The Acetylation of Tricarbonyl-(*trans*-1,3-dimethylindane)chromium

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ACETYLATION of tricarbonyl-(*trans*-1,3-dimethylindane)chromium (I), followed by chromatography of the product on alumina, gave a mixture of the diastereoisomeric acetyl compounds (IIa) and (IIb) (14%) in which the isomer (IIa) predominated by a factor of *ca.* 9:1. Recrystallisation of a portion (100 mg.) of the crude mixture gave pure (IIa) (40 mg.), m.p. 163—164°. Other products isolated were: recovered (I) (60%); a small amount (1·5%) of the 4- and 7-acetyl compounds; and 5-acetyl-*trans*-1,3-dimethylindane. The stereoselectivity in the kinetically controlled acetylation reaction[1] must arise from a dissymmetric interaction of the tricarbonylchromium residue with the transition states leading to (IIa) or (IIb), as electronic interactions of the alicyclic ring must be symmetrical towards reactions at C-5 or C-6. This stereoselectivity clearly demonstrates the conformational influence of metal bonding on ligand reactivity.

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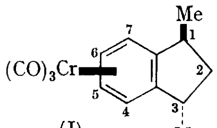
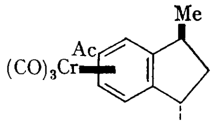
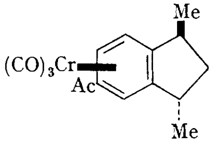
The n.m.r. spectrum of tricarbonyl-(*trans*-1,3-dimethylindane)chromium can be interpreted in terms of the tricarbonylchromium residue adopting a preferred conformation as in (III) owing to non-bonded interaction[2] with the *cis*-methyl group at C-1. The proton assignments are then H-7, τ 4·57 (doublet); H-5, τ 4·64 (triplet); H-4, τ 4·88 (doublet); and H-6, τ 5·0 (triplet). Previous work has shown that protons lying under superimposed metal–carbonyl bonds are deshielded relative to those in the alternant, exposed positions.[2] The protons H-5 and H-6 could be expected to have very similar τ values in the absence of conformational effects in the tricarbonylchromium residue as the effects of intrinsic asymmetry have been shown to be extremely small for proton spectra.[3]



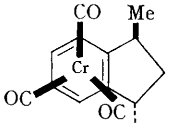
(I)



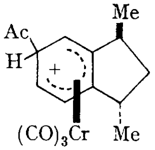
(IIa)



(IIb)



(III)



(IV)

The stereoselectivity in the acetylation reaction could be associated with adverse steric interactions between the superimposed carbonyl group and the transition state for acetylation at C-5, if the molecule reacts predominantly in conformation (III).[1] Alternatively the transition state may involve a displacement of the chromium atom away from the incipient tetrahedral carbon atom, in which case displacement towards the *trans*-methyl group would be favoured as in (IV), leading to preferential formation of (IIa).‡

The stereochemistry of the diastereoisomeric acetyl compounds (IIa) and (IIb) was assigned from the following n.m.r. data. The major component had three aromatic protons H-7, τ 3·88 (singlet); H-5, τ 3·92 (doublet); and H-4, τ 4·88 (doublet). The minor component had H-7, τ 4·62 (doublet); H-6, τ 4·21 (doublet); and H-4, τ 4·12 (singlet). The protons H-7 and H-5 in the major component (IIa) are deshielded both as a result of the superimposed metal–carbonyl bond and by the *ortho*-acetyl group, whereas H-4 is *meta* to the acetyl group and does not have a superimposed metal–carbonyl bond. In the minor isomer the two effects are now in opposition, *i.e.* the non-superimposed protons are *ortho* to the acetyl group, thus leading to a much smaller spread of τ values. The n.m.r. spectrum of the mixture of 4- and 7-acetyl compounds (ratio 1·5 : 1) was interpreted in a similar manner. The diastereoisomer ratio in this case cannot be interpreted solely in terms of the conformational influence of the tricarbonylchromium residue as the neighbouring methyl group can exert a different steric effect in the isomeric transition states§

The absence of thermodynamic effects in the acetylation ratio was also suggested by a reaction of 5-acetyl-*trans*-1,3-dimethylindane with hexacarbonylchromium in boiling diglyme. A mixture of (IIa) and (IIb) in the ratio 1·2 to 1 was obtained, which indicates that the thermodynamic stability of the isomers is similar under these conditions where the product ratio is equilibrium controlled.[4]

(*Received, January* 1*st*, 1968; *Com.* 002.)

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‡ We thank Dr. R. Pettit, University of Texas, for this suggestion.

§ In the acetylation of (I) at C-4 the neighbouring methyl group is *trans* to the tricarbonylchromium residue, whereas for reaction at C-7 the neighbouring methyl group is *cis*.

[1] W. R. Jackson and W. B. Jennings, *Chem. Comm.*, **1966**, **824**; G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *J. Amer. Chem. Soc.*, **1964, 86,** 2203.

[2] *Cf.* D. E. F. Gracey, W. R. Jackson, W. B. Jennings, S. C. Rennison, and R. Spratt, *Chem. Comm.*, **1966, 231.** Spectra were measured in $CDCl_3$ solution at 100 MHz.

[3] G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Amer. Chem. Soc.*, **1964, 86,** 2628.

[4] W. Strohmeier and E. H. Staricco, *Z. phys. Chem.* (*Frankfurt*), 1963, **38,** 315 and references therein; D. E. F. Gracey, H. B. Henbest, W. R. Jackson and C. H. McMullen, *Chem. Comm.*, 1965, 566.