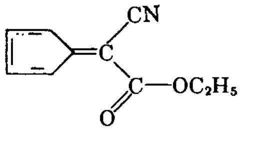
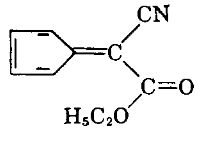
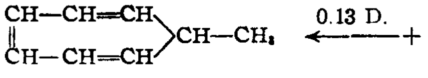
molecular orbital method underestimates, in general, repulsions between electrons, it is plausible that they obtained a moment slightly greater than that of the present investigation. On the other hand, the moment predicted by Julg[4] does not agree with the present experiment in regard to both the direction and the magnitude of the moment. The moment of heptafulvene represents perhaps the greatest one ever reported for a hydrocarbon molecule, but the value is adequate compared with the large moment, 4.17 D., of tropone.[17] Presumably, the lack of stability of heptafulvene is closely associated with the high polarity of the molecule.

The moment of 8-ethoxycarbonylheptafulvene-8-nitrile is hardly feasible for a rigorous theoretical treatment. However, the observed moment is consistent with the structure I, whereas an alternative planar form II gives a too high theoretical moment (>7 D.) incompatible with the observed moment. This is quite understandable, because the molecule will be stabilized with its CN and C=O groups of high polarity separated farthest apart from each other.


I


II

The molecule of ditropylmalononitrile is suitable for the estimation of the moment of 7-methylcycloheptatriene, the simplest molecule having a tropyl group. The moment calculated for this compound is 0.13 D. Although the use of the moment of a tropyl group is open to question, because there is no assurance that the group moment is parallel to the end C—C axis, it leads to a calculated moment, 4.43 D., for tropylmalononitrile in fair agreement with the observed value of 4.12 D. The problem of various valence structures for compounds having a tropyl group has been a subject of considerable dispute among organic chemists[18] and the nuclear magnetic resonance has been employed in order to discuss the structure of some of these compounds. However, the present discussion is independent of choice to be made among conceivable valence structures for a tropyl group.



Mention should be made that the estimated moment for heptafulvene, 3.07 D., is much greater than that for 7-methylcycloheptatriene, 0.13 D., and that the directions of the moments are opposed. The former compound is a typical example of non-alternant hydrocarbons which show a π-electron moment. On the other hand, although the molecule of the latter compound contains an odd-member ring, it has a character of an alternant hydrocarbon as a π-electron system, because one of the carbon atoms in the ring is bonded to four other atoms, the bond type being that of sp^3 rather than of sp^2. Since π-electrons in alternant hydrocarbons are predicted[19] to be uniformly distributed over carbon atoms involved, the π-electron moment vanishes. Thus, the difference in polarity between heptafulvene and 7-methylcycloheptatriene can be explained qualitatively in terms of the theory of molecular orbitals.

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(17) Y. Kurita, S. Seto, T. Nozoe and M. Kubo, *Bull. Chem. Soc. Japan*, **26**, 272 (1953).

(18) W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain and R. B. Williams, THIS JOURNAL, **78**, 5448 (1956).

(19) C. A. Coulson, H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A192**, 16 (1947); C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950).

[CONTRIBUTION FROM THE DETROIT RESEARCH LABORATORIES OF THE ETHYL CORP., DETROIT, MICH.]

The Chemistry of Cyclopentadienylmanganese Tricarbonyl Compounds. II. Sulfonation and Metallated Derivatives[1]

BY MICHAEL CAIS[2] AND JOHN KOZIKOWSKI

RECEIVED MARCH 14, 1960

Cyclopentadienylmanganese tricarbonyl has been sulfonated. A number of sulfones prepared from the sulfinic acid and sulfonyl chloride are reported. The sulfinic acid also served as starting material for the preparation of ring mercurated derivatives of cyclopentadienylmanganese tricarbonyl.

Recently, Piper, Cotton and Wilkinson[3] have carried out a study of the structure of cyclopentadienyl–carbon monoxide compounds of transition metals. These authors point out that the case of cyclopentadienylmanganese tricarbonyl (I) is a very interesting one because the cyclopentadienyl ring is considered to be bound to the metal by a "sandwich" bond, whereas in manganese bis-cyclopentadienide (II) the metal to ring bond appears to be of ionic character.[4,5] A striking difference between the two compounds is that I does not react with maleic anhydride whereas II reacts instantaneously with the latter.[3] This and other differences between compounds I and II, in particular the suggested presence of a "sandwich" bond in I, made it seem desirable to us to investigate the chemical properties of I. This investigation was directed

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(1) Presented in part at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September 14–18, 1959.

(2) Chemistry Department, Technion, Haifa, Israel.

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

(4) G. Wilkinson and J. M. Birmingham, THIS JOURNAL, **76**, 6210 (1954).

(5) G. Wilkinson, F. A. Cotton and J. M. Birmingham, *J. Inorg. and Nuclear Chem.*, **2**, 95 (1956).

not only at a study of the aromatic character of the cyclopentadienyl ring of I but was also largely concerned with obtaining information about the stability of the carbon monoxide-to-metal bonds.

The successful Friedel–Crafts acetylation, benzoylation and alkylation of I in good yields has been reported from these laboratories[6a] and this supports the evidence[6] in favor of the aromatic nature of the cyclopentadienyl ring in I, while at the same time showing the carbon monoxide-to-metal bonds to have a good degree of stability.

The sulfonation of I in very high yields, upon which we now wish to report, brings further confirmation of the last two points. The high conversion obtained in this reaction with I are in contrast to the relatively lower conversion obtained in the sulfonation of ferrocene.[7] One reason for this difference in conversions is probably due to the fact that with I it is not necessary to use an excess of starting material, as with ferrocene where sulfonation can take place in both rings. Another reason might be attributed to the method used by us in working up the reaction product. The (sulfocyclopentadienyl)-manganese tricarbonyl (III), was isolated in the form of its *p*-toluidine salt IV. Compound IV, which turned out to be very sparingly soluble in cold water, could be precipitated directly by adding a solution of *p*-toluidine in dilute hydrochloric acid to the water-diluted, filtered, reaction mixture. This obviates the necessity of evaporating off the large volume of water resulting from the work-up of the reaction mixture. Compound IV can be easily purified through recrystallization from hot water or from alcohol. Furthermore, IV can be used directly to react with phosphorus pentachloride to obtain (chlorosulfonyl cyclopentadienyl)-manganese tricarbonyl (V) in quantitative yield.[8] Reduction of V with sodium sulfite afforded the (sulfinocyclopentadienyl)-manganese tricarbonyl (VI) in nearly quantitative yield.

The high yields obtained in all these reactions testify to the stability of the carbon monoxide-to-metal bonds in I. Furthermore, one is inclined to believe that the substitution of the $-SO_3H$ group in the cyclopentadienyl ring of I goes beyond the expected deactivating effect of such a group, substituted in an aromatic ring, in that it imparts increased stability to the molecule as a whole, including the carbon monoxide-to-metal bonds. This is shown by the smooth reaction of IV with phosphorus pentachloride in contrast to the fact that, under similar reaction conditions, phosphorus pentachloride appears to cause complete breakdown of all the bonds in I, manganese chloride being formed in a yield of more than 75%.[9] Rosenblum observes[10] that formylation of ferrocene does not proceed beyond the introduction of one aldehyde group even in the presence of a large excess of N-methylformanilide and phosphorus oxychloride. He regards this as support for the view[11] that an electron-withdrawing substituent in one ring deactivates not only the substituted ring but transmits this effect also to the second unsubstituted ring.

The availability of (sulfocyclopentadienyl)-manganese tricarbonyl(III) and its derivatives, the sulfonyl chloride V and the sulfinic acid VI, prompted us to attempt the synthesis of sulfones which would incorporate the cyclopentadienyl-manganese tricarbonyl moiety.[12]

Of the many methods available for the preparation of sulfones[13] we tried three procedures which allowed us to use compounds V and VI as starting materials. Thus, V and anisole under Friedel–Crafts conditions[12] produced two isomeric sulfones. The two isomers were separated through fractional crystallization from methanol and they differed by about 50° in their melting points. These two isomers are probably the [(*o*-methoxyphenylsulfonyl)-cyclopentadienyl]-manganese tricarbonyl and the corresponding *p*-isomer VIII and IX, respectively, but no chemical attempts have been made to assign the exact structure to them. However, a fairly reasonable idea as to the correct structure of the two isomers can be obtained from an investigation of their infrared spectra. Thus, the lower-melting (134-136°) isomer has a strong band at about 840 cm.$^{-1}$ and very weak absorption about 750 cm.$^{-1}$; on the other hand, the higher melting (184–186°) isomer has a very strong absorption at 756 cm.$^{-1}$ and a weak absorption at about 850 cm.$^{-1}$. Bellamy[14] points out that *o*-disubstituted aromatics absorb strongly in the range 770–735 cm.$^{-1}$ and 1,4-disubstituted aromatics absorb strongly in the range 860–800 cm.$^{-1}$, the latter showing no, or only weak, absorption in the 750–700 cm.$^{-1}$ region. This would indicate, therefore, that the lower melting material is the *p*-isomer, and the higher melting one the *o*-isomer.

Sulfinic acids have been reported[15] to add readily to quinones forming dihydroxyaryl sulfones. The sulfinic acid (VI) underwent this reaction smoothly to produce [(2,5-dihydroxyphenylsulfonyl)-cyclopentadienyl]-manganese tricarbonyl (X). The yield (71%) was reasonably good considering that technical grade *p*-benzoquinone was used in the

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[6] (a) J. Kozikowski, R. E. Maginn and M. Sizen-Klove, 134th Meeting of the A.C.S., Chicago, Ill., September, 1958; see also: (b) F. A. Cotton and J. R. Leto, *Chemistry & Industry*, 1368 (1958); (c) E. O. Fischer and K. Pleszke, *Ber.*, **91**, 2719 (1958); (d) R. Riemschneider and H.-G. Kassahn, *Z. Naturforsch.*, **14b**, 348 (1959).

[7] (a) V. Weinmayr, THIS JOURNAL, **77**, 3011 (1955), reports yields of about 55% of crude ferrocene disulfonic acid and about 72% of ferrocene monosulfonic acid calculated on the reacted material, with over 70% of the starting material having been recovered in the latter case. (b) A. N. Nesmeyanov, E. G. Perevalova and S. S. Churanov, *Doklady Akad. Nauk S.S.S.R.*, **114**, 335 (1957), report a yield of 62% of ferrocene monosulfonic acid calculated on the reacted material, over 55% of the starting material having been recovered in the reaction. (c) G. R. Knox and P. L. Pauson, *J. Chem. Soc.*, 692 (1958), using chlorosulfonic acids as the sulfonating agent, obtained a yield of 66% crude ferrocene monosulfonic acid dihydrate, calculated on unrecovered ferrocene.

[8] After this work was completed, Knox and Paulson, ref. 6c, reported the preparation of ferrocene sulfonyl chloride in 82% yield using phosphorus trichloride. These authors report that the use of phosphorus pentachloride or thionyl chloride with ferrocene monosulfonic acid causes extensive oxidative decomposition.

[9] Unpublished observation by these authors.

[10] M. Rosenblum, *Chemistry & Industry*, 52 (1957).

[11] P. L. Pauson, *Quart. Revs.*, **9**, 409 (1955).

[12] An excellent review article by A. N. Nesmeyanov and E. G. Perevalova [*Uspecki Khim.*, **27**, 3 (1958)] includes references to sulfones in the ferrocene series.

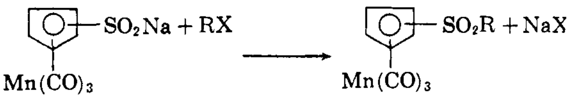
[13] C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 658 ff.

[14] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 66.

[15] V. Migrdichian, "Organic Syntheses," Vol. II, Reinhold Publishing Corp., New York, N. Y., 1957, p. 1712.

TABLE I

SULFONES FROM REACTION



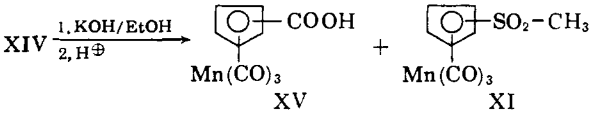
R–X	Reflux time, hr.	Sul-fone	Yield, %	M.p., °C.	Recrystn. solvent	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Manganese, % Calcd.	Manganese, % Found	Sulfur, % Calcd.	Sulfur, % Found
CH_3I	2	XI	97	156–158	B[a]	38.3	37.9	2.50	2.42	19.4	19.4	11.3	11.6
$ClCH_2[(CH_3)_3C]_2C_6H_2OH$[b]	20	XII	84	170–171	E[a]	56.8	56.8	5.63	5.66	11.3	11.3	6.6	6.6
CH_3COCH_2Cl[c]	2	XIII	75	123–124	B					16.9	16.9		
$BrCH_2COC_5H_4Mn(CO_3)$[d]	3	XIV	94	167–168	E/B	42.1	42.2	1.95	2.19	21.4	21.5	6.28	6.24

[a] B = benzene; E = ethanol. [b] 2,6-Di-*t*-butyl-α-chloro-*p*-cresol. [c] The 2,4-dinitrophenylhydrazone of sulfone IX formed very readily, m.p. 190–191° (from chloroform–methanol). *Anal.* Calcd. for $C_{17}H_{13}MnN_4O_9S$: C, 40.4; H, 2.57; Mn, 10.9. Found: C, 40.5; H, 2.60; Mn, 10.9. [d] The preparation of (bromoacetylcyclopentadienyl)-manganese tricarbonyl will be described by us elsewhere.

reaction. Furthermore, no attempt was made to improve the yield of this or any of the other reactions reported herein.

By treating alkyl or arylalkyl halides with the sodium salt[13] of VI, in refluxing ethanol for varied periods, we prepared four sulfones, XI, XII, XIII and XIV. The pertinent data are summarized in Table I.

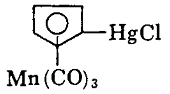
The sulfonyl ketone XIV proved to be a convenient intermediate for the preparation of (carboxycyclopentadienyl)-manganese tricarbonyl (XV) in good yield. The method involved in this preparation, represented by the equation did not offer,



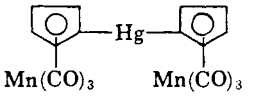
XV XI

however, any particular advantage over a different route[16] for the preparation of XV.

In our search for new ring-substituted cyclopentadienylmanganese tricarbonyl derivatives, we treated the sulfinic acid derivative VI with mercuric chloride[17] and obtained (chloromercuricyclopentadienyl)-manganese tricarbonyl (XVI) in good yield. When XVI was treated with *n*-butyllithium in an attempted transmetalation, the symmetrical (mercuridicyclopentadienylene) bis-(manganese tricarbonyl) (XVII) was isolated.



XVI



XVII

This result is analogous to that obtained by Rausch, Vogel and Rosenberg[18] who attempted to transmetalate chloromercuriferrocene with dispersed sodium and instead of the expected carboxylic acid, after carbonation, they isolated diferrocenylmercury. We used equimolar amounts of *n*-butyllithium and the chloromercuri derivative XVI and it appears possible that all the *n*-butyllithium, XVII might have reacted further to form the transmetalated product.[19]

This possibility as well as the direct mercuration of cyclopentadienyl-manganese tricarbonyl are presently under investigation.

Experimental[20]

(Sulfocyclopentadienyl)-manganese Tricarbonyl-*p*-toluidine Salt (IV).—To a suspension of cyclopentadienylmanganese tricarbonyl (306 g., 1.5 moles) in acetic anhydride (400 ml.) there was added dropwise over one hour with continuous stirring 100% sulfuric acid (220 g., 2.2 moles) keeping the temperature at 25–30°. As the addition of sulfuric acid proceeded, all the solid went into solution and the latter became very dark. Stirring was continued at room temperature for 2 hours after the addition was completed and then, after raising the temperature to 60°, for 1 hour at 55–60°.

The cooled mixture was poured over ice, allowed to stand for 1 hour and then filtered. A small amount (5 g.) of insoluble precipitate was collected which was shown by melting point and infrared spectrum to be the starting material I. The dark colored filtrate (2 l.) was mixed with a solution of *p*-toluidine (170 g.) in water (700 ml.) and concd. hydrochloric acid (150 ml.). A cream-colored precipitate formed instantaneously. This was filtered, washed with ice-water and air-dried to yield a solid (540 g., 93% yield) of m.p. 204–207°.

Recrystallization from absolute ethanol afforded the analytical sample, pale yellow needles, m.p. 209–210°.

Anal. Calcd. for $C_{16}H_{14}MnNO_6S$: C, 46.0; H, 3.60; Mn, 14.0; S, 8.22. Found: C, 46.4; H, 3.88; Mn, 13.7; S, 8.56.

In another experiment, under slighly different conditions, 32% of the starting material was recovered, and the yield of the *p*-toluidine sulfonate of I, calculated on reacted material, was quantitative.

To obtain the potassium sulfonate of I from IV, the latter was heated for a short time with an aqueous solution of potassium hydroxide, filtered, cooled and the filtrate saturated with potassium chloride. The potassium salt of III salted out as pale yellow plates.

Heating to 260° did not melt the crystals. Recrystallization from ethanol afforded the analytical sample.

Anal. Calcd. for $C_8H_4KMnO_6S$: C, 29.8; H, 1.21; Mn, 17.1; S, 9.94. Found: C, 29.8; H, 1.34; Mn, 16.9; S, 10.1.

(Chlorosulfonylcyclopentadienyl)-manganese Tricarbonyl (V).—A mixture of crude, dry *p*-toluidine sulfonate IV (70 g.) and phosphorus pentachloride (70 g.) was stirred vigorously for 10 minutes at room temperature; heat was evolved and a viscous liquid was formed. The mixture was then heated gently, with stirring, on the steam-bath for 45 minutes. After cooling, benzene (500 ml.) was added to the reaction mixture, stirred well and poured over ice, allowed to stand for 1 hour and filtered. The benzene layer was separated, washed once with water, mixed with anhydrous sodium sulfate and activated charcoal (Norit-A), allowed to stand for 30 minutes and filtered. The benzene solution was concentrated to a small volume, diluted with petroleum ether and the precipitate formed was filtered

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(16) J. Kozikowski and M. Cais, to be published.

(17) See ref. 15, Vol. I, p. 755.

(18) M. Rausch, M. Vogel and H. Rosenberg, *J. Org. Chem.*, **22**, 900 (1957).

(19) The transmetalation of organomercury compounds is generally carried out on the dialkyl- or diarylmercury derivatives; see for example ref. 15, Vol. I, p. 739.

(20) Melting points were taken in a capillary and are uncorrected.

off to collect 54 g. of yellow crystals (quantitative yield) m.p. 95–105°.

One recrystallization from carbon tetrachloride afforded the analytical sample, m.p. 112–113°.

Anal. Calcd. for $C_8H_4ClMnO_5S$: C, 31.7; H, 1.33; Mn, 18.1; S, 10.5. Found: C, 31.6; H, 1.38; Mn, 17.8; S, 10.7.

[(*p*-Tolysulfamoyl)-cyclopentadienyl]-manganese Tricarbonyl (VII).—The sulfonyl chloride derivative V (3 g.) and *p*-toluidine (3 g.) were mixed together and heated on steam-bath until a melt was formed. Ethanol (50 ml.) was then added, the mixture heated to reflux for 15 minutes, cooled, diluted with potassium hydroxide aqueous solution and filtered. The filtrate was acidified with hydrochloric acid and the precipitate formed collected by filtration; yield 2 g. of yellow powder, m.p. 197–199°. One crystallization from ethanol afforded yellow crystals, m.p. 199–201°.

Anal. Calcd. for $C_{15}H_{12}MnNO_5S$: C, 48.2; H, 3.27; Mn, 14.7; S, 8.6. Found: C, 48.5; H, 3.39; Mn, 14.5; S, 9.2.

(Sulfinocyclopentadienyl)-manganese tricarbonyl (VI).—The sulfonyl chloride V (12 g.), sodium sulfite (24 g.) and water (200 ml.) were stirred together for 2 hours at room temperature. The mixture was then filtered and the clear yellow solution acidified with 60% sulfuric acid (50 ml). Upon standing for 1 hour a yellow precipitate was formed which upon filtration yielded 9 g. (theoretical yield) of yellow crystals, m.p. 95–105°. If the filtered reaction mixture was not acidified but allowed to stand at room temperature for 16 hours, the sodium sulfinate crystallized out. One recrystallization of the sodium sulfinate from methanol afforded crystals with m.p. 213–215°.

Anal. Calcd. for $C_8H_4MnNaO_5S$: C, 33.1; H, 1.40; Mn, 18.9; S, 11.3. Found: C, 32.6; H, 1.66; Mn, 18.8; S, 11.3.

[(Methoxyphenylsulfonyl)-cyclopentadienyl]-manganese Tricarbonyls by Friedel–Crafts.—(Chlorosulfonyl-cyclopentadienyl)-manganese tricarbonyl (V, 3 g., 0.01 mole), anisole (7 g.), which also served as solvent, and aluminum chloride (3 g.) were refluxed together, with stirring, for 30 minutes. After cooling, the mixture was poured over ice and extracted with ether. The ether extract, after drying (sodium sulfate) was evaporated to dryness (water-pump vacuum and steam-bath heating). The brown residue was dissolved in hot methanol (50 ml.), boiled with Norit-A, filtered and the filtrate was concentrated on the steam-bath until the appearance of crystals. After cooling and filtering, 1 g. of yellow crystals was obtained, m.p. 130–152°, which after two more recrystallizations from methanol yielded 0.3 g., m.p. 186–188°.

Anal. Calcd. for $C_{15}H_{11}MnO_6S$: C, 48.1; H, 2.94; Mn, 14.7. Found: C, 48.3; H, 3.04; Mn, 14.9.

The methanol mother liquor from the original filtration was further concentrated and on cooling yielded 0.8 g. of yellow crystals, m.p. 120–132°. One recrystallization from benzene–petroleum ether afforded 0.5 g. of crystals, m.p. 134–136°.

Anal. Found: C, 48.1; H, 2.97; Mn, 14.8.

The infrared spectra of the two isomers were similar but not identical. The main differences occurred in the "finger print" region (above 900 cm.$^{-1}$), but some significant differences could be observed even at the lower frequencies. Both isomers exhibited the typical sulfone bands[21] in the 1100 and 1300 cm.$^{-1}$ regions.

[(2,5-Dihydroxyphenylsulfonyl)-cyclopentadienyl]-manganese Tricarbonyl (X).—(Sulfinocyclopentadienyl)-manganese tricarbonyl (3.5 g., 0.013 mole) in ethanol (50 ml.) was mixed with a solution of technical grade *p*-benzoquinone (1.5 g.) in ethanol (50 ml.). The mixture was heated for 10 minutes on the steam-bath, cooled and diluted with water (400 ml) containing a few drops of concd. hydrochloric acid. The brown precipitate formed was filtered off, dissolved in ether, boiled with Norit-A, filtered, the filtrate dried over sodium sulfate and diluted with petroleum ether; 2.5 g. of cream-colored precipitate, m.p. 197–199°. The mother liquor filtrate was evaporated and the residue after crystallization from benzene yielded 0.9 g. of crystals, m.p. 197–199°, thus bringing the total yield of material, m.p. 197–199°, to 70.5%. The analytical sample was obtained by one recrystallization from benzene and had m.p. 198–199°. The infrared spectrum of X in KBr pellet showed the two typical strong sulfone bands[21] in the 1100 and 1300 cm.$^{-1}$ regions.

Anal. Calcd. for $C_{14}H_9MnO_7S$: C, 44.7; H, 2.41; Mn, 14.6; S, 8.52. Found: C, 45.0; H, 2.50; Mn, 14.5; S, 8.72.

General Procedure for the Preparation of Sulfones Shown in Table I.—The sodium salt derivative of VI was dissolved in ethanol and refluxed with a slight excess of the alkyl or aralkyl halide. The cooled mixture was filtered to remove the sodium halide formed and the ethanolic filtrate concentrated on the steambath until crystals began to appear. After cooling, the crystals were collected and were generally of a high degree of purity. An additional crop of crystals could be obtained by diluting the ethanolic mother liquor with water. All the sulfones in Table I exhibited the typical sulfone bands in the infrared spectrum.[21]

(Chloromercuricyclopentadienyl)-manganese Tricarbonyl (XVI).—The sulfinic acid derivative VI (0.7 g., 0.0026 mole) dissolved in a mixture of ethanol (30 ml.) and water (20 ml.) was refluxed for 45 minutes with a solution of mercuric chloride (1.5 g., 0.0055 mole) in ethanol (10 ml.) and water (10 ml.). The solution was then filtered hot and part of the solvent was removed under vacuum (water-pump), until crystals began to appear. On cooling and filtering, 0.9 g. (79.5% yield) of yellow crystals, m.p. 135–136°, was obtained. One recrystallization from ethanol did not produce any change in the melting point.

Anal. Calcd. for $C_8H_4ClHgMnO_3$: C, 21.9; H, 0.92; Mn, 12.5. Found: C, 22.0; H, 1.04; Mn, 12.5.

Scaling up the experiment, under the same reaction conditions, produced slightly lower yields.

Attempted Transmetalation of (Chloromercuricyclopentadienyl)-manganese Tricarbonyl.—To an ether suspension of *n*-butyllithium[22] [prepared from 1.4 g. (0.01 mole) *n*-butyl bromide] was added with stirring, at 10–15°, (chloromercuricyclopentadienyl)-manganese tricarbonyl (4.3 g., 0.01 mole) and stirring continued at this temperature for 1 hour. The mixture was then poured over solid carbon dioxide, allowed to stand for 1 hour and filtered. The ether filtrate was washed once with water, dried over sodium sulfate and concentrated to a small volume, until crystals began to appear. On cooling and filtering, 1.5 g. of solid, m.p. 160–164°, was obtained. Two recrystallizations from benzene, or carbon tetrachloride, gave the analytical sample, m.p. 178–179°.

Anal. Calcd. for $C_{16}H_8HgMn_2O_6$: C, 31.6; H, 1.32; Mn, 18.1; Hg, 33.0. Found: C, 31.9; H, 1.67; Mn, 17.7; Hg, 32.2.

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(21) See ref. 14, p. 297.

(22) R. G. Jones and H. Gilman in "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 352.