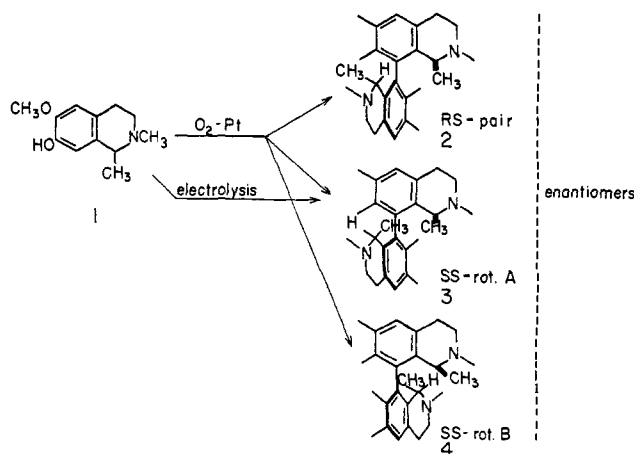


at the diphenyl linkage and at C-1 of the isoquinoline systems (Scheme I). The same three pairs of isomers

Scheme I. Oxidative Coupling of Racemic **1**



were obtained in our laboratory when the $K_3Fe(CN)_6$ oxidation of racemic **1**³ was repeated. We have now found that the electrolytic oxidation⁴ of racemic **1** yields *only one* (tlc, nmr, and isolation) of the enantiomeric pairs in 69% yield (77% conversion). The carbon-oxygen dimer² was isolated in 7% yield.

This single isomer, mp 226–227°, corresponds to one of the two crystalline isomers of the dimer. The structure is thought to be **3** based upon the following evidence. Electrolytic oxidation of the pure enantiomers of **1**⁵ gave the enantiomers of the same dimer which was isolated from racemic **1** [*S* isomer, 62% yield, 72% conversion; *R* isomer, 66% yield, 87% conversion]. The dimers had equal and opposite ORD curves. Thus, C-1 of the two isoquinoline rings in the electrolysis product must have the same configuration, as in **3** and **4**. Furthermore, ferricyanide oxidation of the enantiomers of **1** gave a mixture of two isomers which must be **3** and **4**. One was identical with the product from the electrolytic oxidation, and the other had spectral properties identical with those of another one of the original isomers.² The final establishment of **3** as the structure of the electrolysis product depends upon the nmr spectra of these two compounds. In **4**, the methyl groups are close to the oxygens and the protons should exhibit nmr peaks downfield from those generated by the methyl protons of **3** which lie more over the benzene rings (partially due to a methyl-methyl repulsion which does not exist in **4**). The spectra in dimethyl-*d*₆ sulfoxide of the two isomers from the $K_3Fe(CN)_6$ oxidation show C-methyl doublets at δ 0.71 and 1.17. The product of the electrolysis shows the δ 0.71 peak and is therefore **3**. In **1**, this peak appears at δ 1.22, slightly downfield from both **3** and **4** due to the absence of any positive

(3) M. Tomita, Y. Masaki, and K. Fujitani, *Chem. Pharm. Bull.*, **16**, 257 (1968).

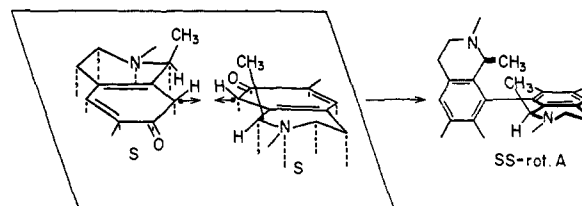
(4) The oxidation was carried out on a graphite felt electrode in excess sodium methoxide (3.3 mol) in wet CH_3CN at a potential of 0.04 V vs. standard calomel electrode using tetraethylammonium perchlorate as an electrolyte. A conventional two-compartment system was used.

(5) Racemic **1** was resolved through its *p*-toluoyltartaric acid salts. The enantiomers were correlated with carnegine of known absolute configuration (A. R. Battersby and T. P. Edwards, *J. Chem. Soc.*, 1214 (1960); E. Späth, *Chem. Ber.*, **62**, 1021 (1929)): *R* isomer, mp 182–182.5°, $[\alpha]_D^{25} +29.2^\circ$ (c 1, $CHCl_3$); *S* isomer, mp 182.5–183°, $[\alpha]_D^{25} -29.8^\circ$ (c 1, $CHCl_3$).

effect of the ring current (of the additional aromatic ring in the dimers).

These results are best explained as resulting from a surface reaction on the graphite electrode as shown in Scheme II between two radicals. Such radicals

Scheme II. Oxidative Coupling of (*S*)-**1** on a Surface



are considered⁶ to be the reacting species in oxidative coupling reactions. If the reacting molecules are adsorbed to the surface with the methyl groups sticking up, only those having identical configurations can come close enough together to couple. Otherwise methyl-methyl hindrance is severe. The formation of **3** in preference to **4** requires that the molecules lie in planes which are not parallel with the electrode surface. These planes are so tipped that the aromatic ring, or the flatter portion, is closer to the surface than the more bulky heterocyclic rings, a quite logical circumstance.

Thus, the reaction is stereoselective in that only molecules of identical configuration couple, and stereospecific in that only one of two possible rotational isomers is formed.

(6) H. Musso in "Oxidative Coupling of Phenols," W. I. Taylor and A. R. Battersby, Ed., Marcel Dekker, New York, N. Y., 1967, p 1.

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Received December 30, 1970

Complexes of Ozone with Carbon π Systems

Sir:

π complexes have frequently been proposed as the result of the initial attraction between ozone and olefinic or aromatic systems.¹⁻⁵ For example, in the competition between ozonolysis and epoxide formation during ozonation of hindered olefins (e.g., 1-mesityl-1-phenylethylene), a π complex precursor is suggested either to enter into 1,3-dipolar cycloaddition (ozonolysis route) or convert to a σ complex (epoxide route *via* O_2 loss).²

We wish now to report data which to our knowledge constitute the first characterization of complexes between ozone and sp^2 carbon systems.

Ozonation of 1-mesityl-1-phenylethylene at -78° in various solvents² or even at -120° (Freon-11 or -12) resulted in the ready absorption of 1 mol equiv of ozone and the simultaneous release of molecular oxygen with formation of the corresponding epoxide.

(1) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

(2) P. S. Bailey and A. G. Lane, *J. Amer. Chem. Soc.*, **89**, 4473 (1967).

(3) R. W. Murray, R. D. Youssefeyeh, and P. R. Story, *ibid.*, **89**, 2429 (1967).

(4) D. G. Williamson and R. J. Cvetanovic, *ibid.*, **90**, 4248 (1968).

(5) P. S. Bailey, F. E. Potts, III, and J. W. Ward, *ibid.*, **92**, 230 (1970).

At -150° (Freon-12 or isopentane solvent, isopentane-liquid N_2 bath), however, ozone was readily absorbed, but no molecular oxygen was evolved; the reaction mixture became Burgundy red in color upon the absorption of 1 equiv of ozone. When the reaction mixture was allowed to warm slightly (-145 to -135°), molecular oxygen was evolved and the epoxide was produced. Table I shows the nmr bands for the

Table I. Ozonation of 1-Mesityl-1-phenylethylene Nmr Bands (δ)

	Phenyl protons	Mesityl ring protons	Vinyl or epoxide protons	Mesityl methyl protons
Olefin (-150°)	7.69, 7.09	6.74	5.92, 5.03	2.29, 2.06
Complex (-150°)	7.52, 6.96	6.58	5.79, 4.90	2.15, 1.97
Epoxide (-135°)	6.99	6.68	2.97	2.17, 2.04

olefin at -150° , the red complex at -150° , and the -135° reaction mixture containing the epoxide. The fact that the nmr spectrum of the complex differs from that of the olefin only in that each peak is shifted very slightly upfield indicates a π complex with very little charge transfer. Analogies are iodine and tetracyanoethylene complexes of certain aromatic systems.⁶

Confirming evidence for the existence of a complex came from comparison of the visible spectra of frozen solutions of ozone on the one hand and the red complex on the other in isopentane at -195° (liquid N_2). The ozone solution absorbed strongly with double peaks occurring over the range 570–610 $m\mu$, as previously reported.⁷ The complex also absorbed broadly, peaking in the range 450–460 $m\mu$. There was only a very slight absorption in the free ozone range.

Similar complexes were obtained between ozone and the following compounds: mesitylene, 1-mesityl-1-phenylethane, and the methyl ether of trimesitylvinyl alcohol (prepared from the vinyl alcohol with NaH in tetrahydrofuran, recrystallized from pentane, mp 161 – 162° . *Anal.* Calcd for $C_{30}H_{36}O$: C, 87.33; H, 8.79. Found: C, 87.27; H, 8.70). Nmr spectra were taken of the complexes of the latter two compounds and, again, these showed only slight or negligible upfield shifts in comparison to the spectra of the pure compounds. Visible spectra of the mesitylene and the vinyl ether complexes showed absorption peaks in the range 435–460 $m\mu$, very similar to that of the complex of 1-mesityl-1-phenylethylene. Along with the absorption peak for the complex, in each case, was a smaller band for pure ozone, which, however, was considerably stronger than the very weak pure ozone absorption found in the visible spectrum of the 1-mesityl-1-phenylethylene-ozone complex. This indicates that the equilibrium between the complex and the individual reactants was more strongly toward the complex in the case of the mesitylphenylethylene than with the other compounds. Further indication

of this came from the colors of the other complexes. All ranged from greenish to black, indicating free ozone in addition to another colored species. The reversibility of complex formation and the greater strength of the mesitylphenylethylene complex than of the 1-methoxy-1,2,2-trimesitylethylene complex was further illustrated by adding *cis*-3-hexene to solutions of the complexes at temperatures well below their decomposition temperatures. In the case of the vinyl ether complex all of the ozone was removed, producing the *cis*- and *trans*-3-hexene ozonides, as shown by nmr spectra.⁸ On the other hand only about one-fifth of the ozone was similarly robbed from the 1-mesityl-1-phenylethylene complex, the rest reacting to give the epoxide.⁸ Ozone could be driven from the mesitylene and 1-mesityl-1-phenylethane complexes by sweeping with nitrogen at -100° .

The temperature at which the complexes decomposed⁹ seemed to have more to do with the further reactivity of the π system involved than with the strength of the complex. Conversion of the mesitylphenylethylene complex to epoxide occurs slightly above -150° . On the other hand further ozone reaction with the other systems appeared to involve ozonolysis of the mesityl group or groups and this did not occur to any appreciable extent below -90° .

Complexation in the case of mesitylene and 1-mesityl-1-phenylethane, of course, must involve the mesityl π system. This also appeared to be true with the 1-methoxy-1,2,2-trimesitylethylene complex, due to the steric inaccessibility of the olefinic double bond, as borne out by a La Pine molecular model of the compound. The model also showed that none of the mesityl groups was coplanar with the double bond. In the case of the 1-mesityl-1-phenylethylene, however, a model showed that the phenyl group, but not the mesityl group, could rotate freely and thus be coplanar with the double bond. This is also indicated by nmr spectra of the olefin. At room temperature there is only one phenyl hydrogen peak (at δ 7.18 ppm) but at -150° there are two peaks for the phenyl protons (Table I) which must be conformational in origin. It is quite likely, therefore, that the mesitylphenylethylene-ozone complex involves the conjugated system of the olefin, rather than the mesityl group.

The total significance of these complexes is, of course, still uncertain. It seems reasonable to us that they represent the initial attraction between ozone and the π systems, from which all further reactions evolve. They could, however, represent novel low-temperature interactions which are entirely independent of the reactions which occur at higher temperatures. In this event it is conceivable that the entire course of an ozonation could be changed by going to very low temperatures. Further investigation of low-temperature ozone-organic chemistry is in progress.

(8) The color of the complex disappeared as soon as the 3-hexene was added (at -150°), perhaps due to the heat of reaction between the complex and 3-hexene. The ratio of epoxide to 3-hexene ozonides was then determined by vpc.

(9) There appears to be little danger in handling these complexes in small quantities (usually 1 mmol or less) provided the reaction mixtures are not overozonized and temperature rises are allowed to occur slowly. In one instance, with the mesitylene complex, detonation occurred when the solution was allowed to warm in air (rather than first in acetone-dry and then in ice water).

(6) For references see: (a) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969, Chapters 1–4; (b) R. Foster and C. A. Fyfe, *Progr. Nucl. Magn. Resonance Spectrosc.*, **4**, 1 (1969).

(7) A. D. Kirshenbaum and A. G. Streng, *J. Chem. Phys.*, **35**, 1440 (1961).

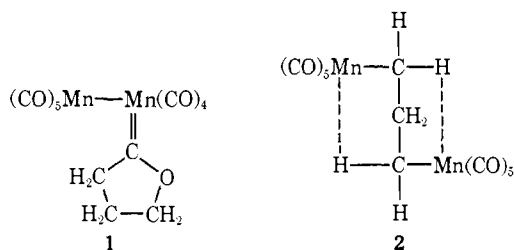
Acknowledgment. The support of this research by the Robert A. Welch Foundation (F-042) and the Petroleum Research Fund of the American Chemical Society (PRF-4534-AC1) is gratefully acknowledged. The authors are also grateful for advice from Drs. Ben A. Shoulders and Clifford Becker concerning the low-temperature nmr and visible spectra techniques.

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Received April 17, 1971

Metal-Carbene Complexes from the Reaction of Methylpentacarbonylmanganese(I) with Sodium Pentacarbonylmanganate(-I)

Sir:

In 1963 King reported that the reaction of $\text{NaMn}(\text{CO})_5$ with either 1,3-dibromopropane or 4-chlorobutyl chloride gave a compound with the empirical formula $\text{Mn}_2(\text{CO})_{10}(\text{CH}_2)_3$.¹ This compound has recently been shown to be the cyclic metal-carbene complex **1**² and not structure **2** as originally proposed by King. We now wish to report a new reaction which clarifies the mechanism of formation of **1** from 1,3-dibromopropane.



The reaction of nucleophiles such as phosphines,³ amines,³ carbon monoxide,⁴ and iodide ion⁵ with $\text{CH}_3\text{Mn}(\text{CO})_5$ to give substituted acetyltetracarbonylmanganese complexes is well known. Here we report that the nucleophilic anion $\text{Mn}(\text{CO})_5^-$ (**3**) reacts with $\text{CH}_3\text{Mn}(\text{CO})_5$ in tetrahydrofuran (THF) to give the dinuclear acetylmanganese anion **4**. Furthermore, we have established this reaction to be a rapid equilibrium process.

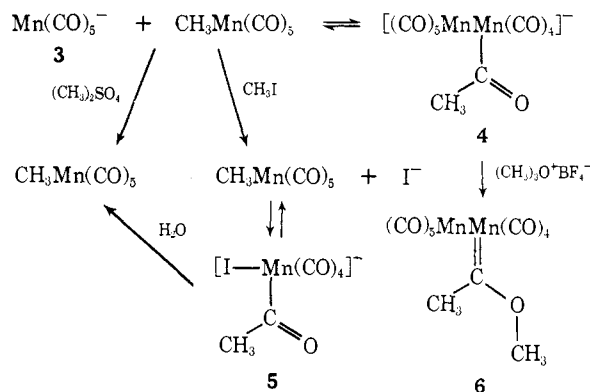
The nmr spectrum of a solution prepared from 0.27 mmol each of $\text{NaMn}(\text{CO})_5$ and $\text{CH}_3\text{Mn}(\text{CO})_5$ in 0.50 ml of THF consists of a singlet at τ 10.10 due to $\text{CH}_3\text{Mn}(\text{CO})_5$ and a new singlet at τ 7.19 which we attribute to the dinuclear acetylmanganese anion **4** in addition to the THF resonances. The relative intensities of the two singlets change upon dilution; the ratio of the area of the peak at τ 7.19 due to the adduct **4** to the area of the $\text{CH}_3\text{Mn}(\text{CO})_5$ peak at τ 10.10 changes from 1.45 to 1.08 when the sample volume is increased from 0.50 to 1.20 ml. The equilibrium has thus been shifted to $\text{CH}_3\text{Mn}(\text{CO})_5$ by dilution, as expected from the law of mass action. A marked change in the relative intensities of the two singlets also occurs upon heating: at 40°, the ratio of the intensity of the peak

due to **4** to the intensity of the $\text{CH}_3\text{Mn}(\text{CO})_5$ peak is 1.45; at 71°, the ratio decreases to 1.03. These changes are reversible below 90° where irreversible line broadening occurs caused by thermal decomposition.

The infrared spectrum of this equilibrium mixture run at nmr concentrations (0.55 M) contains a carbonyl stretch at 1560 cm^{-1} which compares well with the 1566- cm^{-1} band reported for the iodoacetylpentacarbonylmanganese anion **5**. At concentrations sufficiently low to resolve the metal carbonyls, the equilibrium concentration of the dinuclear acetylmanganese anion **4** is so low that it cannot be observed.

The equilibrium has also been shifted by chemical means as shown in Scheme I. Addition of a fourfold

Scheme I



excess of dimethyl sulfate to the equilibrium mixture described above resulted in the disappearance of the peak at τ 7.19 corresponding to the adduct **5** in less than 30 sec; comparison of the increased $\text{CH}_3\text{Mn}(\text{CO})_5$ peak area at τ 10.10 with the area of the methyl singlet of a known amount of *p*-di-*tert*-butylbenzene internal standard indicated the quantitative formation of $\text{CH}_3\text{Mn}(\text{CO})_5$. Addition of methyl iodide to the equilibrium mixture also resulted in rapid disappearance of the acetyl peak at τ 7.19 and an increase in the $\text{CH}_3\text{Mn}(\text{CO})_5$ peak at τ 10.10. The iodide ion produced in this reaction further reacted with $\text{CH}_3\text{Mn}(\text{CO})_5$ to produce a resonance at τ 7.13 corresponding to iodoacetyltetracarbonylmanganese anion **4**, which has been previously isolated as its lithium salt.⁵ The iodo compound **5** readily decomposes upon addition of water to give $\text{CH}_3\text{Mn}(\text{CO})_5$. Addition of sodium iodide to $\text{CH}_3\text{Mn}(\text{CO})_5$ in THF produced the iodo compound **5** with a sharp singlet at τ 7.13. Neither dimethyl sulfate nor methyl iodide gave any O-alkylation of **4**.

The acyl anion **4** can be alkylated on oxygen with trimethyloxonium fluoroborate to give the corresponding methylmethoxycarbene complex **6**, previously prepared by Fischer and Offhaus.⁶ In a typical reaction, $\text{CH}_3\text{Mn}(\text{CO})_5$ (0.50 g, 2.4 mmol) and $\text{NaMn}(\text{CO})_5$ (4.3 ml, 0.55 M, 2.4 mmol) in 30 ml of THF were stirred for 5 min at room temperature. Solvent was evaporated under aspirator vacuum to give an orange oil which was dissolved in oxygen-free water and treated with trimethyloxonium fluoroborate until the solution became acidic. The material obtained from pentane extraction of the aqueous solution was sub-

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