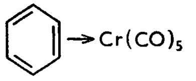
113. *The Organic Chemistry of the Transition Elements. Part I. Tricarbonylchromium Derivatives of Aromatic Compounds.*

By B. Nicholls and M. C. Whiting.

Many aromatic compounds, ArH, displace carbon monoxide from chromium hexacarbonyl with the formation of complexes $Cr(CO)_3(ArH)$ (I). These are stable and may carry any of several functional groups. The effects of the metallic residue upon typical properties of these groups and of the aromatic system as a whole are outlined, and methods for the regeneration of the aromatic components are described.

Tricarbonylbenzenechromium (I) was first obtained by Fischer and Ofele[1] in 27% yield from chromium hexacarbonyl and dibenzenechromium in benzene in a sealed system at 220°. We had independently discovered a simpler and more general method for preparing compounds of this type which involves heating chromium hexacarbonyl under reflux in an excess of the aromatic compound or with a molar quantity in an inert solvent.

(I)



(II)

Shortly after our preliminary communication,[2] Natta and his co-workers also described[3] the direct preparation of several of these compounds, but used a pressurised system (with intermittent release of carbon monoxide) and higher temperatures (200—235°). The work of Fischer and his school[1] shows that equilibria are involved in these reactions—an excess of carbon monoxide converts the dibenzenechromium complex into the hexacarbonyl—and therefore it is advantageous in principle, as well as much easier in practice, to employ an open system, the free escape of carbon monoxide then driving the reaction to completion.

In early experiments decalin was employed as solvent, but because the commercial product contains tetralin as an impurity, and perhaps because of hydrogen-transfer processes, products containing the tricarbonylchromium complex of tetralin were often obtained. Since the final product has a considerable dipole moment and is formed from more or less non-polar components, the reaction should be facilitated by the use of a polar solvent. Of the many tried, diethylene glycol dimethyl ether was the most suitable. Its use made possible the direct preparation of the parent member of the series, tricarbonylbenzenechromium, and also greatly improved the yields of other complexes. A list of complexes, $(ArH)Cr(CO)_3$, is given in Table 1; all are stable, yellow or orange, and crystalline; all gave correct analyses for carbon and hydrogen, and in one case for oxygen.

The rate of formation of these complexes is of obvious interest. The conversion of an aromatic compound into such a complex results ultimately in approximately equal bonding to all six aromatic carbon atoms, and although it can, and should, be regarded as an

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[1] Fischer and Ofele, *Angew. Chem.*, 1957, **69**, 715; *Chem. Ber.*, 1957, **90**, 2532.

[2] Nicholls and Whiting, *Proc. Chem. Soc.*, 1958, 152.

[3] Natta, Ercoli, and Calderazzo, *Chim. e Ind.*, 1958, **40**, 287.

electrophilic attack on the aromatic system it cannot be grouped either with typical attacks on single carbon atoms giving σ-complexes as intermediates (nitration, etc.), or with attacks on individual double bonds giving initially one-bond π-complexes (formation of silver complexes, ozonolysis, dihydro-diol formation). The qualitative experiments already made show that electronic effects roughly parallel those observed in nitration studies, the reaction being facilitated by electron-repelling substituents, *e.g.*, NMe_2 and retarded by electron-attracting groups, *e.g.*, Cl and CO_2Me. A second important factor is the steric effect of substituent groups. Thus the rate sequence $o \sim m > p$ was always observed with disubstituted benzenes, while *tert.*-butylbenzene reacted much more slowly than toluene. The latter result tends to disprove the rate-determining formation of a one-bond π-complex (II), followed by intramolecular displacement of carbon monoxide, since in that case the reactivity of the molecule would depend only upon the environment of its most reactive C–C bond. [The possibility that complex (II) is formed rapidly and reversibly and that its transformation into (I) by intramolecular displacement of carbon monoxide is the rate-determining step is not thereby excluded, but seems most unlikely.] The observed rate sequence is consistent with participation of the aromatic sextet as a whole in the rate-determining stage, since any transition state involving this and chromium hexacarbonyl would suffer more interference from *para-* than from *ortho-* or *meta*-substituents.

TABLE 1. *Direct preparation of tricarbonyl(arene)chromium compounds.*

Aromatic compound	Method	Time (hr.)	Yield (%)	M. p.	Analysis Found (%) C	Analysis Found (%) H	Analysis Calc. (%) C	Analysis Calc. (%) H
Benzene	C	9·0	30	165·5—166·5°	50·3	3·2	50·45	2·8
Toluene	A	12·0	10	82·5—83·5	52·2	3·6	52·6	3·5
	C	5·0	80					
o-Xylene	A	6·0	81	90—91·4	54·5	4·4	54·5	4·15
m-Xylene	A	6·0	27	107—108·5	54·35	4·1	54·5	4·15
p-Xylene	A	3·0	20	99—100	53·95	4·4	54·5	4·15
	A	16·0	87					
Mesitylene *	A	3·8	84	177—178	57·1	4·9	56·25	4·7
Hexamethylbenzene	C	4·0	51	211—213 (dec.)	60·4	6·2	60·4	6·05
Tetralin	A	3·0	85	116—117·5	58·3	4·65	58·2	4·5
Anisole	A	6·0	94	86—87	49·5	3·5	49·2	3·3
Methyl *o*-tolyl ether	A	3·0	99	75—77	51·45	3·85	51·15	3·9
Methyl *p*-tolyl ether	A	4·5	70	52—53·5	51·2	4·05	51·15	3·9
Aniline	B	3·0	91	173—175 (dec.)	46·8	3·2	47·15	3·05
o-Toluidine	B	1·5	98	130—131·8	49·65	3·65	49·4	3·7
m-Toluidine	B	1·5	97	137—138·7	49·4	3·65	49·4	3·7
p-Toluidine	B	8·0	46	156—157·5	49·4	3·7	49·4	3·7
N-Methylaniline	B	3·0	88	122·5—124	49·65	3·7	49·4	3·7
NN-Dimethylaniline	B	3·0	91	145·8—146·5	51·3	4·35	51·35	4·3
NN-Dimethyl-*o*-toluidine	B	3·0	99	76·5—78	52·7	4·55	53·1	4·75
Methyl benzoate	A	4·5	72	97·5—98·5	48·3	3·1	48·55	2·95
Ethyl phenylacetate	B	2·5	88	oil	—	—	—	—
Fluorobenzene	C	3·0	23	122·5—124	46·6	2·5	46·55	2·15
Chlorobenzene	C	3·0	52	102—103	—	—	—	—
Benzyl alcohol	A	3·0	54	95·5—96·5	49·1	3·2	49·2	3·3
Acetophenone	C	4·5	35	91—92·5	51·5	3·25	51·55	3·1
tert.-Butylbenzene	A	6·0	5	83·5—84·5	57·7	5·2	57·75	5·2
				Molybdenum complex				
Mesitylene	B	3·0	70	150 (dec.)	48·15	4·15	48·0	4·0

Method: A, Aromatic compound as solvent. B, Decalin as solvent. C, Diethylene glycol dimethyl ether as solvent.

* Found: O, 18·1. Calc.: O, 18·7%.

Limitations to the reaction were encountered in the presence of certain functional groups (CO_2H, CHO, CN, and NO_2); the chromium hexacarbonyl then suffered decomposition before the complex-forming reaction became appreciable. The complexes derived from phenol and quinol were very readily oxidised and so could not be easily purified.

The characteristic properties of functional substituents are largely preserved in these complexes. Thus, the unstable tricarbonylphenolchromium can be methylated and acetylated to the anisole and phenyl acetate analogues and the aniline complex converted into the corresponding acetanilide derivative. This makes possible the preparation of some otherwise inaccessible complexes, such as those of benzoic and phenylacetic acid, which were prepared by alkaline hydrolysis of the corresponding esters. However, attempts to prepare the nitrobenzene complex by oxidation of the aniline analogue with peroxytrifluoroacetic acid were unsuccessful, the reagent disrupting the molecule, probably by first oxidising the chromium atom (cf. the behaviour of ferrocene[4]). Similarly the attempted indirect synthesis of tricarbonylbenzonitrilechromium failed, owing to our inability to prepare the analogous amide from the benzoic acid complex by using thionyl chloride and ammonia or from the methyl ester and alcoholic ammonia. Both molecules were disrupted, although from the latter reaction a small amount of tricarbonyl(benzoic acid)chromium could be isolated. Methylation of the aniline complex by methyl iodide and sodium carbonate stopped at the monosubstituted stage.

The aromatic tricarbonylchromium complexes are recovered unchanged, provided the molecule contains no reducible function, after treatment with sodium ethoxide in boiling ethanol or with lithium aluminium hydride at temperatures up to 30°. By using the latter reagent tricarbonyl(benzyl alcohol)chromium, identical with the product from benzyl alcohol and chromium hexacarbonyl, was prepared in high yield from the methyl benzoate complex.

Without exception, all the oxidising agents examined attacked the tricarbonylchromium residue with evolution of gas and generation of tervalent chromium. For example, manganese dioxide instantly destroyed the benzyl alcohol complex and then slowly oxidised the liberated benzyl alcohol to benzaldehyde. Similar observations were made in the attempted permanganate oxidation of the toluene complex and diazotisation of the aniline derivative.

In ferrocene, the electrons involved in the bonding between the hydrocarbon residue and the metal atom show mobility characteristic of aromatic or conjugated ethylenic systems. Although easily oxidised by nitric acid, bromine, etc., ferrocene readily undergoes Friedel–Crafts acylation. Dibenzenechromium is not substituted under similar conditions, although its much lower stability precludes more drastic treatment.[5] The tricarbonylchromium derivatives of anisole and mesitylene could, however, be heated under reflux with acetyl chloride and aluminium chloride in methylene dichloride for several hours and then recovered unchanged in 10—50% yield. This lack of reactivity toward electrophilic reagents is not unexpected, since pK_a measurements on the benzoic and phenylacetic acid derivatives (see below) show that the tricarbonylchromium π-grouping has a similar electron-withdrawing power to a *p*-nitro-group, and the inertness of nitrobenzene in Friedel–Crafts acylations is well known. The result, however, makes it unlikely that electrophilic substitution will prove useful synthetically in this field.

The presence of an electron-deficient aromatic ring in these tricarbonylchromium derivatives suggests that they might undergo nucleophilic substitution much more easily than the parent compounds. This proved so; the derivative of chlorobenzene could be converted into the anisole analogue in high yield at 65°. The synthetical use of this observation and the mechanism of substitution are now under investigation. As yet attempts to effect free-radical substitution have not proved successful.

Synthetical applications would require that the π-bound tricarbonylchromium residue could be cleanly and satisfactorily removed when desired. The oxidative methods described suffer from the disadvantage that the aromatic component may undergo further

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[4] Woodward, Rosenblum, and Whiting, *J. Amer. Chem. Soc.*, 1952, **74**, 3458.

[5] Fritz and Fischer, *Z. Naturforsch.*, 1957, **12b**, 67.

transformation. Thermal decomposition of the toluene complex proceeds smoothly at about 200°, giving a mixture of toluene (76%), chromium hexacarbonyl (67%), and pyrophoric chromium. For many purposes it would, however, be preferable to displace the aromatic component by attack on chromium with a more powerful ligand. Displacement by a more nucleophilic aromatic ring does not proceed to a measurable extent, the toluene complex being recovered after prolonged treatment with boiling dimethylaniline or mesitylene. Electron donors such as pyridine, dimethylphenylarsine, and triphenylphosphine, on the other hand, were very efficient and both the aromatic component and the *p*-complex could be isolated. The nature of these and other *p*-complexes will be dealt with in greater detail in a subsequent paper.

The dissociation constants of ferrocenecarboxylic acids are comparable with those of typical aliphatic or aromatic acids,[4] and a carbon atom bonded to a transition-metal atom by an electron system of this type may thus be comparable in electronegativity with one bonded by sp^3 or sp^2 electrons to carbon and hydrogen atoms. Unfortunately the limited range of diarenechromiums available does not include a carboxylic acid. As a first approximation of the extent of electron availability at a carbon centre in a π-tricarbonylbenzenechromium derivative and as a check on the steric effects of the π-bound tricarbonylchromium grouping, the dissociation constants of the derivatives of benzoic and phenylacetic acid were determined in 50% ethanol, along with the unsubstituted and *p*-nitro-acids (Table 2). The derivative of phenylacetic acid had the same dissociation constant as *p*-nitrophenylacetic acid, but in the benzoic acid series the organochromium acid was appreciably weaker than the *p*-nitro-acid. These results suggest that the π-bound tricarbonylchromium group withdraws electrons at least as strongly as a *p*-nitro-group (though by quite a different combination of mechanisms) and that it also exerts a steric effect, hindering solvation and weakening any process of ionisation, comparable with that of a large *ortho*-substituent.

TABLE 2. *Dissociation constants* (p*K**) *of substituted benzoic and phenylacetic acids.*

$Ph{\cdot}CO_2H$	5·68	$Ph{\cdot}CH_2{\cdot}CO_2H$	5·64
π-$Cr(CO)_3(Ph{\cdot}CO_2H)$	4·77	π-$Cr(CO)_3(Ph{\cdot}CH_2{\cdot}CO_2H)$	5·02
p-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$	4·48	*p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$	5·01

Molybdenum hexacarbonyl reacts much more rapidly than chromium hexacarbonyl with aromatic compounds to form similar derivatives $Mo(CO)_3(ArH)$. Unfortunately they are generally less stable than the chromium analogues.

[*Note Added December 3rd,* 1958.—Fischer, Öfele, Essler, Fröhlich, Mortensen, and Semmlinger (*Z. Naturforschung*, 1958, 13b, 458) have also discovered the direct synthesis of these complexes from aromatic compounds and chromium hexacarbonyl.]

EXPERIMENTAL

Only representative examples of the use of the three methods of direct preparation are given in full; for other complexes the procedure differs inappreciably, except as regards reaction time. Analytical data are given in Table 1. Unless otherwise stated, all complexes are yellow crystalline solids, stable to light and air at moderate temperatures when pure but slowly attacked under these conditions when dissolved. " Method B " is seldom, if ever, preferable to " method C "; and " method A " is of little value with compounds which boil below 120°.

Method A. Tricarbonylmesitylenechromium.—A solution of chromium hexacarbonyl (1·07 g.) in mesitylene (10 c.c.) was heated under reflux in an atmosphere of nitrogen. Chromium hexacarbonyl which sublimed was returned to the reaction mixture mechanically, until sublimation ceased (4 hr.). The deep yellow solution was cooled, diluted with ether (100 c.c.), and filtered through deactivated alumina (5 g.). Concentration to dryness afforded the *complex* (1·04 g.; 84%) as needles, m. p. 177—178°, from di*iso*propyl ether.

Method B. Tricarbonyl(NN-*dimethylaniline*)*chromium.*—A solution of chromium hexacarbonyl (2·10 g.) and dimethylaniline (4 c.c.) in decalin (20 c.c.) was heated under reflux during 3 hr. (chromium hexacarbonyl being returned mechanically), allowed to cool, and diluted with ether (100 c.c.). The turbid solution was filtered through deactivated alumina (5 g.), the filtrate evaporated to 25 c.c., and the precipitate filtered off and thoroughly washed with light petroleum. Recrystallisation from di*iso*propyl ether furnished the *complex* (2·26 g; 91%), m. p. 145·8—146·5°.

Method C. Tricarbonyl(fluorobenzene)chromium.—The reaction solution from chromium hexacarbonyl (2·06 g.) and fluorobenzene (3 c.c.) in diethylene glycol dimethyl ether (7 c.c.) was worked up as above to yield a solid (504 mg.; 23%), m. p. 117—120°. Two recrystallisations from light petroleum gave the *complex* (321 mg.), m. p. 122·5—124°, as long needles.

Tricarbonylacetanilidechromium.—A solution of tricarbonylanilinechromium (715 mg.) and acetic anhydride (477 mg.) in pyridine (3·5 g.) was set aside overnight at room temperature in the dark. The resulting dark brown solution was poured into water (50 c.c.; at 0°) and the precipitated oil isolated with ether. Removal of solvent and crystallisation from di*iso*propyl ether–chloroform afforded the *complex* (756 mg.; 90%), m. p. 134—134·5° (Found: C, 48·4; H, 3·45. $C_{11}H_9O_4NCr$ requires C, 48·7; H, 3·3%).

Tricarbonylanisolechromium.—A solution of chromium hexacarbonyl (1·26 g.) and phenol (5 g.) in decalin (10 c.c.) was heated under reflux for 3 hr. and worked up in the usual manner to give tricarbonylphenolchromium as an unstable solid (1·20 g.). This was dissolved in aqueous potassium hydroxide (2·5 g. in 20 c.c. of water) and treated dropwise with dimethyl sulphate (7 g.). The resultant solution was heated under reflux for 2 hr. and diluted, and the organochromium complex was isolated with ether and crystallised from di*iso*propyl ether, giving the complex (1·11 g.; 87%), m. p. 86—87°, identical with that prepared directly.

Tricarbonyl(phenyl acetate)chromium.—The oil (1·01 g.) obtained from the reaction of chromium tricarbonyl (1·21 g.) with phenol (0·61 g.) in decalin (10 c.c.) during 4 hr. at 190—195° was dissolved in pyridine (5 c.c.) and acetic anhydride (2·5 g.) was added. After 16 hr. at room temperature in the dark, the mixture was diluted with water, and the product isolated with ether. Removal of solvent under reduced pressure yielded the *complex* (1·01 g.; 85% from phenol analogue), m. p. 92—95°. An analytical sample had m. p. 94—95·5° (from light petroleum) (Found: C, 49·0; H, 3·1. $C_{11}H_8O_5Cr$ requires C, 48·6; H, 2·95%).

Tricarbonyl(benzoic acid)chromium.—A solution of tricarbonyl(methyl benzoate)chromium (687 mg.; prepared directly) and potassium hydroxide (327 mg.) in water (0·5 c.c.) and methanol (20 c.c.) was kept for 16 hr. at room temperature in the dark. The mixture was diluted with water, unchanged ester was removed by ether extraction, and the aqueous layer was acidified with hydrochloric acid. Isolation with ether yielded the *complex* (617 mg.; 96%; decomp. at 194°) as orange-red clusters (from di*iso*propyl ether–chloroform) (Found: C, 46·4; H, 2·45. $C_{10}H_6O_5Cr$ requires C, 46·5; H, 2·35%).

Tricarbonyl(phenylacetic acid)chromium.—Hydrolysis of the crude ethyl phenylacetate complex (2·30 g.) with potassium hydroxide (1·0 g.) in water (1 c.c.) and methanol (20 c.c.) during 15 hr. at 17° followed by isolation in the usual manner gave the *complex* (2·03 g.; 97%), m. p. 134—135·5° (from di*iso*propyl ether) (Found: C, 48·35; H, 3·15. $C_{11}H_8O_5Cr$ requires C, 48·5; H, 3·0%).

Tricarbonyl(methyl benzoate)chromium.—A solution of tricarbonyl(benzoic acid)chromium (115 mg.) in methanol (25 c.c.) containing concentrated sulphuric acid (1 c.c.), after being kept overnight at room temperature, was poured into water, and the neutral product isolated with ether. Removal of solvent and crystallisation from light petroleum afforded the *complex* (27 mg.; 20%), m. p. 97·5—98·8°, identical with a sample prepared directly (Found: C, 49·3; H, 3·1. $C_{11}H_8O_5Cr$ requires C, 48·9; H, 3·0%).

Tricarbonyl(benzyl alcohol)chromium.—Tricarbonyl(methyl benzoate)chromium (910 mg.) in ether (10 c.c.) was cooled to −70° and treated with lithium aluminium hydride (200 mg.) in ether (10 c.c.). The solution was allowed to warm slowly to −45°; a vigorous reaction then occurred. After a few minutes the mixture was treated with ethanol (5 c.c.) and poured into dilute sulphuric acid (at 0°). Isolation with ether furnished the complex (784 mg.; 96%), m. p. 95·5—96·5°, identical with a sample prepared directly.

Reaction of Tricarbonyl(methyl benzoate)chromium with Ammonia.—A suspension of the ester complex (52 mg.) in aqueous ammonia (5 c.c.; *d* 0·88) was treated with ethanol (5 c.c.), and the mixture was heated under reflux for 12 hr. The cooled solution was diluted with water, washed with ether (2 × 20 c.c.), acidified (dilute sulphuric acid), and extracted with ether. Tricarbonyl(benzoic acid)chromium (14 mg.; 30%) was obtained; it had decomposition point 190° and was identical with a sample prepared directly.

Methylation of Tricarbonylanilinechromium.—A mixture of the amine (124 mg.), sodium carbonate (641 mg.), and methyl iodide (1 c.c.) in methanol was heated under reflux for 5 hr. Isolation in the usual manner afforded tricarbonyl(*N*-methylaniline)chromium (87 mg.; 67%), m. p. 121·5—124°, undepressed on admixture with a sample prepared directly.

Manganese Dioxide Oxidation of Tricarbonyl(benzyl alcohol)chromium.—Manganese dioxide (1·0 g.) was added portionwise to a solution of the complex (240 mg.) in methylene dichloride (25 c.c.). A vigorous evolution of gas occurred after each addition. After being stirred for 24 hr. at room temperature in the dark the solution was filtered, the solid washed well with ether, and the filtrate dried ($MgSO_4$). Solvent was removed through a Fenske column, and the pale yellow oil treated with excess of methanolic 2 : 4-dinitrophenylhydrazine reagent. The precipitate (279 mg.) in benzene–light petroleum (1 : 9) was adsorbed on deactivated alumina (50 g.). Elution with the same solvent yielded benzaldehyde 2 : 4-dinitrophenylhydrazone (131 mg.; 42%), m. p. 236—238° (from di*iso*propyl ether–light petroleum).

Attempted Acetylation of Tricarbonylmesitylenechromium.—The complex (249 mg.) in methylene dichloride (10 c.c.) was mixed with a solution of acetyl chloride–aluminium chloride in methylene dichloride (10 c.c.; 0·3 molar) and heated under reflux for 1 hr. Isolation afforded only the starting material (102 mg.), m. p. 175—176·5°.

Replacement of Chlorine by the Methoxyl Group.—Tricarbonyl(chlorobenzene)chromium (235 mg.) and sodium methoxide (from 500 mg. of sodium) in methanol (20 c.c.) were heated under reflux for 24 hr. Isolation in the usua lway yielded tricarbonylanisolechromium (207 mg.; 90%), m. p. 85·5—86·5° (from light petroleum). (Silver nitrate estimation of chloride ions liberated showed a 97% conversion.)

Thermal Decomposition of Tricarbonyltoluenechromium.—The complex (654 mg.) was slowly heated in a microdistillation unit to 200°. At about 170° chromium hexacarbonyl (219 mg.; 67%) sublimed and the liquid became very dark. At 200° toluene (197 mg.; 76%) distilled leaving a residue of metallic chromium.

Displacement Reactions with π-Complexes.—(a) *Using* NN-*dimethylaniline.* A solution of tricarbonyltoluenechromium (292 mg.) in dimethylaniline (5 c.c.) was heated under reflux for 12 hr. and allowed to cool, and the neutral product was isolated with ether. Removal of solvent furnished unchanged tricarbonyltoluenechromium (247 mg.), m. p. 82—83°.

(b) *Using dimethylphenylarsine.* A solution of tricarbonyltoluenechromium (293 mg.) in dimethylphenylarsine (1 c.c.) was maintained at 150—160° for 1 hr. Isolation gave tricarbonyltris(dimethylphenylarsine)chromium (358 mg.; 41%) as bright yellow prisms, m. p. 98—100°.

(c) *Using triphenylphosphine.* A mixture of triphenylphosphine (3·02 g.) and tricarbonyltoluenechromium (467 mg.) was slowly warmed to 160° and maintained for 2 hr. The resulting deep-red solution was cooled and volatile components were taken off into a trap (acetone–carbon dioxide) at 12 mm. This distillate contained toluene (95·3 mg.; 52%) (estimated from the ultraviolet absorption spectrum in ethanol). The residue was recrystallised twice from chloroform to yield a *p*-complex (971 mg.), m. p. 175—176·8°. This, and the arsenic compound mentioned above, will be discussed in a later communication.

(d) *Using Pyridine.* Tricarbonyltetralinchromium (131 mg.) in pyridine (1 c.c.) was heated under reflux for 1 hr., the red solution was cooled and diluted with ether, and the brown pyridine complex was filtered off. The neutral product was isolated with ether, the solvent was removed through a Fenske column, and the residue was co-distilled with ethanol at 0·02 mm. into a cold trap. Ultraviolet estimation showed the presence of tetralin (27·3 mg.; 42%) in the distillate.

Tricarbonylmesitylenemolybdenum.—A solution of molybdenum hexacarbonyl (1·81 g.) and mesitylene (10 c.c.) in decalin (10 c.c.) was heated under reflux for 3 hr. On cooling, pale yellow needles (1·40 g.; 70%) were deposited and removed by filtration. Recrystallisation from di*iso*propyl ether yielded the complex which decomposed above 150°.

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THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, August* 19*th*, 1958.]