

picrate melted at 140–142° after recrystallization from ethanol. The literature¹¹ reports a melting point of 149°.

Anal. Calcd. for C₁₆H₁₆N₆O₉: C, 44.05; H, 3.67. Found: C, 44.11; H, 3.91.

The methiodide after recrystallization from a mixture of ethanol and ethyl acetate melted at 197–198°. The literature¹² reports a melting point of 198°. A mixture with

- (11) G. M. Bennett and G. H. Willis, *J. Chem. Soc.*, 256 (1929).
 (12) E. Stedman, *ibid.*, 1902 (1927).

an authentic sample melted at 197–198°. The infrared spectra of the two methiodides were identical in Nujol.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, CALIF.]

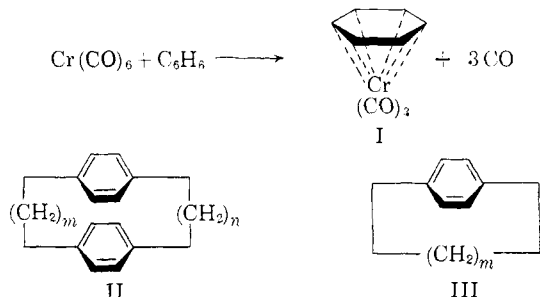
Macro Rings. XXIII. Carbonylchromium Complexes of Paracyclophanes and Model Compounds¹

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Tricarbonylchromium complexes of the paracyclophanes and model open-chain compounds have been prepared. With the [*m.n*]paracyclophanes, only mono-complexes formed when *m* and *n* ≤ 4. Bis-complexes were prepared with difficulty from cycles with *m* = 4, *n* = 5, and *m* = *n* = 6. Complexes of the smaller cycles possessed abnormal ultraviolet absorption spectra compared to either spectra of the larger cyclic, or of open-chain model organometallic compounds. Attempts to convert [4.4]paracyclophane tricarbonylchromium to [4.4]paracyclophanechromium with the metal between the two benzene rings failed.

The description of a general method² for the synthesis of tricarbonylchromium complexes of aromatic hydrocarbons³ (e.g., I) provided a new tool for the study of transannular effects in the paracyclophanes⁴ (II and III). Points of interest in such a study are as follows. (1) Compounds



that possess structure II might complex with either one or two moles of tricarbonylchromium. If the lower homologs of II formed mono-complexes and the higher bis-complexes, this might be taken as evidence for transannular electronic interactions between the two rings in the former substances. (2) Differences in spectral properties of the complexes of II might correlate with changes in the distances between the two benzene rings as the values of *m* and *n* change. (3) Possibly mono-complexes of II could be induced to lose three moles of carbon monoxide to form an organometallic compound with chromium between the two rings and bound directly to each. In these studies, complexes of hydrocarbons such as III and open-chain analogs of II served as models.

Twenty-one different paracyclophanes were used in this study, and their preparations have been described in previous papers in this series.⁵ All of these hydrocarbons formed mono-tricarbonylchromium complexes when heated with hexacarbonylchromium in diethylene glycol dimethyl ether. The names of the compounds employed, and the analytical and physical data pertaining to their complexes are reported in Table I. All of the open-chain model compounds listed in Table I gave mono-complexes. A mixture of complexes which could not be separated was obtained with 1,4-bis-(4-ethylphenyl)-butane. Only two bis-complexes, those of [4.5]- and [6.6]paracyclophane, were obtained, and then in poor yield. Variation in the relative amounts of hexacarbonylchromium employed and changes in solvent did not seem to affect the relative amounts of mono- and bis-complexes formed from [6.6]paracyclophane.

Discussion

Clearly the mono-complexes with structure IV show little inclination to react with hexacarbonylchromium, particularly those homologs in which *m* and *n* are 4 or less. This fact suggests that the electron-withdrawing character of the tricarbonylchromium group² exerts its influence both on the aromatic ring to which it is directly bonded, and on the second aromatic nucleus. Thus the two benzene rings of the [*m.n*]paracyclophanes have to be able to get as far apart as in the [4.5]- or [6.6]-homologs before the two rings can behave as independent units, and form bis-complexes (V). This effect is similar to that observed in the one-to-one complexes formed between the [*m.n*]-

(1) This work was sponsored by the Office of Ordnance Research, U. S. Army.

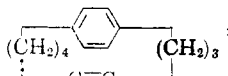
(2) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

(3) (a) E. O. Fischer and K. Ofele, *Angew. Chem.*, **69**, 715 (1957); (b) E. O. Fischer and K. Ofele, *Chem. Ber.*, **90**, 2532 (1957); (c) E. O. Fischer, *et al.*, *Z. Naturforschung*, **13b**, 458 (1958); (d) G. Natta, R. Ercoli and F. Calderazzo, *Chim. e ind.*, **40**, 287 (1958).

(4) D. J. Cram, *Rec. Chem. Prog.*, **30**, 71 (1959).

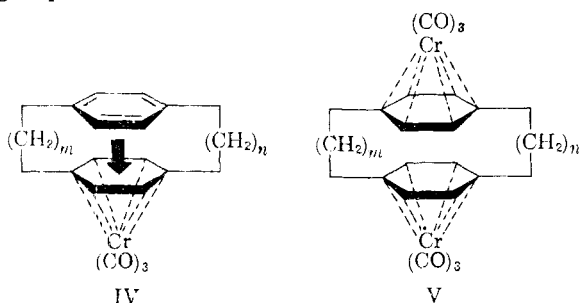
(5) (a) D. J. Cram and H. Steinberg, *THIS JOURNAL*, **73**, 5691 (1951); (b) D. J. Cram and N. L. Allinger, *ibid.*, **76**, 726 (1954); (c) N. L. Allinger and D. J. Cram, *ibid.*, **76**, 2362 (1954); (d) D. J. Cram and H. U. Daeniker, *ibid.*, **76**, 2743 (1954); (e) J. Abell and D. J. Cram, *ibid.*, **76**, 4406 (1954); (f) D. J. Cram, N. L. Allinger and H. Steinberg, *ibid.*, **76**, 8132 (1954); (g) D. J. Cram and M. F. Antar, *ibid.*, **80**, 3103 (1958); (h) D. J. Cram and M. F. Antar, *ibid.*, **80**, 3109 (1958); (i) D. J. Cram and K. Dewhirst, *ibid.*, **81**, 5963 (1959).

TABLE I
 ANALYTICAL DATA AND PHYSICAL PROPERTIES TRICARBONYLCHROMIUM COMPLEXES OF THE PARACYCLOPHANES

[<i>m, n</i>]Paracyclophane carbonylchromium ^a		Mol. formula	Carbon, %		Hydrogen, %		M.p., °C.	Yield, %	Ultra- violet spectra ^b λ _{max} , mμ	ε	Recrystn. solvent	
<i>m</i>	<i>n</i>		Calcd. C	Found C	Calcd. H	Found H						
2	2	5a	C ₁₉ H ₁₉ CrO ₃	66.28	66.53	4.65	4.71	253-255	71	343	10,900	Benz. ^d -pent. ^e
2	3	5a	C ₂₀ H ₁₃ CrO ₃	66.61	65.95	5.03	5.23	125 dec.	50	337	10,800	Benz.-pent.
3	4	5c	C ₂₂ H ₂₂ CrO ₃	68.39	68.17	5.69	5.80	148 dec.	50	324	11,000	Benz.-pent.
4	4	5b	C ₂₃ H ₂₄ CrO ₃	69.00	68.97	6.00	5.94	240 dec.	80	319	11,000	Benz.-hex. ^f
4	5	5c	C ₂₄ H ₂₆ CrO ₃	69.57	69.81	6.28	6.14	129-130	87	319	10,500	Pent.
4	5 bis ^g	5c	C ₂₇ H ₂₆ Cr ₂ O ₆	58.91	58.86	4.73	4.76	275 dec.	4	322	22,250	Benz.-pent.
4	6	5e	C ₂₅ H ₂₈ CrO ₃	70.08	69.89	6.52	6.71	117-118	74	319	10,300	Pent.
5	5	5c	C ₂₅ H ₂₈ CrO ₃	70.08	70.13	6.52	6.59	148-149	16	Pent.
5	6	5e	C ₂₄ H ₂₆ CrO ₃	70.59	70.36	6.83	6.80	136-137	4	Pent.
6	6	5e	C ₂₇ H ₃₂ CrO ₃	71.06	71.31	7.02	7.02	117-118	68	319	10,500	Pent.
6	6 bis ^g	5e	C ₃₀ H ₃₂ Cr ₂ O ₆	60.81	60.58	5.40	5.34	290 dec.	4	320	21,250	Benz.-pent.
1	8	5e	C ₂₄ H ₂₆ CrO ₃	69.57	69.63	6.28	6.32	145-146	53	324	11,100	Is.eth. ^h -pent.
1	9	5g	C ₂₅ H ₂₈ CrO ₃	70.06	69.83	6.54	6.64	166-171	57	322	11,800	Is.eth.-pent.
1	10	5g	C ₂₆ H ₃₀ CrO ₃	70.59	70.48	6.79	6.66	135-136	69	Pent.
1	11	5g	C ₂₇ H ₃₂ CrO ₃	71.05	70.67	7.02	7.25	138-142	52	Pent.
1	12	5g	C ₂₈ H ₃₄ CrO ₃	71.49	71.46	7.23	7.14	129-131	46	320	9,400	Pent.
[<i>m</i>]Paracyclophane <i>m</i>		Ref. no. ^c										
9	5h		C ₁₄ H ₂₂ CrO ₃	63.90	64.27	6.51	6.69	121 dec.	51	323	11,000	Benz.-pent.
10	5d		C ₁₉ H ₁₄ CrO ₃	64.77	64.81	6.82	6.83	149-151	32	320	8,000	Benz.-pent.
12	5f		C ₂₁ H ₂₆ CrO ₃	66.31	66.45	7.37	7.53	133 dec.	22	320	8,200	Pent.
Hydrocarbon carbonylchromium												
Diphenylmethane			C ₁₆ H ₁₆ CrO ₃	63.15	63.24	3.95	4.00	97-98	31	318	10,000	Pent.
1,1-Diphenylethane			C ₁₇ H ₁₇ CrO ₃	64.15	63.76	4.40	4.27	70-71	23	318	10,650	Pent.
1,3-Diphenylpropane			C ₁₈ H ₁₈ CrO ₃	65.06	64.86	4.82	4.66	75	33	Pent.
1,4-Diphenylbutane			C ₂₀ H ₁₈ CrO ₃	65.89	66.00	5.20	5.24	52	28	317	10,700	Pent.
[2.2.2]Paracyclophane ^d			C ₂₇ H ₂₄ CrO ₃	72.32	72.38	5.36	5.50	167 dec.	73	321	10,300	Benz.-pent.
			C ₁₈ H ₁₈ CrO ₃	64.67	64.83	5.39	5.86	152-154 dec.	12	321	10,600	Pent.

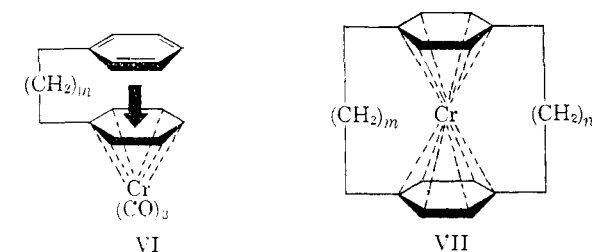
^a *m* and *n* stand for the numbers of methylene groups in the bridges. One Cr(CO)₃ group is complexed with each hydrocarbon molecule unless otherwise specified. ^b Taken in chloroform. ^c References to articles mentioned in text which describe the preparation of the parent hydrocarbons. ^d Benzene. ^e Pentane. ^f Hexane. ^g Bis-tricarbonylchromium complexes. ^h Isopropyl ether. ⁱ Preparation reported in ref. 5i. ^j Preparation reported in ref. 5h.

paracyclophanes and the π-acid, tetracyanoethylene.⁶ Similarly, the smaller cycles underwent only mono-acylation in the Friedel-Crafts reaction under conditions which the larger cycles underwent di-acylation.⁷ These results taken together provide strong evidence for transannular electron release of one benzene to the second when the second is bound to an electron-withdrawing group.



The formation of only mono-complexes (VI) between tricarbonylchromium and diphenylmeth-

ane, 1,3-diphenylpropane and 1,4-diphenylbutane suggests that the uncomplexed ring folds back to some extent over the bound ring to provide some



intramolecular π-electron interaction. The different behavior of 1,4-bis-(4-ethylphenyl)-butane indicates that the two ethyl groups provide some steric barrier to such a configuration, and the two benzene rings to some extent behave as independent π-electron systems.

The distance between the two benzenes in dibenzenechromium are estimated to be less than 3.4 Å.⁸ Calculations with normal bond angles and distances indicate that the distance between the benzene rings in [4.4]paracyclophane can be as great as 3.7 Å.^{5f} Yet under a variety of condi-

(i) D. J. Cram and R. H. Bauer, *THIS JOURNAL*, **81**, 5971 (1959).
 (7) (a) D. J. Cram and J. Abell, *ibid.*, **77**, 1179 (1955); (b) D. J. Cram and R. W. Kierstead, *ibid.*, **77**, 1186 (1955); (c) D. J. Cram and N. L. Allinger, *ibid.*, **77**, 6289 (1955).

(8) E. Weiss and E. O. Fischer, *Z. anorg. Chem.*, **286**, 142 (1956).

tions, the mono-complex of the [4.4]- and [6.6]-cycles failed to eliminate carbon monoxide to give compounds of structure VII. Such a reaction would involve rotation of the complexed benzene ring through 180° about the axis of the bonds extending from its 1,4-position. Such rotation is possible in [4.4]paracyclophane itself,⁹ but the additional bulk of a chromium atom attached to one face of the benzene ring would provide considerable steric resistance to such a rotation in the [4.4]-system, and possibly even in the [6.6]-cycle.

Ultraviolet absorption spectral data for the complexes are recorded in Table I. These spectra exhibit a single λ_{\max} in the region from 317 to 343 m μ . The open-chain compounds absorb at the shortest wave lengths (317-318), the larger paracyclophanes ($m = 12$, $m = n = 4$ and larger) at slightly longer, and the smaller paracyclophanes at the longest wave lengths. In general, the smaller the values of m and n , the greater the bathochromic shift, which reaches a maximum when $m = n = 2$. This effect is attributed to transannular electronic interactions as well as to distortions of the benzene rings from their normally planar configurations.

The infrared spectra of a few of the complexes were examined. Mono-complexes exhibit strong bands at 1876-1881 and 1963-1967 cm.⁻¹, and a weak band at 2900 cm.⁻¹ (chloroform solution), and an additional strong band at 1842-1856 cm.⁻¹ (potassium bromide disk). Bis-complexes have similar spectra, with an additional weak band at 3400 cm.⁻¹ (potassium bromide disk).

Experimental

General Procedure for Preparation of Paracyclophane and Model Tricarbonylchromium Complexes.—The hydrocarbon (0.001 mole) was dissolved in purified diethylene glycol dimethyl ether (10 ml.) and hexacarbonylchromium (0.0011 mole) was added. The solution was held at reflux for 3 hr. (bath temperature, 170-175°). Reagent

(9) D. J. Cram, R. J. Wechter and R. W. Kierstead, *THIS JOURNAL*, **80**, 3126 (1958).

which sublimed into the condenser was returned periodically to the solution with a glass rod. The solution was cooled, diluted with an equal volume of water, and filtered. The complex was separated from inorganic chromium by extraction of the solid with methylene chloride. In many cases filtration was not convenient, and the mixture was extracted several times with methylene chloride. The extract was evaporated under reduced pressure, and finally dried as a film on a rotatory drier at 0.05 mm. and 40-50° to remove diethylene glycol dimethyl ether.

The crude complex was dissolved in benzene or pentane-ether (3 to 1) and chromatographed on neutral, activity I alumina. Elution of the column with the same solvent removed first unchanged hydrocarbon, and then the mono-complex. In the two cases in which bis-complexes were formed, these were eluted with benzene-methanol (10 to 1). The complexes were recrystallized from the solvents indicated in Table I as rapidly as possible, and were stored at 0° or lower.

Use of 2 to 1 molar ratios of hexacarbonylchromium to hydrocarbon did not affect the character of product or yield to any extent. With [2.2.2]paracyclophane, a 4 to 1 molar ratio was used, but only the mono-complex could be isolated.

Pyrolysis of Paracyclophane Tricarbonylchromium Complexes.—The tricarbonylchromium complex of [4.4]paracyclophane (0.088 g.) was heated under nitrogen to 300° for 5 minutes and cooled. Chromatography on alumina of the residue yielded 0.024 g. of [4.4]paracyclophane, m.p. 145-146°, undepressed by admixture with an authentic sample. No other product was isolated. When heated to 180° under nitrogen for 5 minutes, the complex underwent no change and was recovered.

The tricarbonylchromium complex of [6.6]paracyclophane (0.040 g.) was heated to 180° under nitrogen for 5 minutes, cooled, and the residue was recrystallized from pentane to give 0.034 g. of starting material, m.p. 117-118°, undepressed by admixture with an authentic sample. Similar pyrolyses of other complexes gave back either starting material or the parent hydrocarbon.

Attempted Decarbonylations of [4.4]Paracyclophane Tricarbonylchromium Complexes.—(a) A solution of 0.055 g. of complex and 0.050 g. of triphenylphosphine in 20 ml. of benzene was heated at reflux for 4 hours. The cooled solution was chromatographed on alumina to give 0.020 g. of unchanged complex and 0.010 g. of [4.4]paracyclophane.

(b) A mixture of complex (0.120 g.) and aluminum trichloride (0.039 g.) in 1 ml. of methylene chloride was cooled at 0° for 10 minutes. Ice was added to the solution, the layers were separated, and the aqueous extract was washed with methylene chloride. From the organic phase was isolated 0.018 g. of starting complex and 0.035 g. of [4.4]paracyclophane.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

Carbenes from Alkyl Halides and Organolithium Compounds. I. Synthesis of Chlorocyclopropanes¹

BY GERHARD L. CLOSS AND LISELLOTE E. CLOSS

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Alkylolithium compounds react with methylene chloride in the presence of olefins to form chlorocyclopropanes. This reaction is believed to proceed through the intermediate chlorocarbene. Seven alkyl-substituted chlorocyclopropanes have been prepared by this method. Configurations are assigned to the products by considerations of predictable non-bonded interactions in the transition states of the addition of chlorocarbene to the olefins. The configurations are confirmed by n.m.r. spectra.

Introduction

The chemistry of dihalocarbenes (dihalomethylenes) has been rather intensively investigated over the past decade. After Hine² demonstrated by kinetic methods that the alkaline hydrolysis of

(1) Reported in part in a preliminary communication to the editor, G. L. Closs and L. E. Closs, *THIS JOURNAL*, **81**, 4996 (1959).

(2) J. Hine, *ibid.*, **72**, 2438 (1950).

chloroform proceeds through dichloromethylene, many more reactions have been reported in which this intermediate has been postulated. Thus the reaction of haloforms with potassium *t*-butoxide leads to the formation of these divalent carbon species³ as does the decarbalkoxylation of alkyl

(3) W. v. E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6182 (1954).