ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE DETROIT RESEARCH LABORATORIES OF ETHYL CORPORATION]

The Chemistry of Cyclopentadienylmanganese Tricarbonyl Compounds. I. Acylation and Alkylation[1]

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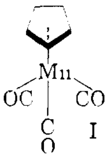
Cyclopentadienylmanganese tricarbonyl has been acetylated and benzoylated and the cyclohexyl and *t*-butyl derivatives prepared. By a series of competitive reactions it has been shown that as regards reactivity toward acylation, a series can be established in order of decreasing activity—anisole > methylcyclopentadienylmanganese tricarbonyl > cyclopentadienylmanganese tricarbonyl > benzene. Benzoylation of methylcyclopentadienylmanganese tricarbonyl gives rise to two isomeric compounds in the ratio 3 to 2.

Ferrocene, which has a type of penetration-complex bonding, shows many of the reactions typical of aromatic compounds.[2-7] However, other similarly bonded compounds such as dibenzenechromium do not show aromatic character,[8] and even biscyclopentadienyltitanium dichloride fails to undergo acylation under Friedel–Crafts conditions.[9] The present investigation relates to cyclopentadienylmanganese tricarbonyl,[10-12] which is a penetration complex, differing in that dissimilar ligands are bonded to the central metal atom.

The parent compound I has been reported to be stable to air, iodine in carbon tetrachloride, hydrogen chloride in ethanol and to treatment with maleic anhydride in boiling benzene.[11] Further, the infrared spectrum of I is markedly similar to that of ferrocene in regions where the cyclopentadienyl portion absorbs, and is cited as evidence for the same type of metal-to-ring bonding.[11] The structure proposed[13] for this compound might be compared to a piano stool with the ring serving as the seat and the CO groups symmetrically arranged as the legs. Our work tends to substantiate this structure insofar as we have never detected the presence of more than one molecular species in a monosubstituted cyclopentadienylmanganese tricarbonyl compound.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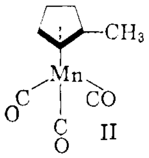
II

Cyclopentadienylmanganese tricarbonyl was alkylated and acylated using aluminum chloride as a catalyst. The alkylation reactions required only catalytic quantities of aluminum chloride. For acylation, where one mole of aluminum chloride coördinates strongly with the oxygen of the resulting ketone, only slightly more than one mole of catalyst was required.

Acylation of these materials was the method of choice for studying the relative reactivity since (1) only monosubstitution takes place and (2) acylation differs from alkylation in being virtually irreversible.[14] The method whereby two compounds are permitted to compete for a limited amount of a third substituent has been so widely used in the past as to obviate the necessity for further comment here. Suffice it to say that in order for valid conclusions to be drawn from the products of such a reaction, AC must be incapable of breakdown under the conditions of the reaction to give BC, and *vice versa*. The literature[15] refers to a somewhat similar study in the chemistry of ferrocene.

$$\begin{matrix}\mathrm{A}\\ \\ \mathrm{B}\end{matrix} + \mathrm{C} \longrightarrow \mathrm{AC} \text{ or } \mathrm{BC}$$

The acylation of I gives rise to only one isomer, but similar substitution of II can give rise to two positional isomers, *i.e.*, the 2- or α-position and the 3- or β-position.[16] Thus when II was benzoylated, two isomers were isolated which differed by 64° in their melting points, gave differing infrared spectra and yielded 2,4-dinitrophenylhydrazones possessing different melting points. The ratio of isomers was established by infrared analysis as 64:37 with the lower melting form predominating. The authors wish to refrain from assigning structure to these materials, but if the analogy to ferrocene holds true it would be expected that the low melting form, since it predominates, would be the β-isomer.[16]

The results of the competitive acylations are summarized in Table I.

It has been reported[15] previously that when one mole of ferrocene and ten moles of anisole in chloroform solution were allowed to compete for a limited

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(1) Presented in part at the 134th Meeting of the American Chemical Society in Chicago, Ill., September 10, 1958.

(2) R. B. Woodward, M. Rosenblum and M. C. Whiting, THIS JOURNAL, **74**, 3458 (1952).

(3) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. A. Nesmeyanova, *Proc. Acad. Sci. USSR*, **97**, 459 (1954).

(4) R. Riemschneider and D. Helm, *Ber.*, **89**, 155 (1956).

(5) A. N. Nesmeyanov and N. S. Kochetkova, *Proc. Acad. Sci., USSR*, **109**, 543 (1956).

(6) P. L. Pauson, *Quart. Revs.*, **9**, 391 (1955).

(7) A. N. Nesmeyanov, *Proc. Royal Soc. (London)*, **246**, 495 (1958).

(8) H. P. Fritz and E. O. Fischer, *Z. Naturforsch.*, **12B**, 67 (1957).

(9) G. Wilkinson and J. M. Birmingham, THIS JOURNAL, **76**, 4281 (1954).

(10) E. O. Fischer, *Z. Naturforsch.*, **9B**, 618 (1954).

(11) T. S. Piper, F. A. Cotton and G. Wilkinson, *J. Inorg. and Nuclear Chem.*, **1**, 165 (1955).

(12) J. E. Brown, H. Shapiro and E. G. DeWitt, U. S. Patent 2,818,417, Dec. 31, 1957. This patent describes the preparation and properties of methylcyclopentadienylmanganese tricarbonyl.

(13) F. A. Cotton, A. D. Liehr and G. Wilkinson, *J. Inorg. and Nuclear Chem.*, **1**, 175 (1955).

(14) R. C. Fuson, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1950 p. 338.

(15) G. D. Broadhead, J. M. Ogersby and P. L. Pauson, *J. Chem. Soc.*, 650 (1958).

(16) K. L. Rinehart, Jr., K. L. Motz and Sung Moon, THIS JOURNAL, **79**, 2749 (1957).

TABLE I

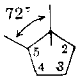
COMPETITIVE ACYLATIONS

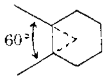
Competing reactants (moles)	Substituent (mole)	Products, %[a]
I (0.25) Benzene (1.25)	$CH_3\underset{\substack{\| \\ O}}{C}$ (0.25)	54.4 9.3
I (0.3) II (0.3)	$C_6H_5\underset{\substack{\| \\ O}}{C}$ (0.3)	31 ± 2 68 ± 7[b]
II (0.3) Anisole[c] (0.6)	$C_6H_5\underset{\substack{\| \\ O}}{C}$ (0.3)	. . 90.8[d]

[a] Yield based on the number of moles of substituent. [b] Total yield of two isomers; roughly in the same ratio as obtained when II was acylated alone. [c] Anisole was chosen because it is reported to acylate only in the *p*-position.[17] [d] *p*-Methoxybenzophenone.

amount of acetyl chloride–aluminum chloride complex, only acetylferrocene was formed. Thus the series, in order of decreasing reactivity, becomes ferrocene > anisole > II > I > benzene.

Alkylation of I and II proceeds more sluggishly than does acylation and determination of products is complicated by polysubstitution. Thus, dialkylation can give α- and β-isomers and trialkylation can yield the 1,2,3- and 1,2,4-isomers. In





the materials which are designated as di- and tributylated derivatives of I, the possibility exists that these may contain C_8H_{17} groups arising as a consequence of the dimerization of isobutylene prior to reaction with I. We believe this to be a remote possibility and indeed we were unable to find any report in the literature which would parallel such a course of reaction. The authors do not wish to imply that the structure of these materials is known unequivocally, but that the designation as butyl derivatives seems most probable. It has been suggested[18] that *o*-di-*t*-butylbenzenes would be very difficult to prepare. However, when dealing with cyclopentadienyl compounds the steric factors are somewhat reduced because of the increased bond angles.

Experimental[19]

Benzoylcyclopentadienylmanganese tricarbonyl[20] was prepared by treatment of the cyclopentadienyl compound I with benzoyl chloride and aluminum chloride in the usual Friedel–Crafts manner. Addition of aluminum chloride (8.7 g., 0.065 mole) in small portions to a stirred mixture of 10.2 g. (0.05 mole) of I, 7.05 g. (0.05 mole) of benzoyl chloride and 100 ml. of carbon disulfide resulted in a small rise in temperature and evolution of hydrogen chloride. When addition was complete (*ca.* 30 min.) the mixture was heated to reflux for 4 hr., cooled, hydrolyzed with cold dilute hydrochloric acid and the organic layer separated.

The solution was evaporated to dryness, and the solid residues dissolved in hexane and dried over calcium sulfate. Concentration of the solution yielded 14 g. (0.0454 mole), 91%, m.p. 69.5–73.5°. Recrystallization from benzene–petroleum ether raised the m.p. to 73.5–74.5°.

Anal. Calcd. for $C_{15}H_9MnO_4$: C, 58.5; H, 2.92; Mn, 17.8. Found: C, 58.9; H, 3.11; Mn, 17.4.

The 2,4-dinitrophenylhydrazone[21] melted at 229–230°.

Anal. Calcd. for $C_{21}H_{13}MnN_4O_7$: Mn, 11.3. Found: Mn, 11.5.

Competitive Acetylation of I and Benzene.—To a stirred mixture of 51 g. (0.25 mole) of I, 97.5 g. (1.25 moles) of benzene and 19.7 g. (0.25 mole) of acetyl chloride in 200 ml. of carbon disulfide were added 40 g. (0.31 mole) of aluminum trichloride in small portions. In the course of the hour required for the addition, the temperature rose to 45°. Stirring was continued for an hour, then the mixture was chilled in an ice-bath and hydrolyzed by the dropwise addition of a large excess of cold dilute hydrochloric acid. The organic layer was separated, dried by shaking with anhydrous sodium carbonate and finally the solvents were removed by distillation at atmospheric pressure.

The residues were distilled at reduced pressure through a small spinning band fractionating column to give two fractions: fraction A (16.5 g.) boiling at temperatures up to 110° at 23 mm. and fraction B (33.4 g.) boiling at 104° at *ca.* 2 mm. The latter fraction, acetylcyclopentadienylmanganese tricarbonyl, could be crystallized by dissolution in a minimum of ether and isoöctane and then judiciously cooling, m.p. 41.5–42.5°.

Anal. Calcd. for $C_{10}H_7MnO_4$: C, 48.8; H, 2.85; Mn, 22.4. Found: C, 49.2; H, 2.89; Mn, 21.9.

The red 2,4-dinitrophenylhydrazone melted at 223–224°.

Anal. Calcd. for $C_{16}H_{11}MnN_4O_7$: Mn, 12.9. Found: Mn, 13.5.

Examination of the infrared spectrum of fraction A showed the material to contain *ca.* 17% (2.8 g., 0.023 mole, 9.3% of theory based on acetyl chloride) of acetophenone together with a larger percentage of unreacted I and a small amount of the acetyl derivative.

Benzoylation of II.—When II was treated with benzoyl chloride and aluminum chloride under conditions similar to those described for the preparation of benzoylcyclopentadienylmanganese tricarbonyl a total yield of 73.4% of benzoylated product was obtained. The product was separated into two fractions depending on solubility in petroleum ether. That which was most soluble was recrystallized from carbon disulfide to a constant m.p. 53–54°.

Anal. Calcd. for $C_{16}H_{11}MnO_4$: C, 59.6; H, 3.42; Mn, 17.1. Found: C, 59.7; H, 3.41; Mn, 16.8.

The 2,4-dinitrophenylhydrazone formed most rapidly from this isomer, m.p. 198–200°.

Anal. Calcd. for $C_{22}H_{15}MnN_4O_7$: Mn, 11.0. Found: Mn, 11.4.

The fraction least soluble in petroleum ether was recrystallized from it, m.p. 117–118°.

Anal. Calcd. for $C_{16}H_{11}MnO_4$: C, 59.6; H, 3.42; Mn, 17.1. Found: C, 59.9; H, 3.66; Mn, 17.1.

The 2,4-dinitrophenylhydrazone of this isomer formed slowly, m.p. 210–211°.

Anal. Calcd. for $C_{22}H_{15}MnN_4O_7$: Mn, 11.0. Found: Mn, 11.3.

Examination of the infrared spectrum of the original benzoylated products, prior to separation, indicates the ratio of the two isomers to be about 64:37 with the lower melting isomer predominating.

Competitive Benzoylation of I and II.—To a solution containing 61.2 g. (0.3 mole) of I, 65.4 g. (0.3 mole) of II and 42.3 g. (0.3 mole) of benzoyl chloride in 400 ml. of carbon disulfide was added 52.2 g. (0.39 mole) of aluminum trichloride in small portions. Addition required one hour, and stirring was continued for an additional 2 hours.

Standard procedures were used for the work-up of the products. The residues remaining after removal of solvents were fractionally distilled through a Nester spinning band column. The forecut boiling in the range 74–86° at 3–4 mm. amounted to 51 g. and analysis, using vapor-phase chromatography, showed this material to be 76% (38.8 g.) I and 24% (12.2 g.) II.

The main fraction, b.p. 174–176° at 2–3 mm., weighed

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(17) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, p. 302.

(18) H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 24 (1953).

(19) Boiling points and melting points are uncorrected.

(20) During preparation of this manuscript, the authors learned of Prof. E. O. Fischer's report of the benzoylation of cyclopentadienylmanganese tricarbonyl under Friedel–Crafts conditions; Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

(21) All 2,4-dinitrophenylhydrazones were prepared by the method described by R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

75.8 g. Comparison of the infrared spectrum of this fraction with that of mixtures of known composition shows it to contain 43 ± 2% of the low-melting benzoyl derivative of II, 25 ± 5% of the high-melting derivative and 31 ± 2% of benzoylcyclopentadienylmanganese tricarbonyl.

Competitive Benzoylation of II and Anisole.—To a stirred solution containing 65.4 g. (0.3 mole) of II, 64.8 g. (0.6 mole) of anisole, 42.3 g. (0.3 mole) of benzoyl chloride in 400 ml. of carbon disulfide was added 52.2 g. (0.39 mole) of aluminum chloride. The addition required 90 min. and occasional cooling was required to maintain the temperature at 25°. After standing overnight, the mixture was subjected to the customary work-up. Fractional distillation through a Nester spinning band column yielded 22.9 g. of anisole; 60.1 g., 92%, of II; and 57.8 g., 90.8%, of *p*-methoxybenzophenone, m.p. 62.5–63.5° (lit.[22] 61–62°).

The *p*-methoxybenzophenone was further identified by hydrolysis to the *p*-hydroxy derivative, m.p. 133–134° (lit.[22] 135°).

Butylation of I.—Isobutylene (32 g., 0.57 mole) was bubbled slowly into a stirred mixture containing 102 g. (0.5 mole) of I, 13.3 g. (0.1 mole) of aluminum chloride and 350 ml. of carbon disulfide. In the course of the 6 hours required for the addition, the temperature rose to a maximum of 39°. The mixture was stirred overnight at room temperature then worked up in the usual manner.

Removal of the solvents and then fractional distillation through a small Nester spinning band column gave 60 g. of I and 49.6 g. of alkylated derivatives boiling above 143° at 29 mm. Three fractions were obtained (among others) which analyzed correctly for the mono-, di- and tributylated derivatives of I.

Mono-*t*-butyl, b.p. 150° at 28–29 mm., $n^{20}D$ 1.5600. *Anal.* Calcd. for $C_{12}H_{13}MnO_3$: C, 55.4; H, 5.0; Mn, 21.2. Found: C, 55.6; H, 5.13; Mn, 20.9.

Di-*t*-butyl, b.p. 164–168° at 10 mm., m.p. 70–71°. *Anal.* Calcd. for $C_{16}H_{21}MnO_3$: C, 60.8; H, 6.64; Mn, 17.4. Found: C, 60.9; H, 6.76; Mn, 17.2.

Tri-*t*-butyl, b.p. 160–163° at 3.5 mm., $n^{20}D$ 1.5326. *Anal.* Calcd. for $C_{20}H_{29}MnO_3$: C, 64.5; H, 7.80; Mn, 14.8. Found: C, 64.0; H, 7.54; Mn, 14.8.

Alkylation of I with Cyclohexyl Chloride.—Cyclohexyl chloride (23.6 g., 0.2 mole) was added dropwise over a one-hour period to a stirred mixture of 40.8 g. (0.2 mole) of I, 3.32 g. of aluminum trichloride and 150 ml. of carbon disulfide. The evolution of hydrogen chloride started almost immediately and the temperature rose slowly to 35°. When addition was complete the mixture was stirred for an additional hour, then chilled, hydrolyzed with cold dilute hydrochloric acid, extracted with ether, dried with sodium carbonate and the solvents removed by distillation. The residues were distilled at *ca.* 2 mm. through a small spinning band fractionating column to yield the fractions

Take-off temp., °C.	Wt., g.	Remarks
70	10	I
70–109	2.3	
109–110	7.5	
110–114	9.05	$n^{20}D$ 1.5686
114–149	2.4	
149–152	4.6	$n^{20}D$ 1.5804
152–160	2	$n^{20}D$ 1.5700

The fraction boiling at 110–114° analyzed well for the **monocyclohexyl** derivative.

Anal. Calcd. for $C_{14}H_{15}MnO_3$: C, 58.7; H, 5.24; Mn, 19.2. Found: C, 58.8; H, 5.17; Mn, 19.1.

The fraction boiling 149–152° analyzed for the **dicyclohexyl** compound.

Anal. Calcd. for $C_{20}H_{25}MnO_3$: C, 65.3; H, 6.8; Mn, 15.0. Found: C, 65.8; H, 6.87; Mn, 15.0.

Acknowledgment.—The authors wish to thank Mr. R. T. Lundquist of these laboratories for the determination of the ratio of isomers in the benzoylated products.

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[22] "Dictionary of Organic Compounds," Vol. II, Oxford University Press, New York, N. Y., p. 732.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Diaryliodonium Salts. XI. Salts Derived from Phenoxyacetic and β-Phenoxyethanesulfonic Acids[1,2]

BY F. MARSHALL BERINGER AND ROBERT A. FALK

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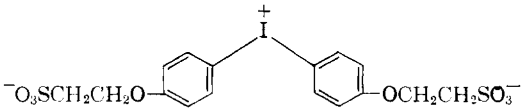
β-Phenoxyethanesulfonyl chloride was condensed with phenyliodoso diacetate, and the product was hydrolyzed to the betaine $4\text{-}C_6H_5\overset{+}{I}C_6H_5OCH_2CH_2SO_3^-$. The same sulfonyl chloride with iodine(III) trifluoroacetate gave a product which was hydrolyzed and isolated as a barium salt, $Ba^{++}/_2 4,4'\text{-}\overset{+}{I}(C_6H_4OCH_2CH_2SO_3^-)_2$. As these materials do not contain the iodonium groups in a cation, their aqueous solutions do not give precipitates with halide ions. Symmetrical and unsymmetrical salts were similarly obtained from phenoxyacetic acid. The proofs of structures of all the iodonium salts rest on reactions with iodide ions to give 4-iodophenyl ethers, which were prepared independently.

In studies of the reactions of iodonium salts with nucleophiles in aqueous or largely aqueous solutions, it has been noticed that the appearance of

$$C_6H_5\overset{+}{I}C_6H_5 + \overset{-}{X} \longrightarrow C_6H_5X + C_6H_5I$$

a second phase of insoluble products caused an increase of rate.[3] One method of avoiding this heterogeneity, the use of organic solvents or cosolvents, has the limitation that the empirical kinetic order of the reaction may decrease from second toward first with decreasing solvent polarity.[3,4] A second method would be to have substituents on the iodonium cation such that the products would be water-soluble. One of the compounds here reported has an iodonium-containing anion which meets these requirements.



An additional useful property of such an anion is that it is not precipitated from solution by halide

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[1] Preceding paper, F. M. Beringer, E. M. Gindler, M. Rapoport and R. J. Taylor, THIS JOURNAL, **81**, 351 (1959).

[2] This paper is taken from the dissertation of Robert A. Falk, submitted in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

[3] F. M. Beringer and E. M. Gindler, THIS JOURNAL, **77**, 3203 (1955); F. M. Beringer, E. J. Geering, I. Kuntz and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956).

[4] F. M. Beringer and E. M. Gindler, THIS JOURNAL, **77**, 3200 (1955).