The Stereochemistry of Organometallic Compounds. Part II.[1] Effects of Non-bonded Substituents on the *cis–trans*-Equilibrium Ratios of Tricarbonyl(indane)chromiums[2]

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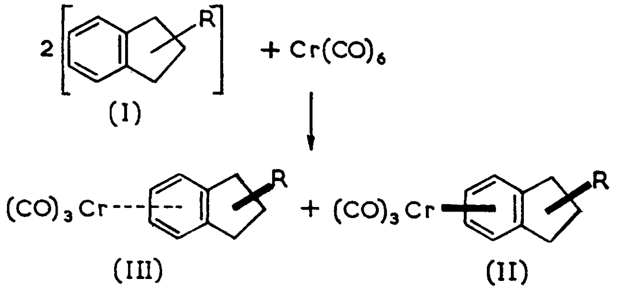
A series of 1- and 2-substituted indanes have been treated with hexacarbonylchromium in three solvents: diglyme, decalin, and cyclohexanol. The ratios of *cis*- to *trans*-tricarbonyl(indane)chromiums thus obtained have been shown to be thermodynamically controlled, as individual isomers come to equilibrium under the conditions used. The ratios are discussed in terms of non-bonded interactions between the substituent and the chromium carbonyl group. Some unusual cases of preferred stabilisation of *cis*-isomers have been found.

TRICARBONYL(ARENE)METAL compounds now form an important and easily accessible class of organometallic compounds since the direct method of preparation from a metal carbonyl and an arene was discovered.[3] We have attempted to study the intramolecular interactions which are possible between metal carbonyl groups and typical organic functional groups. The reaction chosen was that between hexacarbonylchromium and 1- or 2-substituted indanes (I) in boiling 'diglyme,' cyclohexanol, or decalin. In these reactions the compounds *cis*- (II) and *trans*-tricarbonyl(indane)chromium (III) were obtained. Isomer ratios, determined by chromatography on alumina or by gas chromatography (for the alkylindane complexes) were reproducible to ±3%. The ratios for the methyl indane-1- and 2-carboxylate experiments were the only exceptions, in that in some cases considerable hydrolysis occurred on the column. Although attempts were made to estimate the isomeric composition of the hydrolysis products, these ratios are considered to be slightly less accurate.



Stereochemical assignments for the *cis*- and *trans*-tricarbonylchromium compounds from indan-1-ol (I; R = 1-OH), indan-2-ol (I; R = 2-OH) and their acetates, methyl indane-2-carboxylate (I; R = 2-CO_2Me), and 2-hydroxymethylindane (I; R = 2-CH_2OH) have been made previously. The assignments for the *cis*- and *trans*-compounds from 1-cyanoindane (I; R = 1-CN), 2-cyanoindane (I; R = 2-CN), and methyl indane-1-carboxylate (I; R = 1-CO_2Me) were made on the basis of dipole moment measurements. The higher melting isomer of each pair, which was also the more firmly absorbed on alumina columns, was found in each case to have the higher dipole moment and was assigned the *cis*-structure. The stereochemistry of the 1- and 2-methylindane complexes was established by preparing pure isomers from individual methoxycarbonyl compounds. This was accomplished, for example, by reduction of *cis*-tricarbonyl(methyl indane-1-carboxylate)-chromium (II; R = 1-CO_2Me) with lithium aluminium hydride to the *cis*-1-hydroxymethyl compound (II; R = 1-CH_2OH), formation of the toluene-*p*-sulphonate ester (II; R = 1-CH_2OTs), and further reduction with hydride to give *cis*-tricarbonyl-(1-methylindane)chromium (II; R = 1-Me). The stereochemistry of the compounds from 1-isopropylindane (I; R = $CHMe_2$), 1-cyanomethylindane (I; R = CH_2CN), and 1-ethylsulphonylindane (I; R = $SO_2{\cdot}CH_2{\cdot}CH_3$) was assigned on the basis of their n.m.r. spectra. When the n.m.r. spectra of *cis*-tricarbonyl-(1-methylindane and 1-hydroxymethylindane)chromiums were determined, the peaks due to aromatic protons were much more resolved than in the spectra of the corresponding *trans*-compounds. One isomer from each of the above 1-substituted indanes also showed this effect and was assigned the *cis*-structure. This effect will be further discussed in Part V. Pure samples of individual *cis*- and *trans*-tricarbonyl-(2-isopropylindane)chromiums (II and III, R = 2-$CHMe_2$) could not be obtained. The isomer ratios refer to the relative peak areas from gas chromatographic analysis. It was tentatively assumed that the relative peak area response was unity for the two compounds and that the *trans*-isomer had the lower retention time, as was recorded for the other tricarbonyl(alkylindane)chromiums studied. The isomer ratios are given in Table 1.

The *cis* : *trans* ratios presented above represent the relative thermodynamic stability of each of the pairs of isomers, because separate experiments showed that the individual isomers come close to the formation ratio when heated in the presence of the parent ligand under the reaction conditions. Full details of these experiments are given in Table 4. The time taken to reach equilibrium in these experiments was much longer than

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[1] The paper by W. R. Jackson and C. H. McMullen, *J. Chem. Soc.*, 1965, 1170, is considered as Part I; Parts II—VII, following papers.

[2] For a preliminary account of some of this work see D. E. F. Gracey, H. B. Henbest, W. R. Jackson, and C. H. McMullen, *Chem. Comm.*, 1965, 566.

[3] (*a*) B. Nicholls and M. C. Whiting, *Proc. Chem. Soc.*, 1958, 152; (*b*) E. O. Fischer, K. Ofele, H. Essler, W. Frohlich, J. P. Mortensen, and W. Semmlinger, *Chem. Ber.*, 1958, **91**, 2763; (*c*) G. Natta, R. Ercoli, and F. Calderazzo, *Chimica e Industria*, 1958, **40**, 287.

in the formation experiments because more dilute solutions were used (dilution factor *ca.* 30). It was not possible, because of decomposition of the complexes, to heat all these experiments long enough and consequently some did not quite reach equilibrium. All evidence, however, points to the ratios in Table 1 being the equilibrium ratios. In only one case, when *trans*-tricarbonyl-(1(cyanoindane)chromium was heated with the parent ligand in diglyme, did the determined equilibration ratio (74 *cis* : 26 *trans*) overshoot the ratio found in the formation experiment (64 : 36). The equilibration of isomers is in agreement with the work of Strohmeier and his co-workers[4,5] who have shown that exchange occurs when ^{14}C-labelled benzene and tricarbonyl(benzene)chromium are heated in heptane at 140—180°. However these workers derived a rate law for the exchange reaction of the form (1), in which

$$\text{Rate} = k_2[C_6H_6Cr(CO)_3]^2 + k_2'[C_6H_6Cr(CO)_3][C_6H_6] \quad (1)$$

$k_2 \gg k_2'$. In the absence of free organic ligand we found that individual isomers were recovered unchanged after being heated in boiling solvent. Similarly no equilibration of single tricarbonyl(alkylindane)chromiums occurred on gas chromatography. It thus appears that the above rate expression is not generally applicable. An exchange reaction between two complexes which involved retention of stereochemistry in both molecules would be in agreement with the suggested kinetic scheme.

TABLE 1

Isomer ratios from the reactions of hexacarbonylchromium with substituted indanes in boiling diglyme 'A', cyclohexanol 'B', and decalin 'C'

Substituent (Formula I)	Solvent	Ratio * *cis*(II) : *trans*(III)
1-CH_3	A	49 : 51
	B	53 : 47
	C	49 : 51
1-$CH(Me)_2$	A	20 : 80
	B	18 : 82
	C	15 : 85
1-CO_2Me	A	63 : 47
	B	52 : 47
	C	69 : 31
1-CN	A	64 : 36
	B	68 : 32
1-$OCOCH_3$	A	52 : 48
	C	53 : 47
1-CH_2OH	A	50 : 50
1-CH_2CN	A	57 : 43
1-$SO_2CH_2CH_3$	A	5 : 95
2-CH_3	A	31 : 69
	B	16 : 84
	C	33 : 67
2-$CH(Me)_2$ †	A	21 : 79
	A ‡	20 : 80
	B	15 : 85
	C	31 : 69
2-CO_2Me	A	32 : 68
	B	31 : 69
	C	22 : 78
2-CN	A	12 : 88
	B	29 : 71
2-O·$COCH_3$	A	53 : 47
	B	52 : 48
	C	54 : 46
2-CH_2OH	A	26 : 74

* Many of these results are the average of at least two individual experiments. † Stereochemical assignment on the basis of gas-chromatographic retention time only. ‡ Reaction with four times the normal volume of solvent.

A general trend from comparison of the results for 1- and 2-substituted indanes is that a substituent in the 1-position usually leads to a higher proportion of *cis*-isomer at equilibrium than the same substituent in the 2-position, except when the group is very bulky (*e.g.*, isopropyl). In two cases, those of the 1-cyano- and 1-methoxycarbonyl substituents, the *cis*-isomer is preferred at equilibrium. In a discussion of these results it is convenient to group the factors which influence the the relative stability of the isomers into two main categories, steric and electronic effects.

Steric Effects.—Direct adverse interactions between a bulky group and the tricarbonylchromium residue would be expected to be greater in the *cis*-isomer rather than the *trans*, thus leading to a preference for *trans*-isomer at equilibrium. This effect appears to become significant in the 1-substituted indanes for groups as bulky as isopropyl; thus 1-isopropylindane and 1-ethylsulphonylindane give only small amounts of *cis*-isomers at equilibrium. Surprisingly, with the methylindanes the *trans*-isomer is preferred from 2-methylindane but both isomers are equally stable from 1-methylindane. A methyl group at C(1), *cis* to the metal residue, appears to lead to a conformational preference for the tricarbonylchromium group, as the n.m.r. spectrum at 30° shows a highly resolved aromatic region (for full discussion see Part V). The free energy involved in this interaction cannot be very great at 160°, otherwise a significant deviation from the 1 : 1 isomer ratio would be expected. Examination of models shows that substituents in the 1-position are held fairly rigidly at a shallow angle to the plane of the arene ring, and inversion of the five-membered ring has little effect on the magnitude of the interaction with a bonded tricarbonylchromium group. In contrast, a methyl group at C(2), *cis* to the tricarbonylchromium residue, has severe adverse interactions with the metal residue when it is in the *pseudo*-axial position (IVa). The *cis*-isomer is thus forced to adopt a conformation (IVb) with a *pseudo*-equatorial methyl group and thus the entropy of ring inversion is lost. The use of cyclohexanol as solvent leads to a significant decrease in the amount of *cis*-isomer from 2-methylindane as compared with reactions in diglyme and decalin. Cyclohexanol can form hydrogen bonds to the tricarbonylchromium group,[1] thus increasing its effective size and the unfavourable interactions with the 2-methyl group in a *pseudo*-axial conformation. The preference for an equatorial methyl group is thus emphasised.

Electronic Effects.—The tricarbonyl-(1-cyanoindane)-

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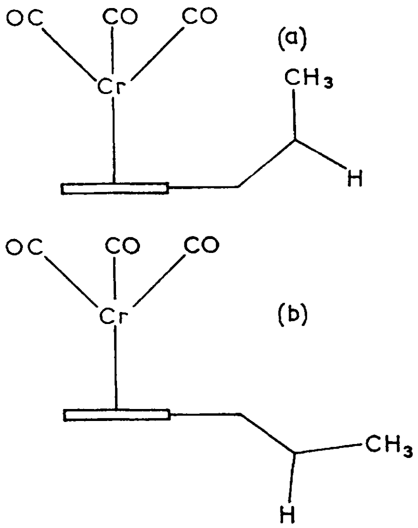
[4] W. Strohmeier and H. Mittnacht, *Chem. Ber.*, 1960, **93**, 2085; W. Strohmeier and H. Mittnacht, *Z. phys. Chem.* (*Frankfurt*), 1962, **34**, 82; W. Strohmeier and E. H. Staricco, *ibid.*, 1963, **38**, 315.

[5] W. Strohmeier and H. Mittnacht, *Z. phys. Chem.* (*Frankfurt*), 1961, **29**, 339.

chromiums show a distinct preference for the *cis*-isomer at equilibrium (68 *cis* : 32 *trans* in cyclohexanol) in contrast to the tricarbonyl-(2-cyanoindane)chromiums where the *trans*-isomer is preferred (29 *cis* : 71 *trans* in cyclohexanol). Equilibration experiments on individual isomers gave similar values. In *cis*-tricarbonyl-(1-cyanoindane)chromium the cyanide group is held fairly close to the metal residue, regardless of the conformation



(IV)

of the five-membered ring. Thus two groups which are both capable of acting as π-donors or π-acceptors are in proximity and it is possible that favourable electrostatic interactions arise. Other pairs of geometric isomers are known in which the isomer with the more bulky groups *cis* is the more stable.[6,7] In both the case of the dihalogenoethylenes[6] and the phenyl thiovinyl ketones[7] a similar juxtaposition of π-donor–π-acceptor groups is achieved in the *cis*-isomer, and favourable electrostatic interactions have been suggested. In tricarbonyl-(2-cyanoindane)chromium similar interactions could be possible only when the cyano-group is held in a *pseudo*-axial conformation. It is thus possible that any gain in electrostatic energy would be more than counterbalanced by a loss of entropy of ring inversion and therefore no *cis*-stabilisation occurs. Dipole moment studies indicate that *cis*-tricarbonyl-(2-cyanoindane)chromium appears to prefer a conformation in which the cyano-group is *pseudo*-equatorial (for a full discussion see Part IV). The trend of *cis*-isomer stabilisation in the 1-substituted indane series is continued in the methyl indane-1-carboxylate complexes but has virtually disappeared for the 1-cyanomethylindane and 1-acetoxyindane complexes. The trend is reversed when the polar group is very bulky, as in 1-ethylsulphonylindane, which gave almost exclusively the *trans*-isomer.

EXPERIMENTAL

All m.p.s. were determined on a hot stage. Light petroleum had b.p. 40—60°. Alumina (Spence, grade H) deactivated with aqueous acetic acid was used for chromatography. A Pye Argon chromatograph, with 4 ft. columns packed with polyphenyl ether (7% w/w) on 100—120 mesh Celite, was used for analytical gas chromatography; argon flow rate 60 ml./min. N.m.r. spectra were measured on a Varian H.R. 100 spectrometer by Mr. R. Spratt, using tetramethylsilane as internal standard and deuteriochloroform as solvent, except where otherwise stated.

1- *and* 2-*Substituted Indanes*.—The 1- and 2-substituted[8–19] indanes shown in Table 2 were prepared by standard literature methods or by slight modifications thereof. Full details will be supplied on request to W. R. Jackson.

2-*Cyanoindane*.—Ethyl 2-cyanoindane-2-carboxylate (1 mol.) b.p. 162—164°/11 mm. (lit.,[20] 169—170°/18 mm.) was heated with potassium hydroxide (1·1 mol.) in aqueous methanol and the acid isolated. The crude acid (20 g.) was dissolved in 2,4,6-collidine (200 ml.) and the solution refluxed for 3 hr. The cold reaction mixture was poured into 2N-hydrochloric acid. The nitrile was extracted into ether. The ether layer was washed with 2N-hydrochloric acid, 10% potassium hydrogen carbonate solution, and water, dried, and the solution evaporated. Fractional distillation of the residue gave 2-*cyanoindane* (13·1 g., 86%), b.p. 79—81°/0·05 mm., n_D^{18} 1·5478 (Found: C, 83·9; H, 6·4; N, 10·1. $C_{10}H_9N$ requires C, 83·9; H, 6·3; N, 9·8%).

1-*Ethylsulphonylindane*.—Ethanethiol (15·5 g.) was added dropwise during 10 min. to a stirred solution of sodium ethoxide in ethanol (150 ml., 5·8 g. of sodium previously dissolved). Freshly distilled 1-chloroindane (38·2 g.) was added during 1 hr. and the emulsion was then refluxed for a further 2 hr. The mixture was allowed to cool, poured on crushed ice (400 g.) whereupon the product separated as a colourless oil, which was extracted into dichloromethane. The extract was washed with water, dried ($MgSO_4$), and the dichloromethane distilled off. Fractionation of the residue gave 1-*ethylthioindane* (34·3 g., 77%), b.p. 128—129°/10 mm., n_D^{18} 1·5706 (Found: C, 74·3; H, 8·2; S, 18·3. $C_{11}H_{14}S$ requires C, 74·1; H, 7·9; S, 18·0%). The sulphide (10 g.) was dissolved in acetic acid (50 ml.) and the solution was heated at 100° while hydrogen peroxide (25·5 g., 30%) in acetic acid (50 ml.) was added. The stirred mixture was heated for a further 1·5 hr., poured on crushed ice (400 g.) and the acid neutralised with potassium hydrogen carbonate. The neutral solution was extracted with dichloromethane, the extract washed with 10% hydrogen carbonate

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[6] H. G. Viehe, *Chem. Ber.*, 1960, **93**, 1697.

[7] D. Landini and F. Montanari, *Chem. Comm.*, 1967, 180.

[8] J. E. Horan and R. W. Schiessler, *Org. Synth.*, 1961, **41**, 53.

[9] W. Huckel, M. Sachs, J. Yantschulewitsch, and F. Nerdel, *Annalen*, 1935, **518**, 155.

[10] W. H. Perkin and G. Revay, *J. Chem. Soc.*, 1894, **65**, 228.

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[12] L. Ruzicka and E. Peyer, *Helv. Chim. Acta*, 1935, **18**, 676.

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[15] W. Wunderlich, *Arch. Pharm.*, 1953, **286**, 512.

[16] M. Tiffeneau and A. Orekhoff, *Bull. Soc. chim. France*, 1920, **27**, 782.

[17] C. Courtot, *Ann. Chim.* (*France*), 1916, **5**, 52.

[18] D. D. Phillips, J. A. Cimildoro, P. Scheiner, and A. W. Johnson, *J. Org. Chem.*, 1958, **23**, 786.

[19] J. F. Bunnet and J. A. Skorcz, *J. Org. Chem.*, 1962, **27**, 3836.

[20] P. E. Gagnon and J. L. Boivin, *Canad. J. Chem.*, 1948, **26**, 503.

solution, and water, and dried (Na_2SO_4), and the dichloromethane distilled off. The solid residue, m.p. 54—58°, was recrystallised from dichloromethane–light petroleum to yield 1-*ethylsulphonylindane* (9·3 g., 86·5%), m.p. 55—56° (Found: C, 62·95; H, 6·75; S, 15·4. $C_{11}H_{14}O_2S$ requires C, 62·8; H, 6·7; S, 15·2%).

1-*Cyanomethylindane*.—Condensation of indan-1-one with cyanoacetic acid in piperidine [21] gave a black tar which was chromatographed on alumina. Elution with ether–light petroleum (1 : 1) gave crude 1-indanylideneacetonitrile (54%) as a gum. Hydrogenation of the crude olefin at atmospheric pressure over platinum oxide in chloroform gave 1-*cyanomethylindane*, b.p. 72°/0·01 mm., n_D^{25} 1·5732 (Found: C, 84·3; H, 7·35; N, 9·25. $C_{11}H_{11}N$ requires C, 84·0; H, 7·05; N, 8·9%).

TABLE 2

Compound	Physical characteristics	Lit. values	Ref.
Indan-2-one	M.p. 57—58°	57—58°	8
Indan-2-ol	M.p. 70°	70°	9
2-Acetoxyindane	M.p. 32°	32°	9
Methyl indane-2-carboxylate	B.p. 125—126°/11 mm.	170°/60 mm.	10
Indane-2-carboxylic acid	M.p. 130°	130°	10
2-Hydroxymethylindane	B.p. 78—80°/0·08 mm. M.p. 33·5°	B.p. 139—140°/11 mm.	11
2-Methylindane	B.p. 68—70°/10 mm.	70°/10 mm.	12
Indan-1-one	M.p. 39—41°	40°	13
Indan-1-ol	M.p. 53—54°	54°	14
1-Acetoxyindane	B.p. 124°/13 mm., n_D^{25} 1·5218	135°/15 mm.	14
Methyl indane-1-carboxylate	B.p. 126°/14 mm.	130—133°/13 mm.	15
Indane-1-carboxylic acid	M.p. 59—60°	59—60°	16
1-Hydroxymethylindane	B.p. 124°/8 mm.	134°/13 mm.	17
1-Methylindane	B.p. 70°/15 mm.	60°/10 mm.	12
1-Isopropylidane	B.p. 114°/5 mm.	100°/2 mm.	18
1-Cyanoindane	B.p. 87°/0·75 mm., n_D^{25} 1·5421	83—84°/0·8 mm.	19

TABLE 3

Reactions of hexacarbonylchromium in (A) diglyme, (B) cyclohexanol, and (C) decalin, with substituted indanes

Compound	Wt. of hexacarbonylchromium (g.) *	Solvent (10 ml.)	Reaction time (hr.)	*cis*-Isomer (%)	*trans*-Isomer (%)
2-Acetoxyindane	1·1	A	3	33	30
	2·0	A	3	32	30
	1·1	B	8	50	46
	1·1	C	3	46	39
Methyl indane-2-carboxylate	1·1	A	5	24	52
	1·1	B	4	21	46
	1·1	C	2·5	19	61
1-Acetoxyindane	1·1	A	3	33·7	30·8
	1·1	C	3	33·5	27·2
Methyl indane-1-carboxylate	1·1	A	1·5	41	23
	1·1	B	2·75	24	18
	1·1	C	2·75	47	21

Full details of the separation and stereochemical assignment of these compounds have been published. * 4 molar equiv. of ligand to hexacarbonyl were used.

General Procedure for the Preparation of Tricarbonyl-(indane)chromiums.—All reactions for which stereochemical ratios are quoted were carried out by the method of Nicholls and Whiting.[3a] A few larger scale preparations were carried out in a Strohmeier apparatus.[22] Hexacarbonylchromium and excess of indane ligand were refluxed in an inert solvent under nitrogen. The hexacarbonylchromium which sublimed was returned mechanically to the mixture. Heating was continued until the hexacarbonylchromium ceased to sublime or until flecks of a green precipitate, indicating decomposition of the metal carbonyl, appeared. The solution, usually deep yellow, was allowed to cool, diluted with ether, and filtered. The ether was evaporated at 40°/10 mm. and the higher-boiling solvent removed at 100°/0·1 mm. The tricarbonylchromium compounds were freed from the last traces of solvents and unchanged ligand by chromatography on alumina.

2-*Methylindane*.—Hexacarbonylchromium (2·2 g.) and 2-methylindane (5·2 g.) were heated in diglyme for 5 hr. The product (1·15 g.) was chromatographed on a long column (1·7 m.) of alumina. The first fractions eluted with light petroleum were recrystallized from the same solvent to give trans-*tricarbonyl-*(2-*methylindane*)*chromium* (0·35 g., 11%), m.p. 82—82·5° (Found: C, 57·8; H, 4·8. $C_{13}H_{12}CrO_3$ requires C, 58·1; H, 4·5%). Mixed fractions (0·51 g.), m.p. 73—106° were eluted and finally cis-*tricarbonyl-*(2-*methylindane*)*chromium* (0·15 g., 5%), m.p. 111—112° from light petroleum (Found: C, 57·6; H, 4·6). Gas chromatography of a mixture of the *cis*- and *trans*-isomers at 165° showed two clearly resolved peaks. The peak-area response was identical for the two isomers. This method of analysis was used to determine the isomer ratio in three solvents.

(a) *Diglyme*. Hexacarbonylchromium (0·5 g.) and 2-methylindane (1·3 g.) were refluxed in 'diglyme' (8 ml.) for 3 hr. The isomeric mixture (0·41 g., 68%) was shown to be 31 *cis* : 69 *trans*.

(b) *Cyclohexanol*. A similar reaction in cyclohexanol

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[21] M. M. Shemyakin and D. M. Traktenberg, *Compt. rend. Acad. Sci. U.S.S.R.*, 1935, **24**, 763; *Chem. Abs.*, 1940, **34**, 3676.

[22] W. Strohmeier, *Chem. Ber.*, 1961, 2490.

(8 ml.) gave a mixture (0·49 g., 80%); ratio 16 *cis* : 84 *trans*.

(c) *Decalin*. A similar reaction in decalin (8 ml.) gave a mixture (0·58 g., 95%) in ratio 33 *cis* : 67 *trans*.

Stereochemical Assignments to the Tricarbonyl-(2-*methylindane*)*chromiums*.—Toluene-*p*-sulphonyl chloride (0·2 g) was added to *trans*-tricarbonyl-(2-hydroxymethylindane)-chromium (0·16 g.) in pyridine (4·4 ml.) at —5°. The mixture was kept at 0° for 24 hr. and then water (5 ml.) was added with stirring to the cold solution. The mixture was extracted with ether, the ether layer washed with 2N-hydrochloric acid, 10% potassium hydrogen carbonate solution, and water, dried ($MgSO_4$), and the ether evaporated. Crystallisation of the residue from light petroleum gave trans-*tricarbonyl*-(2-*toluene*-p-*sulphonyloxymethylindane*)*chromium* (0·22 g., 89%), m.p. 113—122° (Found: C, 55·0; H, 4·4. $C_{20}H_{18}CrO_6S$ requires C, 54·8; H, 4·1%). The ester (0·21 g.) in dry ether (100 ml.) was added during 30 min. to a stirred suspension of lithium aluminium hydride (0·2 g.) in dry ether (50 ml.). The mixture was refluxed for 12 hr., allowed to cool, and the excess of hydride decomposed with 2N-sulphuric acid (100 ml.). Isolation of the product in ether gave a yellow oil which was towered through alumina (150 g.) to give *trans*-tricarbonyl-(2-methylindane)chromium, m.p. and mixed m.p. 81—82·5°, from light petroleum.

Similar treatment of the *cis*-ester (0·1 g.) gave *cis*-tricarbonyl-(2-toluene-*p*-sulphonyloxymethylindane)chromium (0·14 g., 91%) as an unstable oil which was not further purified. Reduction of this oil (0·3 g.) and crystallization from light petroleum and chromatography on alumina gave *cis*-tricarbonyl-(2-methylindane)chromium (50 mg., 27%), m.p. 112—114°, mixed m.p. 111—113° with a sample obtained directly from 2-methylindane.

2-*Cyanoindane*.—(a) *Diglyme*. Hexacarbonylchromium (1·1 g.) and 2-cyanoindane (2·2 g.) were allowed to react in boiling ' diglyme ' (10 ml.) for 2 hr. Some flecks of yellow solid were seen. The cold mixture was diluted with chloroform (150 ml.) and filtered. The solvents were removed, the residue dissolved in benzene–ether, and chromatographed on alumina (350 g.). Elution with ether–light petroleum (1 : 1) gave trans-*tricarbonyl*-(2-*cyanoindane*)-*chromium* (0·7 g., 51%), m.p. 165—166°, from light petroleum–chloroform (Found: C, 56·0; H, 3·25; N, 5·2. $C_{13}H_9CrNO_3$ requires C, 55·9; H, 3·25; N, 5·0%). Elution with ether–methanol (9 : 1) gave cis-*tricarbonyl*-(2-*cyanoindane*)*chromium* (90 mg., 22%), m.p. 325° (decomp.), from light petroleum–chloroform (Found: C, 55·7; H, 3·1; N, 5·0%).

(b) *Cyclohexanol*. A reaction on the same scale in boiling cyclohexanol (10 ml.) gave the *trans*-isomer (0·74 g., 53%), and the *cis*-isomer (0·31 g., 22%).

The stereochemistry of the two isomers was assigned from their dipole moments: *cis*-compound, 8·61 D; *trans*-compound, 5·44 D in dioxan solution at 25° as measured by the method of Guggenheim and Smith.[23]

2-*Isopropylindane*.—(a) *Cyclohexanol*. Hexacarbonylchromium (1·1 g.) and 2-isopropylindane (1·6 g.) were refluxed in cyclohexanol (10 ml.) for 2·5 hr. Isolation in ether gave, after chromatography on alumina (100 g.) in light petroleum, a yellow oil (1·09 g., 77%) (Found: C, 60·85; H, 5·5. $C_{15}H_{16}CrO_3$ requires C, 60·8; H, 5·45%). Analytical gas chromatography at 187—188° showed two peaks with retention times 101 and 118 min. The relative peak areas were in the ratio 85 : 15. All attempts to isolate the pure individual isomers, either by column chromatography, preparative gas chromatography, or fractional crystallisation failed. The more easily eluted compound was tentatively assigned the *trans*-structure.

(b) *Diglyme*. A reaction on an identical scale in diglyme for 3·5 hr. gave an isomer mixture (1·14 g., 79%) of composition 21 *cis* : 79 *trans*. Another reaction in diglyme on twice the above scale for 2 hr. gave isomers (2·96 g., 94%) in ratio 20 *cis* : 80 *trans*.

(c) *Decalin*. Reaction in decalin (10 ml.) under the above conditions for 4·5 hr. gave an isomer mixture (0·13 g., 9%) in ratio 30 *cis* : 70 *trans*.

Methyl Indane-1-*carboxylate*.—(a) *Diglyme*. Hexacarbonyl chromium (1·1 g.) and methyl indane-1-carboxylate (3·57 g.) were heated in diglyme (10 ml.) for 1·5 hr. The crude product, isolated in ether, was chromatographed on alumina (350 g.). Elution with ether–light petroleum (1 : 19) gave methyl indane-1-carboxylate. Elution with ether–light petroleum (3 : 22) gave trans-*tricarbonyl*(*methyl indane*-1-*carboxylate*)*chromium* (0·37 g., 24%), m.p. 74—76° raised to 77° on recrystallization from ether–light petroleum (Found: C, 53·95; H, 3·65. $C_{14}H_{12}CrO_5$ requires C, 53·85; H, 3·9%). Further elution gave cis-*tricarbonyl*(*methyl indane*-1-*carboxylate*)*chromium* (0·63 g., 41%), m.p. 81—84° raised to 86·5° by recrystallisation from ether–light petroleum (Found: C, 53·55; H, 3·8%). The dipole moments of the isomers were determined in carbon tetrachloride solution at 25° by the method of Guggenheim and Smith.[23] The *trans*-isomer had a moment of 4·78 D and the *cis*-isomer 5·33 D.

(b) *Cyclohexanol*. A similar mixture in cyclohexanol (10 ml.) was refluxed for 2·75 hr. The above isolation procedure gave the *trans*-isomer (0·288 g., 18·4%) and the *cis*-isomer (0·377 g., 24%). When this reaction was repeated with a 5 hr. period the *trans*-isomer (0·45 g., 29%) and the *cis*-isomer (0·44 g., 28%) were obtained together with mixed fractions (0·13 g.). A small yellow band persisted at the top of the chromatography column. The alumina from the column was shaken with 6N-sulphuric acid (600 ml.) and the mixture extracted with ether. The ether extract was washed with water and dried ($MgSO_4$), and the ether evaporated. The residue (53 mg.), a yellow gum, was dissolved in ether and treated with excess of diazomethane in ether. The esters regenerated in this manner (the i.r. spectrum was almost identical with that of the original mixture) were combined with the mixed isomer fractions and rechromatographed to yield the *trans*-isomer (67 mg.) and the *cis*-isomer (74 mg.).

(c) *Decalin*. A reaction in decalin (10 ml.) was heated for 2·75 hr. and gave the *trans*-isomer (0·33 g., 21%) and the *cis*-isomer (0·74 g., 47%). A small amount of tricarbonyl-(indane-1-carboxylic acid)chromium (10 mg.) was isolated from the alumina column.

1-*Hydroxymethylindane*.—Hexacarbonylchromium (1·2 g.) and 1-hydroxymethylindane (2·6 g.) were refluxed in diglyme (40 ml.) in a Strohmeier apparatus for 3 hr. The products were isolated in ether and chromatographed on alumina (450 g.). Elution with ether–light petroleum (1 : 1) gave 1-hydroxymethylindane. Further elution with this mixture gave cis-*tricarbonyl*-(1-*hydroxymethylindane*)*chromium* (0·48 g., 30%), m.p. 91—92°, from ether–light petroleum (Found: C, 55·2; H, 4·4. $C_{13}H_{12}CrO_4$ requires

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[23] E. A. Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714: J. W. Smith, *ibid.*, 1950, **46**, 394.

C, 54·95; H, 4·25%). Elution with ether–light petroleum (4 : 1) gave trans-*tricarbonyl-*(1-*hydroxymethylindane*)*chromium* (0·48 g., 30%), m.p. 65—67° raised to 67—69° after one recrystallization from ether–light petroleum (Found: C, 54·95; H, 4·3%). Elution with ether–methanol (9 : 1) gave an unidentified yellow gum (93 mg.).

A second reaction with hexacarbonylchromium (1·5 g.), the alcohol (2·9 g.), and diglyme (40 ml.) for 2·5 hr. gave the *cis*-isomer (0·67 g., 35%), the *trans*-isomer (0·68 g., 35%), and an unidentified gum (0·14 g.).

1-*Methylindane*.—(a) *Decalin*. Hexacarbonylchromium (1·1 g.) and 1-methylindane (2·7 g.) were refluxed in decalin (10 ml.) for 5 hr., the product (1·0 g.) isolated in ether, and chromatographed on a long column of alumina (500 g., 1·8 m.). trans-*Tricarbonyl*-(1-*methylindane*)*chromium* (0·28 g., 21%), m.p. 45—47° from light petroleum (Found: C, 58·3; H, 4·4. $C_{13}H_{12}CrO_3$ requires C, 58·2; H, 4·5%) was eluted in the first fractions. Further elution with light petroleum gave mixed fractions (0·49 g.) as oils followed by cis-*tricarbonyl*-(1-*methylindane*)*chromium* (0·20 g., 15%), m.p. 101—102° from light petroleum (Found: C, 58·5; H, 4·7%).

A similar mixture was heated for 2 hr. and after chromatography on alumina gave an isomeric mixture (1·1 g., 82%) shown by g.l.c. at 158° to contain the *cis*- and *trans*-isomers in ratio 49 : 51.

(b) *Diglyme*. Hexacarbonylchromium (1·1 g.) and 1-methylindane (2·64 g.) were refluxed in diglyme (10 ml.) for 1·3 hr. The isomeric mixture (1·18 g., 88%) contained *cis*- and *trans*-isomers in ratio 53 : 47.

(c) *Cyclohexanol*. A reaction in cyclohexanol (10 ml.) with similar quantities to those above gave mixed isomers (1·04 g., 78%) in ratio 53 *cis* : 47 *trans*.

Assignments of Stereochemistry to the Tricarbonyl-(1-*hydroxymethyl- and* 1-*methylindane*)*chromiums*.—(a) *cis*-Tricarbonyl(methyl indan-1-carboxylate)chromium (0·5 g.) in dry ether (50 ml.) was added during 30 min. to a stirred suspension of lithium aluminium hydride (0·67 g.) in ether (50 ml.). The mixture was stirred overnight, refluxed for 2 hr., the excess of hydride destroyed with moist ether, and the solid products dissolved in sulphuric acid. The product was isolated in ether and filtered through a short column of alumina (10 g.) to yield *cis*-tricarbonyl-(1-hydroxymethylindane)chromium (0·27 g., 59%), m.p. 91—92°, mixed m.p. 92°, from ether–light petroleum. The *cis*-alcohol (0·2 g.) was treated at 0° for 4 hr. with toluene-*p*-sulphonyl chloride (0·201 g.) in dry pyridine (10 ml.). The mixture was taken up in ether (100 ml.) and washed with 2N-hydrochloric acid (6 × 50 ml.), 5% potassium hydrogen carbonate solution, and water, and dried ($MgSO_4$) and the ether removed. The ester was obtained as a gum (0·28 g.) which was not further purified but dissolved in dry ether (25 ml.) and added during 15 min. to a stirred suspension of lithium aluminium hydride (0·3 g.) in dry ether (25 ml.). The mixture was refluxed for 2 hr. and the product isolated as described above. The oil was dissolved in light petroleum and filtered through alumina (30 g.) to give *cis*-tricarbonyl-(1-methylindane)chromium (62 mg.), m.p. and mixed m.p. 101—102° from light petroleum.

(b) The *trans*-ester (0·15 g.) was reduced as above to give *trans*-tricarbonyl-(1-hydroxymethylindane)chromium, m.p. 67—69°, mixed m.p. 67—68°, from ether–light petroleum. A sample of this alcohol (0·19 g.) was converted into its toluene-*p*-sulphonate ester (0·3 g.), isolated as a yellow gum. The ester was reduced as above and after chromatography gave *trans*-tricarbonyl-(1-methylindane)chromium (59 mg.), m.p. and mixed m.p. 46—47° from light petroleum.

1-*Isopropylindane*.—(a) *Diglyme*. Hexacarbonylchromium (1·1 g.) and 1-isopropylindane (1·62 g.) were heated for 3 hr. in diglyme (10 ml.). The product (1·12 g.) was dissolved in a small amount of ether–light petroleum and chromatographed on a long column (1·8 m.) of alumina (500 g.). Elution with light petroleum gave initially trans-*tricarbonyl*-(1-*isopropylindane*)*chromium* (0·12 g.), m.p. 66—67° from light petroleum (Found: C, 61·0; H, 5·65. $C_{15}H_{16}CrO_3$ requires C, 60·8; H, 5·45%. Mixed fractions (0·87 g.) as yellow oils were next eluted. Finally light petroleum elution gave cis-*tricarbonyl*-(1-*isopropylindane*)-*chromium* (0·12 g.), m.p. 95—95·5° from light petroleum (Found: C, 60·7; H, 5·6). The n.m.r. spectrum of the more strongly absorbed compound showed four clearly resolved aromatic protons. On this basis this compound was assigned the *cis*-structure (see Part V).

A repeated mixture on a similar scale was heated for 2·5 hr. and gave a mixture of isomers (1·16 g., 78%) which were shown to be in ratio 20 *cis* : 80 *trans* by chromatography at 187°.

(b) *Cyclohexanol*. A mixture in cyclohexanol (10 ml.) was heated for 2·5 hr. and gave a mixture of isomers (0·97 g., 65%) in ratio 18 *cis* : 82 *trans*.

(c) *Decalin*. Reaction in decalin for 2·5 hr. gave isomers (1·14 g., 77%) in ratio 15 *cis* : 85 *trans*.

1-*Cyanoindane*.—(a) *Diglyme*. Hexacarbonylchromium (1·1 g.) and 1-cyanoindane (1·43 g.) were refluxed for 5 hr. in diglyme (10 ml.). The products were isolated from chloroform and chromatographed on alumina (400 g.). Elution with ether–light petroleum (3 : 17) gave 1-cyanoindane. Elution with ether–light petroleum (3 : 7) gave trans-*tricarbonyl*-(1-*cyanoindane*)*chromium* (0·27 g., 19·5%), m.p. 135—136° from chloroform–light petroleum (Found: C, 55·7; H, 3·4; N, 5·2. $C_{13}H_9CrO_3$ requires C, 55·95; H, 3·2; N, 5·0%). Elution with ether gave cis-*tricarbonyl*-(1-*cyanoindane*)*chromium* (0·47 g., 34%), m.p. 146—148° from chloroform–light petroleum (Found: C, 56·1; H, 3·2; N, 5·25%). The dipole moments of the two isomers measured in dioxan were 7·76 D for the *cis*-isomer and 3·02 D for the *trans*-isomer.

A repeated mixture which was heated for 2·75 hr. gave the *trans*-isomer (0·29 g., 21%) and *cis*-isomer (0·55 g., 39%).

(b) *Cyclohexanol*. A reaction on the above scale in cyclohexanol gave the *trans*-isomer (0·16 g., 12%), and the *cis*-isomer (0·35 g., 25%) after 3·25 hr.

Repetition gave *trans*-isomer (0·26 g., 18%) and *cis*-isomer (0·52 g., 37%) after 2·5 hr.

1-*Cyanomethylindane*.—Hexacarbonylchromium (0·55 g.) and 1-cyanomethylindane (0·78 g.) were refluxed in diglyme (12·5 ml.) for 2 hr. The mixture was pale yellow after 5 min. and became progressively orange, orange-red, and finally red-brown and was no longer clear. The product was isolated with ether and chromatographed on alumina (300 g.). Elution with ether–light petroleum (3 : 17) gave 1-cyanomethylindane. Elution with ether–light petroleum (1 : 3) gave a solid (0·78 mg.), m.p. 112—117°, which on recrystallisation from chloroform–light petroleum gave pale mustard-coloured plates of trans-*tricarbonyl*-(1-*cyanomethylindane*)*chromium* (31 mg.), m.p. 120—121° (Found: C, 57·8; H, 3·8; N, 5·1. $C_{14}H_{11}CrNO_3$ requires C, 57·4; H, 3·8; N, 4·8%). Further elution with the same solvent mixture gave mixed fractions (0·35 g.) as oils. Finally cis-*tricarbonyl*-(1-*cyanomethylindane*)*chromium* (0·12 g.), m.p. 108—110°, yellow prisms from chloroform–light petroleum (Found: C, 57·7; H, 4·1%), was eluted. The n.m.r. of the *cis*-isomer showed four resolved aromatic protons (see Part V).

A second reaction between hexacarbonylchromium (0·22 g.) and 1-cyanomethylindane (0·48 g.) in diglyme (10 ml.) for 2·5 hr. gave a mixture of tricarbonyl-(1-cyanomethylindane)chromiums (0·2 g., 67%). The isomers were calculated to be in ratio 57 *cis* : 43 *trans* from the n.m.r. spectrum and integral.

1-*Ethylsulphonylindane*.—Hexacarbonylchromium (1·1 g.) and 1-ethylsulphonylindane (2·1 g.) were refluxed in diglyme (10 ml.). After 1 hr. extensive decomposition had occurred and the mixture was allowed to cool. The oily product was dissolved in a small amount of chloroform and chromatographed on alumina (250 g.). Elution with ether–light petroleum (3 : 7) gave the starting sulphone. Elution with ether–light petroleum (1 : 1) gave trans-*tricarbonyl*-(1-*ethylsulphonylindane*)*chromium* (0·63 g., 39%) as yellow plates, m.p. 188—190° after crystallisation from ethyl acetate–light petroleum (Found: C, 48·3; H, 3·8; S, 8·9. $C_{14}H_{14}CrO_5S$ requires C, 48·55; H, 4·05; S, 9·25%). Elution with ether gave cis-*tricarbonyl*-(1-*ethylsulphonylindane*)*chromium* (56 mg., 3·2%) as yellow needles, m.p. 168—170° from ethyl acetate–light petroleum (Found: C, 48·7; H, 4·15; S, 8·9%). The n.m.r. spectrum of the *cis*-isomer again showed four clearly resolved protons.

A repeated mixture was heated for 2 hr. before decomposition became extensive. The *trans*-isomer (1·22 g., 70%) and the *cis*-isomer (49 mg., 3%) were obtained.

Equilibration Experiments.—The following attempted equilibration reactions shown in Table 4 were carried out by heating the isomer or the mixture of isomers (0·1 g.) under the described conditions. A thermostatted oil-bath was used and nitrogen was bubbled slowly through the solutions. The products were isolated and the isomer ratios determined as previously described.

TABLE 4

Compound	Solvent	No. of equivs. of ligand added	Time (hr.)	Temp.	Recovery (%)	Isomer ratio *cis* : *trans*
cis-Tricarbonyl-(1-cyanoindane)chromium	B	2·3	18	155°	57	66 : 34
	A	2·3	21·5	155	77	64 : 36
	B	0·0	6	150	94	100 : 0
trans-Tricarbonyl-(1-cyanoindane)chromium	B	2·3	7	Reflux	59	74 : 26
	A	2·3	7	Reflux	58	61 : 39
	A	0·0	6	150	96	0 : 100
cis-Tricarbonyl(methyl indane-1-carboxylate)chromium	B	2·8	16	150	85	48 : 52
	B	2·8	21	150	65	51 : 49
trans-Tricarbonyl-(2-cyanoindane)chromium	A	2·0	4	Reflux	64	27 : 73
	B	2·0	4	Reflux	51	22 : 78
cis-Tricarbonyl-(1-methylindane)chromium	B	2·4	36	Reflux	[a]	51 : 49
	B	0·0	16	150	[a]	100 : 0
trans-Tricarbonyl-(1-methylindane)chromium	B	2·4	64	Reflux	[a]	48 : 52
	A	2·4	64	Reflux	[a]	49 : 51
	C	2·4	64	160/65	[a]	46 : 54
	B	0·0	16	150	[a]	0 : 100
trans-Tricarbonyl-(1-isopropylindane)chromium	B	2·7	36	Reflux	[a]	18 : 82
	A	2·7	36	Reflux	[a]	19 : 81
	C	2·7	36	165	[a]	14 : 86
	B	0·0	5	150	[a]	0 : 100
trans-Tricarbonyl-(2-methylindane)chromium	A	0·0	17	150	[a]	0 : 100
	C	0·0	21	170	[a]	0 : 100
	B	2·0	30	150	[a]	15 : 85
	A	2·0	26	150	[a]	10 : 90
trans-Tricarbonyl-(2-hydroxyindane)chromium	B	2·0	24	150	58	22 : 78
trans-Tricarbonyl-(2-acetoxyindane)chromium	A	4·0	2·5	Reflux	42	44 : 56
	C	4·0	2·5	Reflux	62	25 : 75
cis-Tricarbonyl-(2-acetoxyindane)chromium	A	4·0	2·5	Reflux	62	68 : 32
	C	4·0	2·5	Reflux	69	63 : 37

[a] Not measured; the solution was injected on to a gas chromatograph.

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