Organometallic Photochemistry with Circularly Polarized Light. Synthesis of Optically Active Tropone–Iron Tricarbonyl Complex by Asymmetric Destruction

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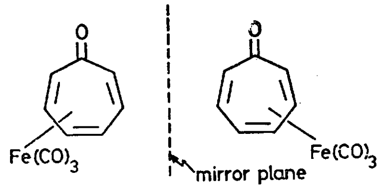
Summary Irradiation of tropone–Fe(CO)$_3$ complex (**1**) with left or right circularly polarized light at λ 380—500 nm induces stable optical activity in the complex by an asymmetric destruction process.

Although the resolution of chiral organometallic compounds has recently become a subject of considerable interest,[1] the related asymmetric induction in co-ordinated compounds by circularly polarized light (C.P.L.)[2] has not received similar widespread attention. Until the present time the use of C.P.L. to induce optical activity in co-ordination compounds has been limited to the partial photoresolution of tris(bidentate ligand) chromium(III) complexes.[3,4] Since the metal co-ordination in organometallic compounds often induces inherent dissymmetry in the organic ligand, it was expected that chiral organometallic complexes will have high rotational strength,[5] comparable to that of the widely studied helicenes.[2] We report here the first example of asymmetric induction in transition metal organometallic compounds by asymmetric destruction photolysis with C.P.L.



(1)

The possible existence of tropone–Fe(CO)$_3$ (**1**)[6] in two enantiomeric forms was first noted by Weiss and Höbel[7] but its resolution has never been achieved. It was later shown by ^{1}H n.m.r. spectroscopy that tropone–Fe(CO)$_3$,[6,8] as well as cycloheptatriene–Fe(CO)$_3$,[9] are non-fluxional compounds at room temperature. Eisenstadt has also noted that no interconversion of tropone–Fe(CO)$_3$ enantiomers occured between 40—120 °C.[10]

Our experimental set up consisted of a high pressure mercury lamp (Conrad Hanovia 450 W) whose light was filtered through an aqueous CuSO$_4$–NH$_3$ solution.[11] The isolated beam in the 380–500 nm region overlapped the weak absorption peak of the complex at 435 nm. This beam was collimated by a Spectrosil B lens (50 mm diameter, 200 mm focal length) and was converted into linearly polarized light by a Glan Taylor quartz prism. A Fresnel Rhomb retarder made of fused silica served as a quarter wave plate to convert the linearly polarized light into circularly polarized light, keeping the phase retardation almost independent of wavelength over a large wavelength range.

Irradiation of (**1**) in n-hexane solution for 6 h in a 1 cm cell, yielded α_D (observed) of $+0{\cdot}012 \pm 0{\cdot}002°$. At shorter irradiation times, a smaller α_D was observed although it was always clear that the observed rotation was larger than $\pm 0{\cdot}002°$, the polarimeter (Perkin Elmer 141) sensitivity limit. When the solution was irradiated by left C.P.L. for *ca.* 6 h the observed α_D was $-0{\cdot}010 \pm 0{\cdot}002°$.

Separation by t.l.c. of the irradiated mixture followed by polarimetric analysis of the various fractions has verified that the source of optical activity resided in the substrate fraction. Thus clearly, one enantiomer of the tropone complex is preferentially destroyed during irradiation.

The extent of the photolytic destruction after 6 h of irradiation was 3%, calculated from the difference in the absorption at 435 nm before and after photolysis. Assuming an optical yield of 0·5%, as compared with the helicenes[12] and other related systems studied so far,[13] a specific rotation of 700° for the pure enantiomer has been calculated. This value corresponds reasonably to systems with inherent asymmetry.[5]

The observation of stable optical activity in (**1**) provides a confirmation for the existence of chirality in the molecule, induced by metal co-ordination and substantiates previous findings[6,8,10] which exclude racemization *via* interconversion of the two enantiomers.

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