Restricted Rotation in Some Tricarbonyl(arene)chromium Compounds

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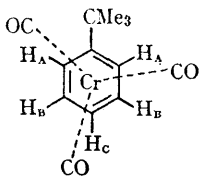
THE aromatic protons of tricarbonyl(isopropylbenzene)chromium have an n.m.r. spectrum which is temperature-dependant.* At 30° the five protons appear as a singlet at τ 4·82 but at −15° a multiplet is obtained. A spectrum in deuterochloroform at −40° showed a broad multiplet (*ca.* 6 peaks) with outer peaks separated by τ 0·17. This multiplet again collapsed to a singlet at 30°. The aromatic protons of tricarbonyl(t-butylbenzene)chromium appeared as a doublet and two triplets at τ 4·55 (2 protons), 4·76 (1 proton), and 4·88 (2 protons) respectively and the spectrum remained unchanged over the range +50 to −15° (−40° in deuterochloroform). The results have been provisionally interpreted in terms of severe restriction of rotation of the chromium–arene bond in tricarbonyl(t-butylbenzene)chromium and less severe restriction in tricarbonyl(isopropylbenzene)chromium.

Tricarbonyl(t-butylbenzene)chromium may be restricted to a conformation (I). The A-protons are deshielded by the superimposed carbonyl groups, relative to the value for tricarbonyl(isopropylbenzene)chromium, while the B-protons are

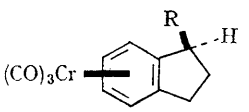
* Spectra were determined at 100 Mc./sec. in *ca.* 5% solutions in carbon tetrachloride. When spectra were determined in deuterochloroform, similar results were obtained but at slightly lower τ-values (τ0—0·15).

relatively shielded. The coupling constants $J_{AB} = J_{BC} = 6{\cdot}5$ c./sec. provided no evidence for bond fixation in the aromatic ring system. The aromatic protons in other tricarbonyl(arene)-chromiums with substituents of a bulky nature were similarly well resolved, *e.g.*, in *cis*-tricarbonyl-(1-methyl-, 1-hydroxymethyl-, and 1-isopropyl-indane)chromiums (II) and in, 1,3-di-t-butyl-benzene. Molecular models, constructed with the aid of previously-determined molecular dimensions for tricarbonyl(arene)chromium compounds,[1,2] were in agreement with the above proposals.

Attempts are being made to determine the barrier to rotation in tricarbonyl(isopropylbenzene) chromium and to investigate possible chemical consequences of the proposed fixed conformation of the tricarbonylchromium group in tricarbonyl-(t-butylbenzene)chromium.



(I)



(II)

(*Received, February 28th*, 1966; *Com.* 131.)

[1] P. Corradini and G. Allegra, *J. Amer. Chem. Soc.*, 1959, **81**, 2271.
[2] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1314.