a less strained six-membered lactone ring is present as is evidenced by the lower energy lactone carbonyl stretching band at 1782 cm^{-1} *. The PMR spectrum of (II) as shown in Fig. 1 is an A_2B_2X pattern and includes a sharp triplet at τ 5.03 which corresponds

* Prof. R. B. King has indicated in a private communication that he has also carried out the reactions of $NaMn(CO)_5$ with glutaryl and adipyl dichlorides and obtained products which have IR spectra and melting points similar to the respective properties of (II) and (VII) described in this paper.

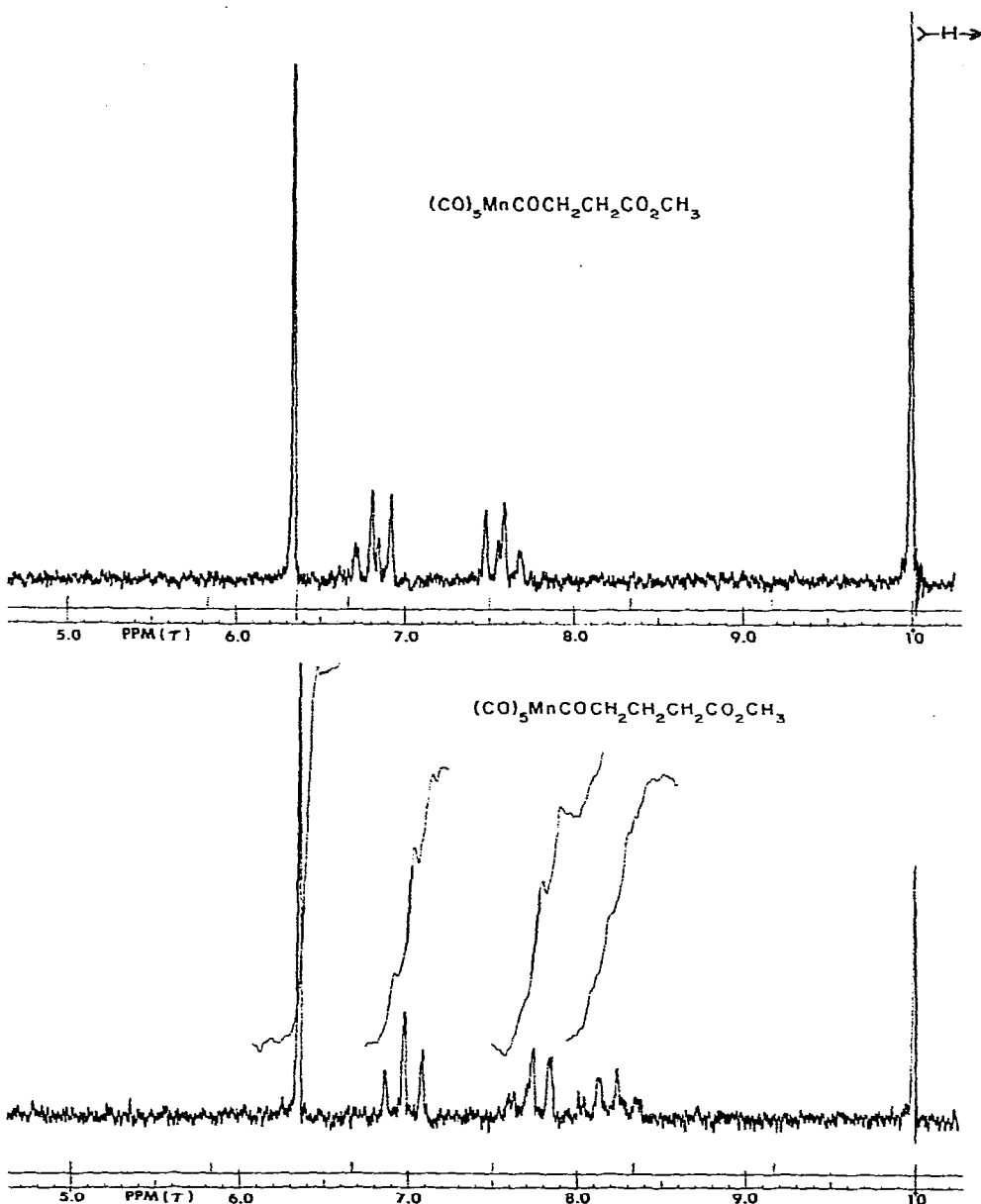


Fig. 2. PMR spectra of compounds (V) and (VI) in carbon tetrachloride with tetramethylsilane as internal standard at τ 10.

to the single vinyl proton split by the central pair of methylene protons. The other part of the PMR spectrum is centered at τ 7.97 with the more deshielded half of the complex pattern readily assignable to the methylene protons adjacent to the lactone carbonyl. Like (I), compound (II) is hydrolyzed by acid and yields (IV) which has been characterized as the ester (VI). The PMR spectrum of (VI) is shown in Fig. 2 and similarities to the spectrum of (V) are readily evident.

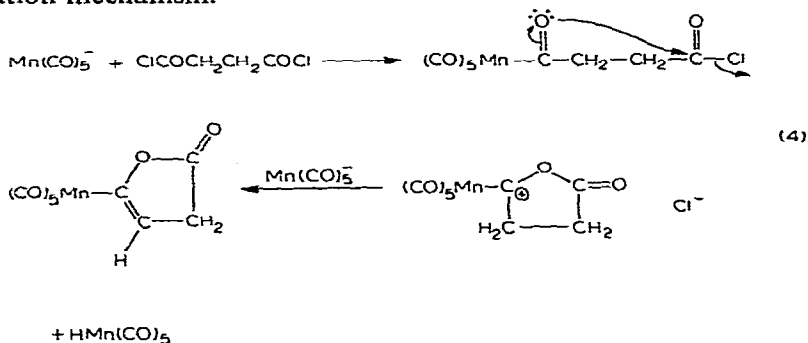
The mass spectral breakdown pattern of (I) and (II) were obtained but owing to a considerable number of accidental mass coincidences (*e.g.* CO and C₂H₄ both have masses of 28) cannot be used as unequivocal structure proofs in themselves. It was noted that following the stepwise loss of five CO units a strong signal appeared at the *m/e* value corresponding to L-Mn for both (I) and (II). Should the rings be intact at this point, the further observed breakdown steps of (I) and (II) were rationalizable. We plan to report further on the mass spectral breakdown patterns of acyl- and alkylmanganese compounds in the near future.

Compounds (VII) and (VIII)

Characterization of the two manganese products obtained in the reactions of adipyl and pimelyl chlorides with Mn(CO)₅⁻ is restricted to elemental analysis and IR spectral data. The analytical information indicates that both (VII) and (VIII) include two manganese atoms for each diacyl group. The IR data (Table 1) suggest the presence of two equivalent Mn(CO)₅ groups and a strong acyl carbonyl stretching band is observed in the region reported for other acyl manganese compounds¹. Unfortunately, the insolubility of these compounds in common organic solvents has precluded an accurate estimation of the structure of the organic portion of the molecules. However, what might be termed the normal product structure does fit the available information and so these products are formulated as (CO)₅MnCO-(CH₂)_nCOMn(CO)₅ with *n*=4 and 5 for (VII) and (VIII), respectively.

DISCUSSION

The two new compounds (I) and (II) are unique in that they represent the first examples of a lactone ring attached to a single metal atom by a simple σ bond. Recently Mills and Robinson⁷ obtained the structure for Co₂(CO)₉HCCH, (IX), in which a carbon atom in the lactone ring serves as a bridging atom between the two metal atoms. Heck⁸ has succeeded in preparing π-(butenolactonyl)cobalt tricarbonyl derivatives (X) by reacting acetylcobalt tetracarbonyl with acetylenes. Whereas the lactone system in both (IX) and (X) arises from the addition of an acetylene to a metal carbonyl complex, the lactone system in (I) or (II) must be generated by an internal cyclization mechanism.



One possible pathway whereby (I), or (II), might be formed is outlined in reaction (4). The first step is a normal reaction for the formation of an acylmanganese

compound. In the second step, an internal attack by the acylmetal carbonyl oxygen on the remaining acyl chloride group is proposed with generation of a carbonium ion from which a proton may be abstracted by the excess manganese pentacarbonyl anion. King⁹ has already shown that $\text{Mn}(\text{CO})_5^-$ is a very potent nucleophile that will even displace other organometallic groups from carbon. Presumably, for succinyl and glutaryl chloride the rate of cyclization is more rapid than the rate of reaction of the second acid chloride group with $\text{Mn}(\text{CO})_5^-$, whereas with adipyl or pimelyl chloride the increased chain length may cause cyclization to be significantly slower or totally unfavorable and a simple dimanganese derivative results. Although it is possible that each of the diacyl chlorides studied yields both types of products, that is cyclic and linear, our methods of isolation have always yielded only the products noted.

In addition to (I) or (II), large quantities of manganese decacarbonyl were recovered from the reactions involving succinyl and glutaryl chlorides. By comparison, very little dimanganese decacarbonyl was recovered from the reactions involving adipyl or pimelyl chlorides. The dimanganese decacarbonyl obtained in the former reactions was not excess starting material, but may have arisen from decomposition of hydridomanganese pentacarbonyl. Although no conclusive evidence for the formation of hydridomanganese pentacarbonyl can be cited, this substance may have been present in the colorless tetrahydrofuran distillate, which was collected at liquid nitrogen temperature, from the glutaryl and succinyl chloride reactions. As noted in the experimental section, manganese carbonyl was formed in these solutions upon warming to room temperature.

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