

Effects of Non-bonded Substituents on the *cis-trans*-Equilibrium Ratios of Tricarbonyl(indane)chromiums

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REACTIONS between hexacarbonylchromium and 1- or 2-substituted indanes (I; R=OH, Me, CN, CO₂Me) for 1.5—5 hours in boiling cyclohexanol gave *cis*- (II) and *trans*- (III) tricarbonylchromium compounds in combined yields of 60—90%.

Isomer ratios, determined by chromatography on alumina or by gas chromatography for the methyl-indane complexes, were reproducible to $\pm 3\%$. The configurations of the complexes (II and III; R=OH) were assigned earlier;¹ those of the cyano- and methoxycarbonyl compounds were obtained from their dipole moments, *e.g.* 7.6 and 3.2D in dioxan for the *cis*- and *trans*-1-cyano-complexes. The structures of the methyl substituted isomers were established by preparing them from individual methoxycarbonyl compounds (*via* CH₂OH, CH₂OTs).

The *cis:trans* ratios obtained represent the relative thermodynamic stability of each of the pairs of isomers, because separate experiments showed that individual isomers (1-CN; 2-OH; 2-Me; 2-CN) come to equilibrium under the conditions used (free ligand present in solution). In the absence of free organic ligand, individual

TABLE

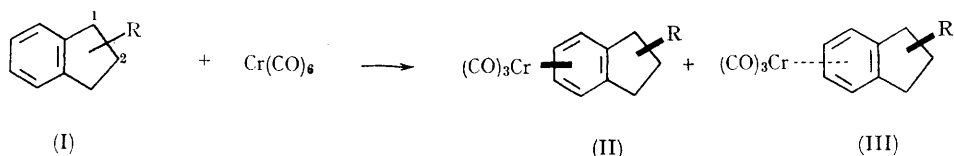
Substituent	<i>cis:trans</i> Ratios	
	1-Substituted indanes	2-Substituted indanes
OH	46 : 54	22 : 78
Me	53 : 47	16 : 84
CO ₂ Me	57 : 43	31 : 69
CN	67 : 33	(30 : 70)*

* The reaction solution did not remain clear.

¹ W. R. Jackson and C. H. McMullen, *J. Chem. Soc.*, 1965, 1170.

isomers were recovered unchanged after being heated in boiling cyclohexanol or decalin (five experiments). This result would not be expected

1-substituted complexes, the ratio changes towards a preference for *cis*-compounds at equilibrium. The possibility that the latter trend may be



on the basis of the kinetic scheme proposed for the equilibration of [¹⁴C]benzene and tricarbonyl(benzene)chromium in heptane at 140—180°. ²

Results obtained from the fairly rigid indane system should provide information concerning the intramolecular interactions possible between a metal carbonyl group and typical organic functional groups. To date they indicate that *trans*-are more stable than *cis*-compounds in the 2-substituted series, and that, in going from 2- to

reversed when bulky alkyl groups are present as substituents is being examined.

The ratios also depend on the solvent, although these variations do not alter the general trends noted above. For example, the proportion of *trans*-2-methylindane complex at equilibrium falls from 84% (cyclohexanol), to 69% (diglyme) and 67% (decalin).

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² W. Strohmeier and H. Mittnacht, *Z. phys. Chem. (Frankfurt)*, 1961, **29**, 339.