ml round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with 1-ferrocenylstyrene (2.0 g, 0.007 mol), CHCl$_3$ (14 g, 0.12 mol), 50% NaOH solution (50 ml), CH$_2$Cl$_2$ (200 ml), and finally 1 g of TEBAC catalyst. The reaction mixture was stirred for *ca.* 5 hr, during which time a mild exotherm was noted. The reaction mixture was worked up as described previously and the crude product was chromatographed over alumina. Elution with Skelly B afforded 2.25 g of the cyclopropane, which was recrystallized from *n*-heptane to give 1.79 g (70%) of a red-orange solid melting at 124–125°. *Anal.* Calcd for C$_{19}$H$_{16}$FeCl$_2$: C, 61.50; H, 4.35; Cl, 19.11. Found: C, 61.53; H, 4.32; Cl, 18.97. Pmr (100 MHz, CDCl$_3$): δ 2.07 (d, 1 H) and 2.18 (d, 1 H) (*gem*-protons, J_{AB} = 7.5 Hz), 3.91 (s, 5 H, C$_5$H$_5$), 4.04 (m, 2 H) and 4.12 (m, 2 H) (C$_5$H$_4$), 7.44 (s, 5 H, C$_6$H$_5$).

1,1′-Bis(α-styryl)ferrocene.—A 500-ml three-necked flask equipped with a stirrer, a reflux condenser, an addition funnel, and a N$_2$ inlet was charged with triphenylmethylphosphonium iodide (33 g, 0.08 mol) and 200° ml of THF. A solution of *n*-butyllithium (40 ml, 2.1 *M* in hexane) was added and the mixture was stirred for *ca.* 10 min. A solution of 1,1′-dibenzoylferrocene[53] (15.6 g, 0.04 mol) in 100 ml of THF was added dropwise. Stirring was continued for 1 hr before hydrolyzing with water. The crude product was chromatographed over neutral alumina (Merck) using Skelly B as eluent: yield 4.0 g (25%) of a red-brown oil; pmr (60 MHz, CS$_2$) δ 3.95 (t, 4 H, J = 4 Hz), 4.05 (t, 4 H, J = 4 Hz, C$_5$H$_4$), 5.03 (d, 2 H, J_{AB} = 2.2 Hz), 5.32 (d, 2 H, J_{AB} = 2.2 Hz), 7.17 (m, 10 H). The base peak in the mass spectrum of 1,1′-bis(α-styryl)ferrocene is the parent ion at *m/e* 390.

1,1′-Bis(1-phenyl-2,2-dichlorocyclopropyl)ferrocene (6).—A 250-ml round-bottomed flask equipped with a stirring bar and a reflux condenser was charged with 1,1′-bis(α-styryl)ferrocene (1.5 g, 0.00384 mol), CH$_2$Cl$_2$ (40 ml), CHCl$_3$ (10 ml), 50% aqueous NaOH (20 ml), and finally 0.5 g of TEBAC catalyst. After stirring for *ca.* 5 hr, the reaction mixture was diluted with water and worked up as described previously. The crude product was chromatographed over Merck neutral alumina; elution with Skelly B, followed by recrystallization from *n*-heptane, afforded a yellow-orange solid (1.5 g, 71%). *Anal.* Calcd for C$_{28}$H$_{22}$FeCl$_4$: C, 60.47; H, 3.99. Found: C, 60.80; H, 4.05. The compound blackens at $\sim$145°, but is not a mobile liquid below 260°. Pmr (100 MHz, CS$_2$): δ 1.56 (d, 2 H) and 1.82 (d, 2 H) (cyclopropane protons, J_{AB} = 7.50 Hz), 3.52 (m), 3.62 (m), and 3.75 (m) (total 8 H, C$_5$H$_4$), and 7.29 (s, 10 H, C$_6$H$_5$).

Registry No.—**2,** 12085-73-3; **3,** 12087-46-6; **4,** 38856-04-1; **5,** 38856-05-2; **6,** 38856-06-3; **7,** 2415-80-7; **8,** 3591-42-2; **9,** 3141-42-2; **10,** 33044-82-5; 2-ferrocenylpropene, 31725-14-1; 2-ferrocenyl-2-propanol, 12093-87-7; ferrocenylbenzyl ketone, 1277-72-1; ferrocene, 102-54-5; 1-ferrocenyl-2-phenylethanol, 12094-28-9; *trans*-2-ferrocenylstyrene, 1272-54-4; 1-ferrocenylstyrene, 35126-64-8; ferrocenophenone, 1272-44-2; 1,1′-bis(α-styryl)ferrocene, 38856-13-2; 1,1′-dibenzoylferrocene, 12180-80-2.

Acknowledgment.—We would like to thank the Caltech President's Fund, NASA Contract NAS 7-100, and the Air Force Office of Scientific Research, Grant 73-2424.

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[53] M. Rausch, M. Vogel, and H. Rosenburg, *J. Org. Chem.*, **22**, 903 (1957).

Organometallic Derivatives of Cymantrene. The Formation of (Fulvalene)hexacarbonyldimanganese[1]

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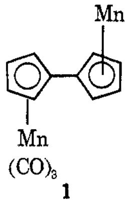
Cymantrene (**2**) has been found to undergo facile mercuration by reaction with mercuric acetate in the presence of perchloric acid. Chloromercuricymantrene (**3**) has been converted into a variety of organomanganese derivatives, including cymantrenylmagnesium iodide (**8**), cymantrenyllithium (**10**), cymantrenylferrocene (**6**), and (fulvalene)hexacarbonyldimanganese (**1**). Complex **1** undergoes Friedel–Crafts acetylation to produce (3-acetylfulvalene)hexacarbonyldimanganese (**11**).

A recent communication by us[2] reported the synthesis and properties of (fulvalene)hexacarbonyldimanganese (**1**), one of the first examples in which fulvalene serves as the sole π ligand in an organo transition metal complex.[3] We now wish to describe in detail the preparation of a number of novel organometallic derivatives of cymantrene (**2**), their utilization as intermediates in the synthesis of **1**, and the results of preliminary studies regarding the reactivity of **1** toward electrophilic substitution.[4]



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During the course of our studies in cymantrene chemistry it became necessary for us to prepare substantial quantities of the monochloromercuri derivative (**3**). We were unable in several attempts to reproduce the original direct mercuration procedure described for cymantrene (**2**),[8] but were successful in reproducing a four-step procedure described by Cais.[9] The latter method was tedious, however, and resulted in low overall yields of product (24% yield of **3** starting

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[1] Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 9–13, 1968, Abstracts INOR-088.

[2] M. D. Rausch, R. F. Kovar, and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **91**, 1259 (1969).

[3] For another example of a fulvalene–transition metal π complex, see F. L. Hedberg and H. Rosenberg, *J. Amer. Chem. Soc.*, **91**, 1258 (1969); see also ref 2.

[4] After our program in this area had been completed,[1] the isolation of **1** from (a) the halogenation of triphenylphosphinegoldcymantrene;[5] (b) the reaction of cymantreneboronic acid with copper acetate;[6] and (c) the coupling of cymantrenylmagnesium iodide (**8**) with cobalt(II) chloride[7] was independently reported.

[5] A. N. Nesmeyanov, K. I. Gandberg, and T. V. Baukova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2032 (1969).

[6] A. N. Nesmeyanov, V. A. Sazonova, and N. N. Sedlova, *Dokl. Akad. Nauk SSSR*, **194**, 825 (1970).

[7] H. Egger and A. Nikiforov, *Monatsh. Chem.*, **100**, 1069 (1969).

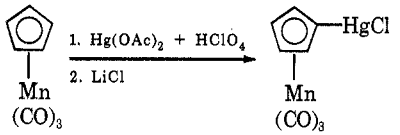
[8] A. N. Nesmeyanov, K. N. Anisimov, and E. P. Valueva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1683 (1962).

[9] N. Cais and J. Kozikowski, *J. Amer. Chem. Soc.*, **82**, 5667 (1960).

from 2). An investigation was therefore begun to develop a more convenient and reliable synthetic route to **3**.

Results and Discussion

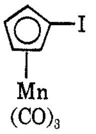
Cymantrene (**2**) was found to undergo facile reaction with mercuric acetate *in the presence of perchloric acid.*[10] Treatment of the resulting acetoxymercuri derivative with lithium chloride produced chloromercuricymantrene (**3**) in 53% yield. The marked effect of perchloric acid in promoting the mercuration reaction was illustrated by treating **2** with mercuric acetate in the absence of catalyst. Analysis of the reaction mixture by thin layer chromatography indicated the presence of only trace amounts of mercurated product.



2 **3**

A purification procedure was devised which facilitated step-by-step removal of the by-products and unreacted starting material from the crude reaction product. Thus, washing the methylene chloride solution of the crude product with water removed the inorganic salts present, while extraction of the residue from that solution with benzene and subsequent filtration through a dry column of Florisil removed polymercuration products. Evaporation of the benzene eluent and extraction of the residue with hexane removed substantial amounts of unreacted **2**. Finally, recrystallization of the residue from methylene chloride–hexane afforded a pure crystalline product which was identical with **3** prepared by the method of Cais.[9] Small amounts of a polymercurated product were obtained by eluting the Florisil column with acetone. The material appeared to be bis(chloromercuri)cymantrene, but attempts at characterization were not completely successful.

Chloromercuricymantrene (**3**) reacted with iodine in methylene chloride solution to form a dark soluble complex. Iodocymantrene (**4**) was obtained in 84% yield by shaking a solution of the complex with aqueous sodium thiosulfate and by chromatographing the crude product on a dry column of Florisil. Attempts to prepare bromocymantrene by treatment of **3** with either bromine or N-bromosuccinimide resulted in decomposition of **3** and evolution of carbon monoxide.



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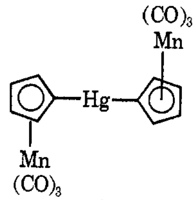

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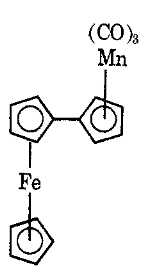

6

Dicymantrenylmercury (**5**) was prepared according to the procedure reported by Nesmeyanov, *et al.*,[8] by treatment of **3** with aqueous sodium thiosulfate, the yield being nearly quantitative. The physical properties of recrystallized material compared favorably with those reported by Cais.[9] An ir spectrum of **5** was virtually identical with that obtained for **3**, exhibiting absorptions due to the terminal carbonyl groups at 2010 and 1900 cm^{-1}.

Our initial attempts to extend the Ullmann biaryl reaction to iodocymantrene (**4**) were unsuccessful. Reaction of **4** with activated copper bronze[11] yielded cymantrene (**2**) as the only product. Modification of the procedure by the use of copper–(Zn) powder,[12] however, afforded (fulvalene)hexacarbonyldimanganese (**1**) in 21% yield. The product was separated from a large amount of hydrogenated product cymantrene (**2**) by dry column chromatography on Florisil. The first band to be eluted contained **2** as identified by its ir spectrum. Further elution of the column yielded a second band which afforded the desired product (**1**). The nmr spectrum of **1** exhibited an A_2B_2 pattern, with two sets of triplets centered at τ 5.04 (four α protons) and 5.26 (four β protons). The α protons were deshielded with respect to cymantrene, while the β protons were virtually unaffected. Thus, a cymantrenyl group exerts a deshielding effect in **1** similar to that observed for a ferrocenyl group in biferrocene.[11] The ir spectrum exhibited strong absorptions at 2000 and 1925 cm^{-1} assigned to the terminal carbonyl substituents.

Attempts to prepare the unsymmetrical product cymantrenylferrocene (**6**) by a mixed Ullmann reaction of **4** with iodoferrocene were unsuccessful, the products being largely biferrocene and **2**, together with small amounts of **1**.

(Fulvalene)hexacarbonyldimanganese (**1**) was also formed in 67% yield when **5** was heated at 265° in the presence of silver powder. The temperature of the reaction was found to be a critical factor in determining the yield of product obtained. Thus, when the pyrolysis was run at 230°, cymantrene (**2**) was the only product obtained. This result is in agreement with an earlier finding that the yield of biferrocene obtained from the pyrolysis of diferrocenylmercury in the presence of silver varies greatly with the reaction temperature.[13]

Pyrolysis of a mixture of diferrocenylmercury (**7**) and dicymantrenylmercury (**5**) in the presence of silver powder yielded a substantial amount (39%) of the mixed product, cymantrenylferrocene (**6**), together with the symmetrical coupling products biferrocene and **1**.

Shechter and Helling prepared the ferrocenyl Grignard reagent by the reaction of a mixture of ethylene bromide and bromoferrocene with powdered magnesium in tetrahydrofuran solution.[14] This reaction has now been successfully extended to the cymantrene system, the cymantrenyl Grignard reagent (**8**) being formed in moderate yield. Treatment of a mixture of ethylene bromide and iodocymantrene (**4**) (2:1 molar ratio) with powdered magnesium in tetrahydrofuran solution produced a dark reaction mixture. Carbonation of the solution thus formed and subsequent

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[10] A. J. Kresg, M. Dubeck, and H. C. Brown, *J. Org. Chem.*, **32**, 745, 752, 756 (1967).

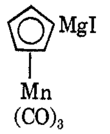
[11] M. D. Rausch, *J. Org. Chem.*, **26**, 1802 (1961).

[12] L. Fieser and M. Fieser, "Advanced Organic Chemistry," Chapman and Hall, London, 1963, p 785.

[13] M. D. Rausch, *Inorg. Chem.*, **1**, 414 (1962).

[14] H. Shechter and J. T. Helling, *J. Org. Chem.*, **26**, 1034 (1961).

hydrolysis afforded cymantrenecarboxylic acid (**9**) in 32% yield. The physical properties of the purified product are in good agreement with properties described for **9** prepared by an alternate procedure.[15,16] A subsequent reaction of **8** with cobalt(II) chloride also produced **1** in 51% yield.



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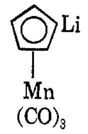

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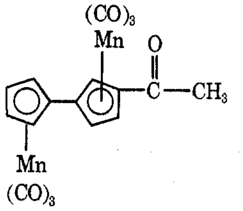

11

Since earlier attempts to prepare cymantrenyllithium (**10**) had been reported to be unsuccessful,[9] we decided to investigate alternate routes to this potentially useful intermediate. The report by Rausch that treatment of diferrocenylmercury (**7**) with an excess of *n*-butyllithium produced lithioferrocene in high yield[13] prompted us to attempt an extension of this exchange reaction to the cymantrene system. Both chloromercuricymantrene (**3**) and dicymantrenylmercury (**5**) were found to undergo transmetalation with *n*-butyllithium to produce cymantrenyllithium (**10**). Thus, treatment of either **3** or **5** with *n*-butyllithium in ethyl ether–benzene solution and subsequent carbonation of the reaction mixture afforded cymantrenecarboxylic acid (**9**) in yields of 40 and 44% respectively. Furthermore, reaction of **10** prepared from either **3** or **5** with cobalt(II) chloride produced **1** in yields of 13 and 16%, respectively.

Since substitution reactions of **1** followed by oxidation of the $Mn(CO)_3$ groups could conceivably lead to a general route to substituted fulvalenes, it was of interest to determine the relative reactivity of **1** in a typical electrophilic substitution reaction.

Attempted acetylation of **1** in carbon disulfide solution using equimolar amounts of acetyl chloride and aluminum chloride yielded starting material and no products of acetylation. These results indicate a lower reactivity of **1** toward electrophilic substitution as compared to cymantrene (**2**), since the latter compound reacts readily under the above conditions.[17] A reaction of **1** in methylene chloride solution with 2 equiv each of acetyl chloride and aluminum chloride, however, afforded (3-acetylfulvalene)hexacarbonyldimanganese (**11**) in 43% yield. The structural assignment of the product as the 3-acetyl isomer (**11**) was made chiefly on the basis of its proton nmr spectrum, which exhibits a doubly deshielded single proton resonance at τ 4.30 (both the acetyl[18] and cymantrenyl[19] groups are known to be deshielding with regard to adjacent protons on a cyclopentadienyl ring). A very small amount of an apparently diacetylated product was also isolated from the reaction, and its structure is presently under investigation.

Experimental Section

Ir spectra were recorded on a Beckman IR-10 spectrophotometer and were calibrated using polystyrene. Nmr spectra were recorded on a Varian A-60 spectrometer using $CDCl_3$ as the solvent and TMS and an internal standard. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. Column chromatography was carried out using CAMAG activity I alumina or Florisil (purchased from Fisher Scientific Co.).

Direct Mercuration of Cymantrene (2).—A 500-ml one-necked flask was equipped for magnetic stirring, and a 250-ml addition funnel was attached. A solution of cymantrene (38.6 g, 0.189 mol) dissolved in 100 ml of methylene chloride was added to the flask. Meanwhile, mercuric acetate (20.1 g, 0.063 mol) and 200 ml of methanol were added to a 500-ml erlenmeyer flask equipped for magnetic stirring. Perchloric acid was added dropwise until the white suspension dissolved (a large excess should be avoided). The mercurating reagent thus formed was then added dropwise to the stirring solution of cymantrene. When the addition was complete, a solution containing 5.4 g (0.126 mol) of lithium chloride dissolved in 25 ml of methanol was added, followed by 100 ml of methylene chloride. The contents of the flask were transferred to a 500-ml separatory funnel, and the solution was washed with two 100-ml portions of water to remove perchlorate salts. The organic layer was filtered and dried over anhydrous sodium sulfate. Evaporation of the solvent to dryness yielded yellow crystals. The residue was extracted with three 100-ml portions of boiling benzene, and the cooled extracts were filtered through a 1 in. × 6 in. column of Florisil. Evaporation of the eluent to dryness yielded a light yellow solid. Unreacted cymantrene (22 g) was removed from the residue by extraction with three 100-ml portions of boiling hexane. The pale yellow product which remained was recrystallized from methylene chloride–heptane to yield 14.6 g (53%) of chloromercuricymantrene (**3**) as yellow needles, mp 132–133° (lit.[9] mp 135–136°). An ir spectrum of this material and **3** prepared by Cais' procedure were identical.

Further elution of the Florisil column with acetone yielded small amounts of what appeared to be bis(chloromercuri)-cymantrene. The crude material was converted by reaction with iodine into an iodinated derivative. Analysis of this product by gas chromatography indicated the presence of two components in approximately equal amounts, possibly 1,2- and 1,3-diiodocymantrene.

Preparation of Iodocymantrene (4).—To a stirred solution containing 10.0 g (23 mmol) of chloromercuricymantrene (**3**) dissolved in a minimum amount of methylene chloride was added a saturated solution of iodine in methylene chloride. Addition was continued until the initially fading purple color persisted. The contents of the flask were transferred to a 250-ml separatory funnel shaken vigorously with two 100-ml portions of sodium thiosulfate solution, and then washed with two 100-ml portions of water. The organic layer was filtered through a 1 in. × 6 in. column of Florisil and the eluent was evaporated to dryness. The residual oil was dissolved in hexane and filtered through a 1 in. × 6 in. column of Florisil. Evaporation of the eluent to dryness yielded 6.4 g (84%) of iodocymantrene as a light yellow oil which solidified upon cooling. The mp was 33–34° (lit.[8] mp 33–34°). An nmr spectrum exhibited a triplet at τ 4.95 (two α protons) and a triplet at 5.28 (two β protons).

Preparation of Dicymantrenylmercury (5).—Chloromercuricymantrene (5.0 g, 11 mmol) was added as a solid to a 250-ml flask containing 200 ml of saturated sodium thiosulfate solution. The resulting mixture was stirred for 5 hr, after which time the suspension was filtered, washed with water, and dried at 100°. Recrystallization of the product from methylene chloride–heptane afforded 3.4 g (99%) of dicymantrenylmercury as yellow platelets, mp 174–175° (lit.[9] mp 174.5–175.5°).

Preparation of (Fulvalene)hexacarbonyldimanganese (1) *via* Ullmann Coupling of Iodocymantrene (4).—To a 6-in. test tube equipped with nitrogen inlet and outlet tubes were added 5.0 g of copper–(Zn) powder[12] and 1.0 g (3 mmol) of iodocymantrene. The tube was thoroughly purged with nitrogen and then immersed in an oil bath maintained at 110° for 24 hr. Subsequently, the contents of the tube were extracted repeatedly with methylene chloride until the extracts were colorless. The combined ex-

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[15] R. Riemschneider and K. Pelzoldt, *Z. Naturforsch. B*, **16**, 627 (1960).

[16] Cymantrenylmagnesium iodide (**8**) has also been used successfully in this laboratory in the synthesis of cymantrenyldiphenylphosphine: G. J. Reilly and W. E. McEwen, *Tetrahedron Lett.*, 1231 (1968).

[17] F. A. Cotton and J. R. Leto, *Chem. Ind.* (*London*), 1368 (1958).

[18] M. D. Rausch and V. Mark, *J. Org. Chem.*, **28**, 3225 (1963).

[19] R. F. Kovar, Ph.D. Thesis, University of Massachusetts, 1969.

tracts were evaporated to dryness, and the remaining residue was chromatographed on a 0.5 in. × 6 in. column of dry-packed Florisil. Elution of the column with hexane produced 0.32 g of cymantrene (2) after evaporation of the solvent. Further elution with benzene and subsequent evaporation of the solvent produced 0.13 g (22% yield) of (fulvalene)hexacarbonyldimanganese (1). Recrystallization of the product from methylene chloride–heptane afforded yellow platelets, mp 145–146°.

Anal. Calcd for $C_{16}H_8Mn_2O_6$: C, 47.32; H, 1.99; Mn, 27.06; O, 23.64; mol wt, 406. Found: C, 47.24; H, 2.02; Mn, 27.23; O, 23.59. mol wt 403 (osmometric in benzene), 406 (mass spectrometry).

Attempted Ullmann Coupling of Iodocymantrene (4) with Iodoferrocene.—A 6-in. test tube equipped with nitrogen inlet and outlet tubes was purged with nitrogen. To this tube were added 5.0 g of copper–(Zn) powder, 0.5 g (1.5 mmol) of iodocymantrene, and 2.0 g (6.4 mmol) of iodoferrocene. The tube was again flushed with nitrogen and was then immersed in an oil bath maintained at 130° for 24 hr. The residue was extracted with methylene chloride until the extracts were colorless, and the combined extracts were evaporated to dryness. Thin layer chromatography of the reaction product showed that complete conversion of iodoferrocene into biferrocene had occurred, along with the formation of cymantrene (2) and a very small amount of (fulvalene)hexacarbonyldimanganese (1). There was no evidence for the presence of the mixed product cymantrenylferrocene (6).

Formation of Cymantrenylmagnesium Iodide (8).—A 100-ml three-necked flask was equipped with a nitrogen inlet tube, addition funnel, and magnetic stirrer. Powdered magnesium (4.0 g, 0.16 g-atom) was added, and the flask was thoroughly flamed and purged with nitrogen. Anhydrous tetrahydrofuran (25 ml) was added, followed by several drops of ethylene bromide to activate the magnesium. A solution of 2.0 g (6 mmol) of freshly chromatographed iodocymantrene and 2.3 g (12 mmol) of ethylene bromide dissolved in 10 ml of tetrahydrofuran was added dropwise over a period of 1 hr, the temperature being maintained at 25°. The reaction was then stirred for an additional 1 hr, at which time Dry Ice was added. The contents of the flask were evaporated to dryness *in vacuo*, and the resulting residue was extracted with three 50-ml portions of water. The combined aqueous extracts were filtered and the filtrate was acidified with phosphoric acid. The precipitate which formed was extracted into ether. The ether extracts were dried over anhydrous sodium sulfate and evaporated to dryness, yielding 0.47 g (32%) of cymantrenecarboxylic acid (9). Recrystallization of the products from methylene chloride–heptane produced yellow platelets, mp 195–197° (lit.[15] mp 187–197°). A mixture melting point with an authentic sample of 9 was undepressed and the ir spectra of both compounds were identical.

Reaction of Cymantrenylmagnesium Iodide (8) with Cobalt(II) Chloride.—A solution of cymantrenylmagnesium iodide (6 mmol) was prepared according to the above procedure. To the Grignard reagent, cooled to −20°, was added 7.8 g (60 mmol) of anhydrous cobalt(II) chloride, and the resulting mixture was stirred for 8 hr. The solvent was then evaporated and the residue chromatographed on a 1 in. × 6 in. column of Florisil. Elution of the column with hexane produced 0.9 g of cymantrene. Further elution of the column with benzene produced, after evaporation of the solvent, 0.61 g (51%) of (fulvalene)hexacarbonyldimanganese (1). Recrystallization of the product from methylene chloride–heptane afforded crystals of mp 145–146°. An ir spectrum of the product was identical with that obtained for 1 synthesized by the Ullmann reaction.

Formation of Cymantrenyllithium (10).—A 250-ml three-necked flask equipped with stirrer, nitrogen inlet tube, syringe cap, and addition funnel was thoroughly flamed and purged with nitrogen. Then 1.0 g (1.6 mmol) of dicymantrenylmercury (5) was added, followed by 100 ml of a 3:1 ethyl ether–benzene mixture. The solution was stirred under nitrogen for 15 min and than 4.7 ml (10 mmol) of *n*-butyllithium was added. The solution immediately darkened and became homogeneous. After the solution had been allowed to stir for an additional 30 min, 100 g of Dry Ice was added. The solution was then extracted with two 50-ml portions of dilute potassium hydroxide solution. The combined extracts were acidified with phosphoric acid, and the precipitate which formed was filtered and dried in air, producing 0.32 g (40%) of cymantrenecarboxylic acid (9). Recrystallization of the product from methylene chloride–heptane yielded yellow platelets, mp 194–196° (lit.[15] 187–197°). A mixture melting point with an authentic sample was undepressed and the ir spectra of both compounds were identical.

Reaction of Chloromercuricymantrene (3) with *n*-Butyllithium.—To a stirred solution of chloromercuricymantrene (1.0 g, 2 mmol) dissolved in a 1:1 mixture of benzene–ethyl ether under nitrogen was added 2.0 ml (4 mmol) of *n*-butyllithium in hexane. After the reaction had been allowed to stir for 15 min, solid carbon dioxide was added and the solvent evaporated to dryness. The residue which remained was extracted with two 50-ml portions of water, and the combined aqueous extracts were filtered. The filtrate was acidified with phosphoric acid, and the resulting precipitate was extracted into ethyl ether. The ether extracts were dried over anhydrous sodium sulfate, and the solvent was evaporated to give 0.22 g (44%) of cymantrenecarboxylic acid (9). The product was recrystallized from methylene chloride–heptane, affording crystals of mp 195–197° (lit.[15] mp 187–197°). A mixture melting point with an authentic sample of 9 was undepressed.

Reaction of Cymantrenyllithium (10) with Cobalt(II) Chloride A. Prepared from Dicymantrenylmercury (5).—A solution of cymantrenyllithium (4 mmol) in 3:1 benzene–ethyl ether was prepared from dicymantrenylmercury according to the above procedure. To this solution, cooled to −20°, were added 5.2 g (40 mmol) of cobalt(II) chloride and 20 ml of anhydrous tetrahydrofuran. The reaction mixture was allowed to warm to room temperature and was then stirred for an additional 8 hr. The solution was concentrated to dryness *in vacuo* and the residue which remained worked up in a manner similar to the procedure described previously, producing 0.11 g (14%) of (fulvalene)hexacarbonyldimanganese (1), mp 146–147°. An ir spectrum was identical with that obtained for a sample of 1 prepared by the Ullmann method.

B. Prepared from Chloromercuricymantrene (3).—A solution of cymantrenyllithium (2 mmol) in 3:1 benzene–ethyl ether was prepared from chloromercuricymantrene according to the procedure previously described. To this solution, cooled to −20°, were added 2.6 g (20 mmol) of cobalt(II) chloride and 20 ml of anhydrous tetrahydrofuran. The reaction mixture was allowed to warm to room temperature and was then stirred for an additional 8 hr. Work-up as described above produced 0.07 g (17%) of (fulvalene)hexacarbonyldimanganese (1), mp 146–147°.

Pyrolysis of Dicymantrenylmercury (5) and Silver Powder.—An intimate mixture of 1.0 g (1.65 mmol) of dicymantrenylmercury and 6.0 g (0.05 g-atom) of silver powder[20] was added to a 1 in. × 8 in. test tube equipped with nitrogen inlet and outlet tubes. The system was flushed with nitrogen and then immersed in bath of Wood's metal maintained at 265°. After 15 hr, the reaction mixture was extracted repeatedly with methylene chloride until the extracts were colorless, and the combined extracts were concentrated to dryness. The residue which remained was chromatographed on a 1 in. × 6 in. column of Florisil. Elution of the column with hexane produced a small initial band containing 63 mg of cymantrene (2). Further elution with benzene and subsequent evaporation of the solvent afforded 0.45 g (67%) of (fulvalene)hexacarbonyldimanganese (1), mp 146–147°. A mixture melting point with a sample of 1 prepared by the Ullmann method was undepressed, and the ir spectra of both compounds were identical.

Preparation of Cymantrenylferrocene (6).—A 1 in. × 8 in. test tube equipped with nitrogen inlet and outlet tubes was thoroughly flushed with nitrogen and an intimate mixture of 1.7 g (2 mmol) of dicymantrenylmercury, 1.2 g (2 mmol) of diferrocenylmercury, and 5.0 g (0.04 g-atom) of silver powder[14] was added. The tube was then flushed with nitrogen and immersed in a bath of Wood's metal maintained at 265°. After 15 hr, the contents of the tube was extracted repeatedly with methylene chloride until the extracts were colorless; the combined extracts were concentrated to dryness. Chromatography of the residue on a 1 in. × 6 in. dry column of Florisil (elution with 6:1 hexane–benzene) produced three bands.

Band I upon evaporation of the solvent yielded 430 mg of biferrocene, identified by its ir spectrum. Band II produced 300 mg (39%) of cymantrenylferrocene (6). Several recrystallization of the product from heptane afforded orange platelets, mp 89–91°.

Anal. Calcd for $C_{18}H_{13}MnFeO_3$: C, 55.71; H, 3.38. Found: C, 55.61; H, 3.38.

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[20] G. Brauer, "Handbuch der Praparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, 1954, p 766.

An ir spectrum (KBr) exhibited absorptions at 3110 (w), 2000 (s), 1925 (s), 1100 (w), 1100 (m), 1030 (m), 840–880 (m, br), 690 (w), 660 (s), and 635 cm^{-1} (s). An nmr spectrum exhibited a multiplet at τ 5.03 (two α protons on cymantrene ring), a multiplet at 5.24 (two β protons on cymantrene ring), a multiplet at 5.60 (two α protons on ferrocene ring), a multiplet at 5.70 (two β protons on ferrocene ring), and a singlet at 5.87 (five protons on unsubstituted ferrocene ring).

Elution of band III and subsequent evaporation of the solvent afforded 640 mg of (fulvalene)hexacarbonyldimanganese (**1**), identified by its ir spectrum.

Acetylation of (Fulvalene)hexacarbonyldimanganese (1).—A 100-ml three-necked flask was equipped with a magnetic stirrer, condenser, and a nitrogen inlet tube. To this flask was added 0.5 g (1.2 mmol) of (fulvalene)hexacarbonyldimanganese dissolved in 25 ml of dry methylene chloride, followed by 0.16 g (2.5 mmol) of acetyl chloride and 0.33 g (2.5 mmol) of aluminum chloride. The solution was heated to reflux under nitrogen for 30 min after which time it was poured over 50 g of ice. The organic layer was separated, dried over calcium chloride, and evaporated to dryness. The remaining residue was then subjected to preparative tlc (elution with methylene chloride). Development of the plate yielded three major bands.

Extraction of band I (highest R_f) from the plate and subsequent evaporation of the solvent yielded 0.12 g of unreacted **1**, mp 146–147°. Band II was extracted from the plate and the solvent evaporated *in vacuo*. Sublimation of the residue which remained at 120° (0.01 mm) produced 0.24 g (43%) of (3-acetylfulvalene)-hexacarbonyldimanganese (**11**), mp 116.0–116.5°, as yellow platelets.

Anal. Calcd for $C_{18}H_{10}Mn_2O_7$: C, 48.25; H, 2.25. Found: C, 48.27; H, 2.44.

An ir spectrum (KBr) exhibited absorptions at 2020 (sh), 2000 (s), 1965 (s), 1935 (s), 1915 (s), 1680 (m), 1460 (w), 1425 (w), 1365 (w), 1240 (w), and 620 cm^{-1} (s). An nmr spectrum exhibited a multiplet at τ 4.30 (one proton α to both the acetyl group and the ring junction), a multiplet at 4.50 (one proton α to acetyl group and β to ring junction), a multiplet at 4.92 (three protons; one proton β to acetyl group and α to bridging carbon plus two protons α to bridging carbon), a multiplet at 5.16 (two protons β to bridging carbon), and a singlet at 7.64 (three protons of the acetyl group).

Band III yielded a product tentatively identified as an additional acetylation product of **1**. An ir spectrum of the product (KBr) exhibited strong absorptions at 2020, 1970, and 1680 cm^{-1}.

Registry No.—**1,** 31988-02-0; **2,** 12079-65-1; **3,** 12203-10-0; **4,** 12079-63-9; **5,** 12216-27-2; **6,** 37048-11-6; **7,** 1274-09-5; **8,** 38855-99-1; **10,** 38856-00-7; **11,** 38856-01-8; cobalt(II) chloride, 7646-79-9.

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Semiempirical Calculations on the Ring Opening of Substituted Cyclopropanones

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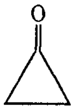
We report the results of INDO and MINDO calculations on the ring openings of cyclopropanone and some of its derivatives and compare the semiempirical results for the parent compound with the *ab initio* results reported earlier. Both semiempirical methods indicate that the substituted cyclopropanones open more readily than the parent compound, but the actual numerical values are not accurate. The major shortcoming of the semiempirical methods is that one never knows when to believe their predictions.

A large number of successful applications of the INDO and MINDO methods have been reported.[2–5] However, in a semiempirical approach the parameters are either not sufficiently flexible or not sufficiently accurate, and examples are bound to exist where these methods fail. It has already been reported that the ring opening of cyclopropanone **1** to singlet oxyallyl **2** is such a case.[6] The INDO method predicts a value in excess of 200 kcal/mol, which is certainly too large.[6,7] The MINDO method has been reported to yield a more reasonable value, 78 kcal/mol, for the isomerization.[5] However, as we shall see, this method also fails in several substituted cases, predicting that the corresponding oxyallyls are considerably more stable. An extended Hückel study on the parent system also predicts oxyallyl to be more stable than cyclopropanone,[8] a result now known to be incorrect.[9,10]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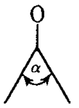

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An *ab initio* study indicates that singlet oxyallyl is 83 kcal/mol less stable than the closed ketone.[7] Because it does not include correlation, this value is probably too high.

Even allowing for some decrease, the energy difference between **1** and **2** is likely to remain large; yet, in contrast to the parent compound, some derivatives of **1** undergo reactions best explained in terms of an oxyallyl intermediate.[11–16] Concerted reactions need not pass

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