

Asymmetric Induction in Cyclopropanation with Homogeneous and Immobilized Chiral Metal β -Diketonate Catalysts

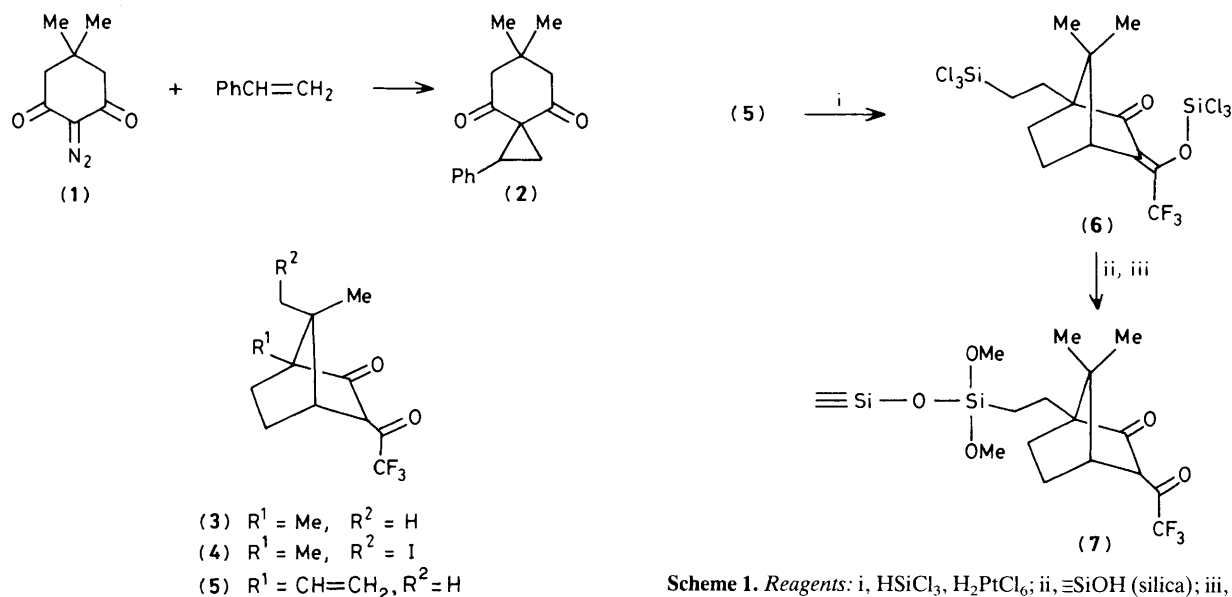
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Copper complexes of 3-trifluoroacetyl-(+)-camphor and two of its derivatives give high optical yields when used as catalysts for the asymmetric cyclopropanation of styrene with 2-diazodimedone; an immobilised analogue of these homogeneous catalysts retains high activity, is readily recovered, and has potential for recycling.

Despite the importance of asymmetric induction in organic synthesis¹ and the high degree of asymmetric induction which has been observed in reactions using chiral catalysts, such as asymmetric hydrogenation² and hydrosilylation,³ little work has been done on asymmetric cyclopropanations using chiral catalysts. A few types of catalyst for this reaction have been reported, involving chiral metal complexes of tribornyl

phosphite⁴ (low optical yields), camphorquinone dioximes⁵ (up to 88% optical yield), and salicylaldehyde imine derivatives⁶ (up to 90% enantiomeric excess). Although β -diketone complexes such as $\text{Cu}(\text{acac})_2$ (acacH = acetylacetonone) are amongst the most popular catalysts for cyclopropanation reactions of alkenes with diazo compounds, none of the asymmetric cyclopropanation catalysts reported hitherto has

Scheme 1. Reagents: i, HSiCl₃, H₂PtCl₆; ii, ≡SiOH (silica); iii, MeOH.Table 1. Reactions of 2-diazodimedone (1) with styrene.^a

Catalyst	Reaction time ^b	Yield ^c of (2)/%	Enantiomeric excess ^d
Cu(acac) ₂	16 h	54	0
Cu(facam) ₂	24 h	36	91.7
Cu(9-iodofacam) ₂	32 h	21	73.3
Cu(10-methylenefacam) ₂	24 h	48	100

^a 3 mmol (1) and 20 mg catalyst refluxed in styrene (15 ml) and benzene (45 ml). ^b Monitored by disappearance of diazo band at 2140 cm⁻¹. ^c Yield of pure product isolated by preparative t.l.c. ^d Optical purity was established by n.m.r. using a chiral shift reagent.

involved a chiral β-diketone. We now report that complexes of a commercially available, chiral β-diketone and some related compounds serve as useful asymmetric induction catalysts and that an immobilized, silica-bonded version of this type of catalyst offers additional advantages in terms of ease of recovery and the potential for catalyst recycling.

The reaction of styrene with 2-diazodimedone (1) using Cu(acac)₂ as catalyst afforded the cyclopropane (2) in 54% yield as a racemic product.† When the reaction was repeated with Cu(facam)₂ [facamH = 3-trifluoroacetyl-(+)-camphor (3)], the cyclopropane obtained was optically active. Similar results were obtained with the copper complexes of two other camphor derivatives, 9-iodo-3-trifluoroacetyl-(+)-camphor [9-iodofacamH (4)] [prepared by trifluoroacetylation⁷ of 9-bromo-(+)-camphor⁸ followed by iodide displacement⁹ on the bromide] and 10-methylene-3-trifluoroacetyl-(+)-camphor [10-methylenefacamH (5)] [from trifluoroacetylation of 10-methylene-(+)-camphor¹⁰]. Of the three chiral complexes, the latter gave the best results in terms of both yield and optical purity (Table 1).

Attention was then directed to the preparation of an immobilized form of the chiral metal β-diketone catalyst. Hydrosilylation¹¹ of the vinyl β-diketone (5) afforded the disilylated compound (6), which was then reacted with Hypersil 5 μm silica under the usual conditions.¹¹ Methanoly-

sis of the silylated β-diketone function followed by capping of residual silanol sites on the silica using trimethylsilyl chloride then gave the silica-bonded trifluoroacetyl-(+)-camphor (7) (Scheme 1).

Microanalysis indicated a surface coverage corresponding to 0.27 mequiv. g⁻¹. The immobilized β-diketone readily complexed a variety of metal cations; reaction with Cu(OAc)₂ led to an uptake of 0.14 mequiv. g⁻¹ in the form of the β-diketone as shown by photoacoustic spectroscopy.¹² The same complex was formed when the immobilized β-diketone (7) was exposed to copper acetate solution in the presence of an excess of 3-trifluoroacetyl-(+)-camphor; there was no additional uptake of Cu²⁺, nor was there any increase in the organic content of the immobilized phase. These results indicated that the bonded phase must be supplying both of the β-diketone groups necessary for complexing the copper and examination of molecular models confirmed that this is geometrically possible for ligands bonded to adjacent silanol sites on the silica surface.

When the reaction between styrene and (1) was catalysed by the copper complex of the immobilized chiral β-diketone (7), the cyclopropane (2) was obtained in 43% yield with an enantiomeric excess of 98.3%. The reaction was complete within 10 h, compared with 24 h for the reaction catalysed by the homogeneous copper complex of the vinyl compound (5), indicating that the immobilized catalyst retains high activity both in terms of yield and extent of asymmetric induction.

The possibility of recovery and reuse of the solid catalyst was examined. In the present work it was found that polystyrene was formed as a by-product during cyclopropanation and this tended to coat the solid catalyst and to reduce its activity substantially during attempted recycling. In further, preliminary experiments to assess the potential for catalyst recycling, indene was therefore examined as a more stable substrate. The decomposition of (1) in refluxing benzene solution containing a fivefold excess of indene in the presence of Cu(10-methylenefacam)₂ was complete in ca. 68 h (monitored by the disappearance of the diazo band in the i.r. spectrum). The copper complex of the immobilized β-diketone gave similar results and when the catalyst was filtered off, washed with benzene, and reused with a new solution of indene and diazodimedone in benzene, the catalyst continued to show activity (i.r. monitoring). The catalyst prepared by uptake of Ni²⁺ into the bonded chiral phase (7) was also

† All new compounds gave satisfactory spectroscopic and microanalytical data.

briefly examined in this reaction and its activity was found to be slightly higher than that of the corresponding Cu^{2+} phase (ca. 61 h for complete disappearance of the diazo compound) and to continue without any loss of activity for at least 3 cycles.

We thank The City University for a postdoctoral fellowship (W. J. L.), the S.E.R.C. for financial support, and the World Health Organization for a Visiting Scientist grant (Z. Z.).

Received, 17th May 1984; Com. 690

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