675. *Cycloheptatriene- and Tropylium-Metal Complexes. Part II.*[1] *The Rearrangement to Benzene Complexes.*

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Sodio-cyclopentadiene or -diethyl malonate causes ring contraction of tricarbonyltropyliumchromium (and molybdenum) salts, giving tricarbonylbenzenechromium. By substitution with tritium and methyl it is shown that the benzene ring is derived entirely from the cycloheptatrienyl ring by extrusion of a carbon atom. The formation of intermediate addition products is demonstrated and a tentative mechanism for the ring contraction is proposed.

As we have reported briefly elsewhere,[2] reaction of tricarbonyltropyliumchromium perchlorate (I) with an excess of cyclopentadienide ion does not follow the " normal " mode established for a variety of other anions in the preceding paper,[1] but affords tricarbonylbenzenechromium (II). The molybdenum analogue behaves similarly. The reaction may be represented formally as:

$$\underset{\text{(I)}}{[C_7H_7Cr(CO)_3]^+ClO_4^-} + C_5H_5^-Na^+ \longrightarrow \underset{\text{(II)}}{C_6H_6Cr(CO)_3} + C_6H_6 + NaClO_4 \quad . \quad . \quad . \quad (1)$$

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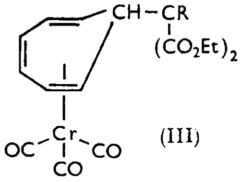
[1] Part I, preceding paper.

[2] Munro and Pauson, *Proc. Chem. Soc.*, 1959, 267.

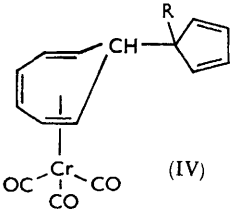
This equation shows that two C_6 fragments may be generated. It was therefore considered necessary to establish whether the benzene ring attached to chromium in the product was derived entirely from the seven-membered ring or in part from the cyclopentadiene ring. A decision in favour of the former view was reached qualitatively by repeating the reaction first with methylcyclopentadienylsodium, whereupon the benzene derivative (II) was again the only chromium complex isolated; then, with tricarbonylmethyltropylium chromium,[1] tricarbonyltoluenechromium was obtained. The conclusion was corroborated more quantitatively by labelling the tropylium complex (I) with tritium and showing that the derived product (II) contained the expected proportion of tritium. Tritium-labelled tricarbonylcycloheptatrienechromium required for this purpose was readily prepared by the Wilzbach technique.[3] As in other examples of this method and notwithstanding the fact that the unsaturated system in our compound is a complex with a metal atom, we observed that the replacement by tritium of the olefinic protons far exceeded replacement of the methylene hydrogen atoms.

The same ring-contraction was again observed when the tropylium complex (I) was treated with an excess of diethyl sodiomalonate. The simultaneous isolation of tricarbonyl-7-di(ethoxycarbonyl)methylcycloheptatrienechromium (III; R = H) suggested that the " normal " anion addition [1] is an intermediate step in these rearrangements. This was confirmed by showing that the ester (III; R = H) is transformed into the benzene complex (II) by the further action of sodiomalonate or other bases such as sodium methoxide. The corresponding intermediate (IV) in the cyclopentadienide reaction was readily isolated when an excess of the tropylium complex (I) was used and was similarly transformed into tricarbonylbenzenechromium (II) by methoxide ion. This complex (IV) had a wide melting range and must be assumed to be a mixture of stereo- (and/or position) isomers. A non-crystalline but otherwise closely similar product (IV) was prepared from cyclopentadienylcycloheptatriene [4] and chromium hexacarbonyl. That the methylmalonate complex (III; R = Me) fails to rearrange indicates that ionisation of the acidic hydrogen (R in III and IV) induced by the basic catalyst is an essential step in the ring contraction. It is for this reason that the t-butylcyclopentadienyl derivative obtained previously [1,2] without ring-contraction is now tentatively formulated as (IV; R = Bu^t).

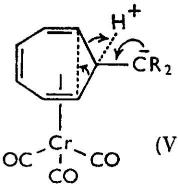
The above observations lead us to propose that the electronic shifts indicated in (V) represent a possible mechanistic picture for this ring-contraction. On this basis the " C_6H_6 " fragment in reaction (1) would be fulvene, and diethyl methylenemalonate would result similarly from (III; R = H). Neither of these products has been isolated, nor indeed would they be expected to survive the reaction conditions, but attempts are in progress to find a case where the corresponding product may be isolated.



(III)



(IV)



(V)

That formulation (V) is at best a first approximation to the actual mechanism is evident since it neglects the function of the tricarbonylchromium grouping. Its importance to the reaction is, however, evident as cyclopentadienylheptatriene is unaffected by sodium methoxide under the conditions employed for rearrangement of

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[3] Wilzbach, *J. Amer. Chem. Soc.*, 1957, **79**, 1013.

[4] Vol'pin, Kursanov, Shemyakin, Maimind, and Neyman, *Chem. and Ind.*, 1958, **1261**.

its complex (IV). In this connection we also treated tricarbonyltropyliumchromium perchlorate (I) with silver oxide and with aqueous hydrogen peroxide under the conditions under which these reagents convert the free tropylium ion into benzaldehyde [5] and benzene [6,7] respectively. However, only the same metal-free products were isolated and it is not known whether ring-contraction preceded or followed cleavage of the hydrocarbon fragment from the metal.

EXPERIMENTAL

For general remarks see Part I (preceding paper).

Reaction of Tricarbonyltropyliumchromium Perchlorate (I) *with an Excess of Cyclopentadienide.*—(*a*) Tricarbonyltropyliumchromium perchlorate (2·80 g., 0·0086 mole), suspended in tetrahydrofuran (50 ml.), was added to sodium cyclopentadienide prepared in the same solvent [from sodium wire (0·5 g., 0·022 mole) and cyclopentadiene (7 ml.)]. The mixture was stirred at room temperature overnight. Removal of solvent *in vacuo*, extraction with ether, evaporation, and sublimation at 50°/0·01 mm. of the residue afforded yellow needles of tricarbonylbenzenechromium (0·86 g., 46%), m. p. 162—163° (lit.,[8] m. p. 161·5—163°) [Found: C, 50·4; H, 2·6; O, 21·8%; *M* (cryoscopic in benzene), 215. Calc. for $C_9H_6CrO_3$: C, 50·5; H, 2·8; O, 22·4%; *M*, 214]. Identity was established by mixed m. p. determination and infrared comparison with an authentic sample.

(*b*) Butyl-lithium (0·006 mole) was prepared from butyl bromide (0·82 g., 0·006 mole) and lithium (0·07 g., 0·01 g.-atom) in light petroleum (10 ml.) at room temperature. Cyclopentadiene (3 ml.) was added dropwise and the mixture stirred at room temperature for 2 hr. Tricarbonyltropyliumchromium perchlorate (1 g., 0·0031 mole) in tetrahydrofuran (30 ml.) was then added and the mixture stirred overnight at room temperature. The solvent was removed *in vacuo* and the residue extracted with ligroin. Evaporation of the ligroin extract gave yellow needles of tricarbonylbenzenechromium (0·204 g., 31%), m. p. 162—163°, identified by mixed m. p. and infrared comparison with an authentic specimen.

Reaction of Tricarbonyltropyliummolybdenum Perchlorate with an Excess of Sodium Cyclopentadienide.—Tricarbonyltropyliummolybdenum perchlorate (2·2 g., 0·006 mole) was treated with sodium cyclopentadienide as described under (*a*) above. The solvent was removed under reduced pressure and the residue extracted with ligroin (2 × 100 ml.). Evaporation of the extract *in vacuo* and rapid recrystallisation of the residue from ligroin gave yellow crystals (0·21 g., 14%), m. p. 118—124° (decomp.) (lit.,[9] m. p. 120—125°), identified as tricarbonylbenzenemolybdenum by mixed m. p. and infrared comparison.

Reaction of Tricarbonyltropyliumchromium Perchlorate with an Excess of Sodium Methylcyclopentadienide.—Sodium methylcyclopentadienide (0·006 mole) was prepared by stirring sodium wire (0·14 g., 0·006 g.-atom) and methylcyclopentadiene (0·5 g., 0·006 mole) in tetrahydrofuran (30 ml.) for 3 hr. at room temperature. Tricarbonyltropyliumchromium perchlorate (1 g., 0·0031 mole) was added and the mixture stirred overnight. The solvent was then distilled *in vacuo* and the brown residue extracted with ligroin. Evaporation of the extract to dryness gave yellow crystals of tricarbonylbenzenechromium (0·286 g., 44%), m. p. and mixed m. p. 162—163°.

Reaction of Tricarbonylmethyltropyliumchromium Perchlorate with an Excess of Sodium Cyclopentadienide.—An excess of sodium cyclopentadienide [from cyclopentadiene (2 ml.) and sodium wire (0·2 g., 0·0087 g.-atom)] in tetrahydrofuran (40 ml.) was added at room temperature to a suspension of tricarbonylmethyltropyliumchromium perchlorate [1] (0·8 g., 0·00236 mole) in tetrahydrofuran (30 ml.), and the mixture stirred overnight. After removal of solvent under reduced pressure, the residue was extracted with ligroin. Evaporation of the extract and recrystallisation from the same solvent yielded tricarbonyltoluenechromium (0·28 g., 52%) as bright yellow needles, m. p. and mixed m. p. 81—82° (lit.,[8] m. p. 80—81°) (Found: C, 52·7; H, 3·7. Calc. for $C_{10}H_8CrO_3$: C, 52·7; H, 3·5%).

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[5] Doering and Knox, *J. Amer. Chem. Soc.*, 1957, **79**, 354.
[6] Vol'pin and Kursanov, *Doklady Akad. Nauk S.S.S.R.*, 1959, **126**, 780.
[7] Vol'pin, Kursanov, and Dulova, *Tetrahedron*, 1960, **8**, 33.
[8] Jackson, Nicholls, and Whiting, *J.*, 1960, 469.
[9] Fischer, Öfele, Essler, Fröhlich, Mortenson, and Semmlinger, *Z. Naturforsch.*, 1958, **13b**, 458.

Ring Contraction of Tritium-labelled Tropylium Complex (I).—(a) *Labelling of tricarbonylcycloheptatrienechromium.* In an apparatus similar to that described by Rydberg and Hanngren,[10] tricarbonylcycloheptatrienechromium (0·1 g.) was exposed to tritium (1 c) for 8 days. The labelled sample was diluted with inactive material (4 g.) and purified to constant count by subjecting it, in turn, seven times to chromatography on alumina, vacuum-sublimation, and recrystallisation from ligroin, benzene, or ether.

(b) *Assay* (method of Banks *et al.*[11]). The samples to be assayed (10 mg.) were rendered electrical conductors by grinding them with an equal weight of graphite in an agate mortar. In the case of the perchlorate, mixing and gentle pressing on filter paper had to be employed to avoid explosion. The mixture was pressed on a recessed nickel planchet with the end of a cylindrical metal rod. The activity was recorded in counts per minute (c.p.m.) as the average of six counts taken on this planchet in a windowless, flow-type Geiger counter with argon–methane as the carrier gas.

(c) *Reactions.* By the methods described above, tritium-labelled tricarbonylcycloheptatrienechromium (1·27 g.; 1080 c.p.m.) afforded active tricarbonyltropyliumchromium perchlorate (1·8 g.) which reached constant count (728 c.p.m.) after three crystallisations from acetone (Calc. count, equivalent labelling of all protons: 660 c.p.m.; calc. count, no labelling of methylene protons: 754 c.p.m.). This salt (1 g.) with an excess of cyclopentadienylsodium afforded tricarbonylbenzenechromium (0·288 g., 43%) which reached its constant count (980 c.p.m.) after four cycles of purification by sublimation, chromatography, and recrystallisation. This count is well within the expected limits of error (5%) of the value (952 c.p.m.) calculated on the assumption that the benzene residue is derived entirely from the tropylium group.

Reaction of Tricarbonyltropyliumchromium Perchlorate with Diethyl Sodiomalonate.—Diethyl malonate (1·28 g., 0·008 mole) was added to sodium ethoxide (0·006 mole) [from sodium (0·138 g., 0·006 g.-atom) and ethyl alcohol (5 ml.)] and the mixture stirred for 30 min. Tetrahydrofuran (20 ml.) and the perchlorate (I) (1·5 g., 0·0046 mole) were then added and the mixture was stirred overnight. The solvent was distilled off *in vacuo* and the red residue extracted with ligroin. Evaporation of the extract to dryness yielded red crystals (0·81 g.), which were chromatographed on neutralised alumina (90 g.) to give two major bands, with traces of two others. Elution with ligroin gave a trace of a red solid and also yellow needles of tricarbonylbenzenechromium (0·236 g., 24%), m. p. 162—163°, identified by mixed m. p. and infrared comparison with an authentic specimen. Ligroin–benzene (1 : 1) eluted *tricarbonyl(diethoxycarbonylmethylcycloheptatriene)chromium* (III; R = H) (0·552 g., 31%), crystallising from ligroin as orange-red plates, m. p. 122—123°, soluble in the common organic solvents (Found: C, 51·8; H, 4·8. $C_{17}H_{18}CrO_7$ requires C, 52·8; H, 4·7%).

Elution with benzene gave a small amount of a green gum (11 mg.), which had no infrared absorption in the carbonyl region and was not examined further.

Rearrangement of Tricarbonyl(diethoxycarbonylmethylcycloheptatriene)chromium (III; R = H).—(*a*) Tricarbonyl(diethoxycarbonylmethylcycloheptatriene)chromium (0·181 g., 0·00047 mole) and diethyl sodiomalonate (0·0033 mole) [from sodium metal (0·076 g., 0·0033 g.-atom) in ethanol (15 ml.) and diethyl malonate (1 g., 0·0062 mole)] were allowed to react at room temperature overnight. The solvent was then distilled *in vacuo* and the orange residue extracted with ligroin. Chromatography of the extract on alumina (50 g.) and elution with ligroin gave tricarbonylbenzenechromium (38 mg., 38%), m. p. 162—163°, identified by mixed m. p. and infrared comparison. Elution with benzene gave unchanged tricarbonyl(diethoxycarbonylmethylcycloheptatriene)chromium (7 mg.) as red plates, m. p. and mixed m. p. 122—123°.

(*b*) In a similar experiment, the malonate complex (III; R = H) (0·2 g.) was treated with sodium methoxide (from 0·2 g. of sodium and 10 ml. of methanol) and afforded tricarbonylbenzenechromium (47 mg., 42%).

Attempted Rearrangement of Tricarbonyl-7-[1,1-*di*(*ethoxycarbonyl*)*ethyl*]*cycloheptatrienechromium* (III; R = Me) *with Diethyl Sodiomalonate.*—The methylmalonyl complex [1] (III; R = Me) (0·4 g.) was recovered unchanged (0·375 g., 94%) when subjected to the reaction conditions (*a*) of the preceding experiment. No tricarbonylbenzenechromium was detected on chromatography.

Reaction of Sodium Cyclopentadienide with an Excess of Tricarbonyltropyliumchromium

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[10] Rydberg and Hanngren, *Acta Chem. Scand.*, 1958, **12**, 322.

[11] Banks, Crawhall, and Smyth, *Biochem. J.*, 1956, **64**, 411.

Perchlorate.—Sodium cyclopentadienide (0·2 mole) was prepared from sodium wire (4·6 g., 0·2 g.-atom) and cyclopentadiene (13·2 g., 0·2 mole) in tetrahydrofuran (100 ml.), and a portion (1·2 ml., *ca.* 0·002 mole) added to a suspension of the perchlorate (I) (1 g., 0·0031 mole) in tetrahydrofuran (25 ml.). The mixture was stirred at room temperature overnight. Filtration, followed by evaporation, yielded a red gum (0·33 g.), which was chromatographed in ligroin–benzene (9 : 1) on alumina (100 g.). Elution with the same solvents gave tricarbonylbenzenechromium (8 mg.), m. p. and mixed m. p. 162—163°, and an orange-red gum (0·27 g., 46%), which crystallised with difficulty from ligroin–ether, then having m. p. 108—114° (decomp.). This product is presumably a mixture of isomers of *tricarbonylcyclopentadienylcycloheptatrienechromium* (IV; R = H) (Found: C, 61·3; H, 4·2. $C_{15}H_{12}CrO_3$ requires C, 61·6; H, 4·1%).

Elution with ligroin–benzene (1 : 1) gave an orange gum (66 mg.) which failed to crystallise. The infrared spectrum showed a strong resemblance to that of the compound, m. p. 108—114° (decomp.).

Reaction of Cyclopentadienylcycloheptatriene with Chromium Hexacarbonyl.—Cyclopentadienylcycloheptatriene [4] (4·05 g., 0·026 mole) and chromium hexacarbonyl (6 g., 0·027 mole) were heated in refluxing ligroin (b. p. 100—120°; 30 ml.) for 12 hr. The solvent was then removed *in vacuo* and the residue chromatographed in ligroin–benzene (9 : 1) on alumina (100 g.). Elution with the same solvents gave a red gum (0·54 g., 7·1%), which was further purified by chromatography on alumina. The infrared spectrum was identical with that of tricarbonylcyclopentadienylcycloheptatrienechromium, m. p. 108—114° (decomp.), described in the preceding experiment. Elution with benzene yielded a second red gum (31 mg.), with strong absorption at 1980 and 1896 cm.$^{-1}$ in the metal–carbonyl stretching region (CCl_4 solution).

Reaction of Tricarbonylcyclopentadienylcycloheptatrienechromium (IV; R = H) *with Sodium Methoxide.*—Sodium methoxide (0·01 mole) and tricarbonylcyclopentadienylcycloheptatrienechromium (200 mg., 0·00068 mole) [prepared from the tropylium complex (I)] in tetrahydrofuran (25 ml.) were stirred at room temperature for 12 hr. The solvent was then removed under reduced pressure and the residue extracted with ligroin. Chromatography on alumina (15 g.) and elution with ligroin gave tricarbonylbenzenechromium (36 mg., 24%) identified as before.

Attempted Rearrangement of Cyclopentadienylcycloheptatriene with Sodium Methoxide.—Cyclopentadienylcycloheptatriene [4] (1·56 g., 0·01 mole) was added to a solution of sodium methoxide [from sodium (2·3 g., 0·1 g.-atom) and methanol (50 ml.)] and stirred for 48 hr. at room temperature. Water (100 ml.) was then added and the mixture extracted with ether. No benzene was detected on vapour-phase chromatography of the washed and dried (Na_2SO_4) ether extract. Evaporation of the solvent and infrared comparison of the residue (1·43 g.) with starting material showed that the product was unchanged.

Oxidation of Tricarbonyltropyliumchromium Perchlorate by Silver Oxide.—The perchlorate (0·65 g., 0·002 mole) in water (180 ml.) was stirred with silver oxide (0·7 g., 0·003 mole) overnight. The mixture was then extracted with ether, and the extract washed with water, dried ($MgSO_4$), and evaporated. Benzaldehyde was obtained (0·14 g., 67%) [2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 236—237°; infrared comparison (Found: C, 54·6; H, 3·5; N, 19·5. Calc. for $C_{13}H_{10}N_4O_4$: C, 54·5; H, 3·5; N, 19·6%)].

Reaction of Tricarbonyltropyliumchromium Perchlorate with Aqueous Hydrogen Peroxide.—The perchlorate (0·65 g., 0·002 mole) in water (200 ml.) at 5° was treated with 30% hydrogen peroxide (1 ml.) in water (5 ml.). Gas evolution took place and, after being stirred overnight, the mixture was extracted with ether. The pale yellow extract was washed with 10% aqueous sodium hydroxide (20 ml.), then water, and dried (Na_2SO_4). Evaporation gave a liquid (34 mg., 21·8%), b. p. 80°, having the same retention time as benzene on vapour-phase chromatography on a Griffin and George Mk2B apparatus, with 20% w/w " embaphase " silicone oil on " Celite-545 " as the stationary phase and nitrogen as the carrier gas.

The authors are indebted to the Ethyl Corporation for financial support which made this work possible.

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[*Received, March 3rd*, 1961.]