

## Stereoelectronic Control of the Regioselectivity of both Electrophilic and Nucleophilic Substitution of $\eta^6$ -(1,1-Dimethylindane)tricarbonylchromium(0)

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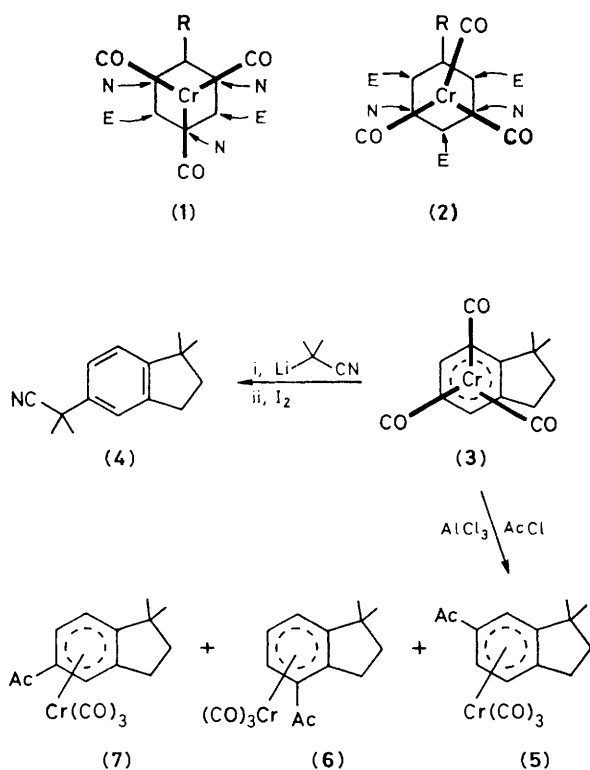
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$\eta^6$ -(1,1-Dimethylindane)tricarbonylchromium(0) reacts with the nucleophile  $\text{LiC}(\text{Me})_2\text{CN}$  at C-5, a position eclipsed by a metal carbonyl bond in the preferred conformation of the molecule, and at C-6 and C-4, positions not eclipsed by metal carbonyl bonds with the electrophile  $\text{MeCO}^+$ , confirming that stereoelectronic effects can dominate the regioselectivity of substitution of arenetricarbonylchromium complexes where the tricarbonylchromium unit adopts a highly preferred conformation.

There is a general correlation between the site of addition of nucleophiles to arene- $\text{Cr}(\text{CO})_3$  complexes and the magnitude of the coefficients at the arene ligand in the lowest energy unoccupied molecular orbital (LUMO) of the complex (and of the free arene ligand).<sup>1</sup> A clear exception to this correlation is the preferred reaction at the *para* position of *t*-butylbenzene- $\text{Cr}(\text{CO})_3$  with the anion  $\text{LiC}(\text{CN})(\text{OR})\text{Me}$ .<sup>1</sup> This special selectivity becomes more significant in the light of the study which showed that while electrophilic addition to alkylarene- $\text{Cr}(\text{CO})_3$  complexes tended to occur in the usual *o/p* directions, *t*-butylbenzene- $\text{Cr}(\text{CO})_3$  again was special, showing a high preference for *meta* substitution.<sup>3</sup> One consistent feature in this behaviour is that where the  $\text{Cr}(\text{CO})_3$  unit adopts a highly

preferred conformation, either for steric reasons or for electronic reasons,<sup>2</sup> then reaction with an electrophile (E) will occur at carbon atoms not eclipsed by metal-carbonyl bonds whereas reaction with a nucleophile (N) will occur at carbon atoms eclipsed by metal-carbonyl bonds.<sup>4</sup>

Recent work with a tricarbonyl-( $\eta^6$ -indane)chromium(0) in which the tricarbonyl chromium residue adopts a highly preferred conformation for steric reasons has confirmed that nucleophilic substitution occurs at a carbon atom eclipsed by a chromium-carbonyl bond [(1) and (2)].<sup>5</sup> No systematic study of both electrophilic and nucleophilic substitution reactions in a single compound with highly preferred conformation appears to have been reported. We report the preparation



of such a molecule in tricarbyl-( $\eta^6$ -1,1-dimethylindane)-chromium(0) (3) and its reaction with the electrophile Ac<sup>+</sup> and the nucleophile LiC(Me)<sub>2</sub>CN.<sup>1</sup>

The complex (3) was prepared in high yield from hexacarbonylchromium and 1,1-dimethylindane using the method of Pauson.<sup>6</sup> The <sup>1</sup>H n.m.r. spectrum of (3) at 90 MHz was in agreement with previous work<sup>7</sup> and was very similar to the spectrum reported previously for (*trans*-1,3-dimethylindane)-tricarbylchromium.<sup>8</sup> It was consistent with the tricarbylchromium residue adopting the preferred conformation (3) in which 4-H and 6-H are shielded relative to 5-H and 7-H.

Reaction with LiC(Me)<sub>2</sub>CN followed by oxidation with iodine of the initially formed anion<sup>9</sup> gave 1,1-dimethyl-5-(2'-cyanoprop-2'-yl)indane (4) in good yield (70%). A single isomer was shown by g.l.c. to predominate (>90%) in the reaction mixture. The structure was clearly established as the 5-substituted isomer (4) on the basis of <sup>3</sup>J(C,H) values determined by <sup>13</sup>C n.m.r. spectra recorded with gated decoupling and by a study of nuclear Overhauser effects in a 250 MHz <sup>1</sup>H n.m.r. of the compound.<sup>†</sup> This reaction has occurred almost exclusively at an eclipsed carbon atom.

The predominant formation of a 5-substituted isomer was almost certainly caused by nucleophilic attack at a carbon which is eclipsed by a chromium-carbonyl bond as depicted in (3). It was presumed that the lack of attack at C-7, which is similarly eclipsed by a chromium-carbonyl bond was due to adverse steric interactions with the *gem*-dimethyl group at C-1. This raised the possibility that the lack of substitution at C-6 in this work was due to adverse steric effects between a nucleophile approaching C-6 and the *gem*-dimethyl group, leaving attack at C-5 as the preferred substitution path. This unlikely possibility was eliminated by a study of the Friedel-Crafts acetylation of (3).

Reaction of (3) with the acetyl chloride-aluminium chloride Perrier complex in dichloromethane for 1.5 h at 20 °C, followed by flash chromatography on silica gave a mixture of

acetyl dimethylindanes (5%), tricarbyl-( $\eta^6$ -acetyl-1,1-dimethylindane)chromiums (63%), and recovered starting material (3), (34%). The <sup>1</sup>H n.m.r. spectrum of the acetylated complex<sup>†</sup> was consistent with the presence of three isomeric acetyl compounds<sup>3</sup> in approximate ratio 65[6-Ac (5)] to 30 [4-Ac (6)] to 5[5-Ac (7)]. Similar ratios were obtained by oxidative removal of the tricarbylchromium residue and g.l.c. of the acetylindanes. The ratios were found to be independent of the yields of acetyl complexes in the range 6–63%. The product ratios show that more than 90% of electrophilic attack on (3) has occurred at C-4 and C-6, positions which are not eclipsed by chromium-carbonyl bonds. The structure assignments of the tricarbyl(acetyl-1,1-dimethylindane)chromiums were based on the n.m.r. spectra<sup>‡</sup> which showed features similar to those of the compounds obtained by acetylation of tricarbyl(*trans*-1,3-dimethylindane)chromium. An authentic sample of a mixture of (5) and (7) was prepared by Friedel-Crafts acetylation of 1,1-dimethylindane and reaction of the resulting mixture of 5- and 6-acetyl compounds with hexacarbonylchromium.

The dominance of conformational effects in directing the regioselectivity of attack of both electrophilic and nucleophilic reagents is thus clearly established.<sup>10</sup> It is interesting that stereoelectronic effects can overcome the normal preferences and promote electrophilic attack at the 4-position of the indane ring. It should be noted that apparently simple steric effects can differentiate between two positions of attack on a tricarbyl-( $\eta^6$ -arene)chromium as in the differentiation between C-5 and C-7 shown by nucleophilic attack in this work.

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<sup>†</sup> Full details of structure assignments will be presented in a full publication.

<sup>‡</sup> <sup>1</sup>H N.m.r. (90 MHz): (5)  $\delta$  6.12 (s, 7-H), 6.03 (d, 5-H), and 5.17 (d, <sup>3</sup>J<sub>ortho</sub> 6.4 Hz) (most abundant); (6)  $\delta$  5.96 (d, 5-H), 5.67 (d, 7-H), and 5.08 (t, 6-H, J<sub>ortho</sub> 6.0 Hz) (second most abundant); (7)  $\delta$  5.94 (s, 4-H), 5.80 (d, 6-H), and 5.37 (d, 7H, J<sub>ortho</sub> 6.7 Hz) (least abundant isomer).