Complete Reversal of Stereoselectivity in Cyclopropanation of 2-Arylidene-1-tetralone Tricarbonylchromium Complexes

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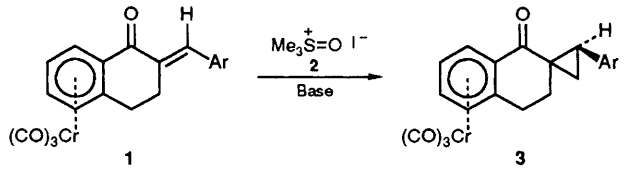
Cyclopropanation of 2-arylidene-1-tetralone tricarbonylchromium complexes with dimethylsulfoxonium methylide under phase-transfer catalysis condition provided cyclopropanes exclusively from the *endo*-face.

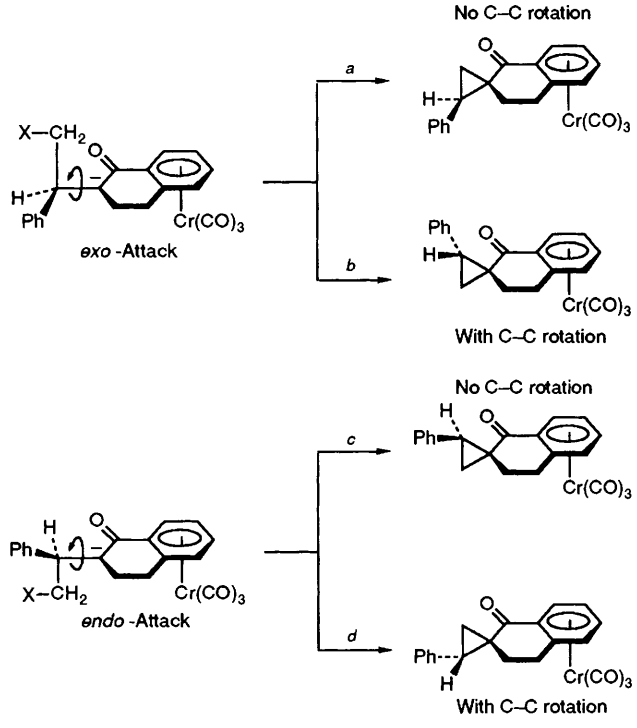
Arene–tricarbonylchromium complexes have found considerable utility in organic synthesis.[1] The tricarbonylchromium unit is often used as a stereoface-directing group whereby a reagent preferentially approaches the substrate from the face away from the metal.[2] The steric bulk of the $Cr(CO)_3$ is sufficient to make such stereocontrol effective. Recent results[3] have shown that the effect can be realised even two or three carbon atoms away from the metal-complexed aromatic ring. We report here a rare instance where a nucleophilic reagent is delivered exclusively from the same face as that occupied by the metal, in direct contrast with the established trend.

When the sulfoxonium ylide **2** was allowed to react with the benzylidenetetralone tricarbonylchromium complexes **1a–c** under phase-transfer catalysis (PTC) conditions[4] in refluxing



Ar	Yield (%) of **3**
a: Ph	87
b: *p*-MeC_6H_4	84
c: *p*-$MeOC_6H_4$	77

Scheme 1



Scheme 2

dichloromethane, the cyclopropanated complexes **3a–c** were obtained in good yield† (Scheme 1). The structures were tentatively deduced from their IR and ^1H–^{13}C NMR data. The cyclopropanation proceeded with excellent stereocontrol and a single diastereoisomer of the product could be detected in each case (200 MHz ^1H NMR). Although the peaks and connectivity could be assigned from the NMR data *via* spin correlation (COSY and HETCOR), the stereochemistry of cyclopropanation was not immediately apparent. The uncomplexed 2-benzylidene-1-tetralone did not undergo any reaction under identical conditions.

Four possible diastereoisomeric products may be formed as depicted in Scheme 2, as a result of *exo*- or *endo*-attack on the enone system. It can be clearly seen that the pathway leading to the product would determine the stereochemical relationship between the phenyl, carbonyl and methylene groups. In order to establish such spatial relationship without ambiguity, the structure of the compound **3a** was determined[5] by single-crystal X-ray diffraction.

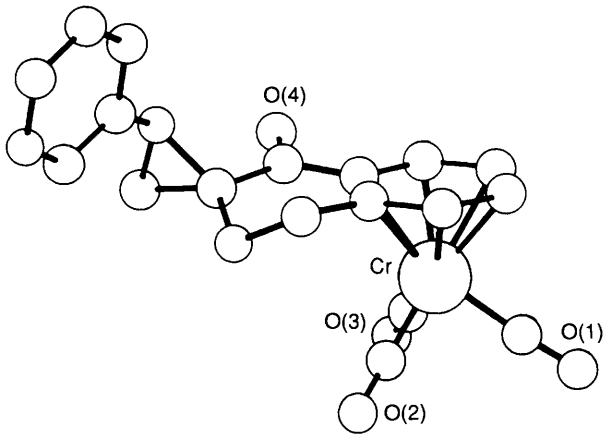


Fig. 1 Crystal structure of complex **3a**

The X-ray diffraction analysis‡ revealed that the cyclopropane was appended from the same face of the molecule as occupied by the $Cr(CO)_3$ group. The PLUTO diagram of **3a** is displayed in Fig. 1. The product has resulted from an unusual *endo*-attack (path *c* in Scheme 2).

It is generally accepted that sulfoxonium ylides react with a double bond activated by an electron-withdrawing group in a manner similar to conjugate nucleophilic addition.[6] Conjugate addition to 2-arylidene-tetralones complexed with $Cr(CO)_3$ has been shown[3a] to proceed with exclusive *exo*-attack.§ The reason for the *endo*-selectivity in the present case is not obvious. An explanation for this unusual stereochemical result should be based on the following two assumptions: (*i*) the attack of the sulfur ylide is reversible, and (*ii*) the ring closure of the *endo*-adduct is fast enough to shift the equilibrium in its favour.¶ Thus, the cyclopropanes **3a–c** are kinetic products. No change in stereoselectivity was observed when the enone **1a** was allowed to react with a homogeneous ylide solution in tetrahydrofuran at room temperature overnight.

To the best of our knowledge, this is the first example of *endo*-selective nucleophilic addition to arene–chromium complexes.

† *Typical procedure*: To a solution of **1a** (1 mmol), trimethylsulfoxonium iodide (1 mmol) and tetrabutylammonium bromide (2 mol%) in degassed dichloromethane (10 ml) was added 50% aq. NaOH (10 ml) and the mixture was heated under reflux for 16 h (argon atmosphere). The product was isolated by usual work up followed by flash chromatography on silica gel (20% ethyl acetate–hexane) as orange crystals. IR ($CHCl_3$): ν/cm^{-1} 1990, 1920 and 1670; ^1H NMR (200 MHz, $CDCl_3$): δ 1.35–1.55 (m, 2H), 2.15–2.80 (m, 5H), 5.1 (d, *J* 6 Hz, 1H), 5.3 (t, *J* 7 Hz, 1H), 5.6 (dt, *J* 6 Hz, 1 Hz, 1H), 6.2 (dd, *J* 6, 1 Hz, 1H) and 7.3 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 18.3, 24.6, 26.4, 33.3, 37.1, 89.4, 90.2, 90.6, 93.1, 94.0, 115.2, 127.1, 128.2, 128.9, 136.0, 195.8 and 230.9. Elemental analyses were satisfactory.

‡ *Crystal data* for **1a**: monoclinic space group $P2_1/n$, a = 7.616(2), b = 10.100(2), c = 22.916(2) Å, β = 95.92(1)°, V = 1753.4 Å^3, D_c = 1.456 Mg m^{-3}, Z = 4, μ(Mo-Kα) = 0.66 mm^{-1}. 2809 Reflections were recorded on an Enraf-Nonius CAD4 diffractometer [ω–2θ mode, θ_{max} = 23.5°, Mo-Kα radiation (λ = 0.70930 Å), graphite monochromator]. 2586 Unique reflections. Solution by direct methods (MULTAN-80, The NRCVAX Crystal Structure System, PC version[5]). All non-hydrogen atoms were refined anisotropically. H-atoms were included with a common thermal parameter but were not refined. Using 235 parameters R = 0.038, R_w = 0.033 for 1723 'observed' reflections with $F > 2.5\sigma(F)$. $\Delta\rho_{fin}$ (max./min.) = 0.47/−0.29 e Å^{-3}. Absorption corrections were not applied. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The *exo*-attack of nitromethane[3a] has been conclusively established by an X-ray structure determination: R. D. Willett, S. Ganesh and A. Sarkar, unpublished results.

¶ We thank a referee for suggesting this possibility.

The faster rate of cyclisation of the *endo* adduct (compared with the *exo* adduct) would be consistent with the relief of unfavourable steric interaction between the metal carbonyl fragment and the sulfoxide group in this intermediate.

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