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# STERICALLY CROWDED CYCLOPROPANATION CATALYSTS. *SYN*-SELECTIVITY USING RHODIUM(III)PORPHYRINS

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**Abstract**—Rhodium(III)porphyrins catalyze the decomposition of ethyl diazoacetate and the transfer of ethoxycarbonylcarbene to alkenes to form cyclopropanes in moderate to high yields. When compared with other catalysts a large *syn*-selectivity was observed on reaction with *cis*-alkenes. This selectivity increased with the size of the substituents, and suggested a preferential direction of approach of the alkene towards a rhodium–carbene complex.

Although a majority of carbene and carbenoid addition reactions to alkenes show a preference for the formation of the *syn*-cyclopropanes, this is not true for alkoxycarbonylcarbenes.[1-3] In the latter case, the presumably more stable *anti*-isomer is almost always the major product. The easy accessibility of both diazoesters and a large variety of efficient catalysts which allow the reaction to be run under mild and homogeneous conditions explain its great usefulness. Any improvement of the *syn*/*anti* ratio would thus widen the scope of the reaction.

Our study was stimulated by a series of observations: (a) the high reactivity of rhodium derivatives towards diazo compounds;[4] (b) among the very useful rhodium catalysts (rhodium(II)carboxylates)[5] the most hindered (rhodium(II)pivalate)[6] showed the best *syn*/*anti* ratio for transferring ethoxycarbonylcarbene to cyclohexene; (c) sterically hindered cobalt complexes (bis-camphorquinonedioximatocobalt(II)) also gave high *syn*/*anti* ratios;[7] (d) in our laboratory, we observed that rhodium(III)porphyrins reacted catalytically with diazoesters, the products being those expected for carbene transfer (i.e. insertion, cyclopropanation).[8]

The porphyrin macrocycle by itself should have a large steric effect on any reaction occurring at the metallic centre. Also, by modifying the peripheral substituents of the macrocycle one must be able to both shape the catalyst and alter its electronic properties.

We report[9] in this paper that large *syn*-selectivities can be obtained by using such catalysts for the reaction of diazoesters with various olefinic substrates.

## RESULTS

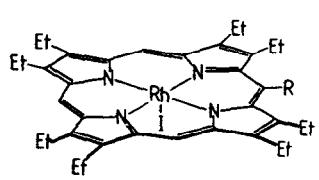
### *Catalysts*

The porphyrin ligands were chosen as a function of the increasing bulkiness of the peripheral substituents. The "flattest" porphyrin used was octaethylporphyrin (porphyrin and octamethylporphyrin are too insoluble). A meso-cyano substituent, necessary for observing adequate reaction rates (see below), was introduced electrochemically.[10] The classical synthesis of meso-tetraarylporphyrins provided the remaining ligands (i.e. meso-tetraphenyl, o-tolyl, mesitylporphyrins).[11] Metalation[12] was achieved using $[Rh(CO)_2Cl]_2$ followed by iodine oxidation of the bis(dicarbonylrhodium)porphyrins to give catalysts **1–5**. For comparison, we also ran a series of reactions using more classical catalysts like Rh(II)pivalate (Rhpiv)[6] and cuprous chloride (CuCl).

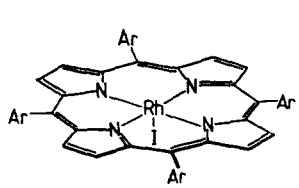
### *Activity of the catalysts towards ethyl diazoacetate*

The reactions were run in excess olefin (olefin/diazoester ratios between *ca* 4 and 10 to 1); only for the sparingly soluble zinc - tetraphenylporphyrin was an excess diazoester added. An inert cosolvent was often added to ensure full solubilization of the catalyst (dichloroethane or chlorobenzene, see Experimental). The catalyst/diazoester ratio was maintained in the $10^{-3}$–$5 \times 10^{-3}$ range. The $N_2$ volume collected reached 100% in most experiments.

The reaction temperature was found to be critical. Catalysts **3–5** decomposed ethyl diazoacetate efficiently at *ca.* 50–60° (reaction at room temperature was very




**1** R = H
**2** R = CN




**3** Ar = phenyl
**4** Ar = o-tolyl
**5** Ar = mesityl

slow). Rhodium(III)octaethylporphyrin iodide **1** did not decompose diazoesters at an appreciable rate even at 60°. The observation that the activity of the meso-cyano derivative **2** compared well with that of **3–5** led us to use **2** instead of **1**; the steric effect of the cyano group was assumed to be negligible.

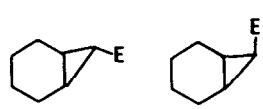
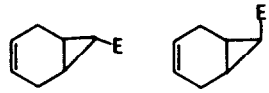
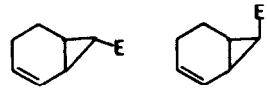
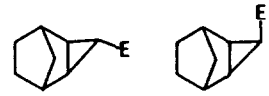
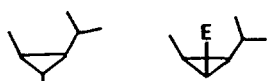
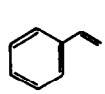
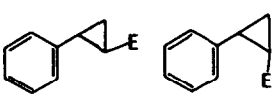
The effect of temperature changes on the product distribution was examined for cyclohexene: no significant deviation was detected between 20–60°. The yields were calculated with respect to the diazoester and were not optimized.

*Cyclopropanation of olefins*

As shown in Table 1, the major products were cyclopropanic *syn* or *anti* esters **6–19**. Minor products were also detected and identified as (a) ethyl maleate and fumarate from carbene dimerization (b) allylic insertion products from cyclohexene (ethyl 2 - cyclohexene - 1 - acetate **20**) and 1,4-cyclohexadiene (actually isolated as ethylphenylacetate from dehydrogenation).

The *syn/anti* ratio was very sensitive to the nature of both the olefin and the catalyst. Mono substituted olefins showed a limited effect, the ratio increasing only slowly in the order CuCl < Rhpiv < **3** < **5**. On the contrary, the reaction with *cis*-disubstituted olefins showed a large increase in the *syn/anti* ratio (up to 6.52 for *cis* - 4 - methyl - 2 - pentene, corresponding to 87% *syn* cyclopropane). Fig. 1. summarizes some of these observations, the catalysts being ordered in accordance to supposed increasing steric hindrance in the vicinity of the metallic centre. The reaction is stereospecific with regard to the configuration of the olefinic substituents (only 2 cyclo-

Table 1. Cyclopropanation of olefins

| Olefin | Cyclopropanic products anti / syn (E = $CO_2Et$) | Catalyst and syn/anti ratio | Total monoester yield (allylic insertion products in %/total monoesters) |
|---|---|---|---|
|  |  6 7 | 2 0.67<br>3 0.74<br>4 0.83<br>5 1.17<br>(CuCl 0.12)[a]<br>(Rhpiv 0.32)[b] | 38 (15)[c]<br>62 (10.5)<br>53 (10)<br>83 (7.5) |
|  |  8 9 | 3 1.4<br>5 3.3<br>(CuCl 0.15)[d]<br>(Rhpiv 0.51) | 90 (17)[e]<br>89.5 (10) |
|  |  10 11 | 3 0.87<br>5 2.16<br>(CuCl 0.2)[f]<br>(Rhpiv 0.43) | 78.5 (<<10)<br>92 (<<10) |
|  |  12 (exo) 13 (exo) | 2 1.0<br>3 1.28<br>4 1.52<br>5 2.14<br>(CuCl 0.02)[g]<br>(Rhpiv 0.44) | 67<br>71<br>74<br>76 |
|  |  14 15 | 3 4.9<br>5 6.52<br>(CuCl 0.56)<br>(Rhpiv 2.2) | 60<br>82 |
|  |  16 17 | 3 0.73<br>5 0.87<br>(CuCl 0.52)[h]<br>(Rhpiv 0.67) | 68<br>85 |
|  |  18 19 | 3 0.88<br>5 0.98<br>(CuCl 0.62)<br>(Rhpiv 0.67)[i] | 71<br>78 |

a. Maximum 0.26 using Moser's catalysts (ref.13), 0.42 using $Br_2CHCO_2Et$ + Cu (ref.14) ; b. Ref.6 and our work ; c. identified as ethyl 2-cyclohexene-1-acetate, see experimental ; d. earlier studies (Cu, $CuSO_4$) indicated a 0.1-0.14 ratio (ref.2) ; e. isolated as ethyl phenylacetate ; f. earlier studies (Cu, $CuSO_4$) indicated a 0.12-0.2 ratio (ref.2) ; g. 0.22-0.33 using CuCN (ref.15) ; h. 0.54 (Cu, ref.2) ; i. 0.71-1.45 using bis-camphorquinone dioximatocobalt(II) (ref.7).

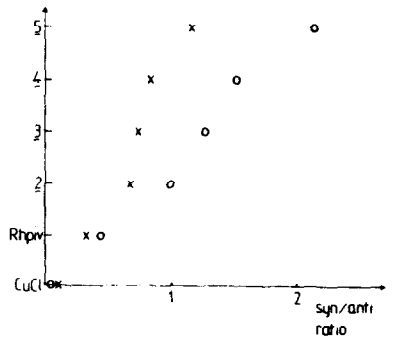



Fig. 1. *Syn/anti* ratio for cyclopropanation of cyclohexene (X) and norbornene (O). Catalysts are ordered as a function of steric hindrance along an arbitrary scale.

propanes with *cis*-methyl and isopropyl groups from *cis* - 4 - methyl - 2 - pentene).

Cyclopropanation of *trans*-disubstituted olefins (*trans* - 4 - methyl - 2 - pentene, *trans* - 2,5 - dimethyl - 3 - pentene) was also investigated but invariably gave mixtures of cyclopropanes and allylic insertion products in low yield accompanied by large amounts of ethyl maleate and fumarate.

*Aromatic substrates*

The same *anti* preference was observed for aromatic substrates as for simple olefins when catalysts were used for ethoxycarbonyl-carbene transfer.[2] In a preliminary experiment, we checked that the rhodium porphyrins were active catalysts for (a) Buchner reaction: benzene was transformed in 46% yield (not optimized) into ethyl cycloheptatrienecarboxylate. Aromatic substrates known to give stable cyclopropanic products were then subjected to our reaction conditions: i.e. ethyl diazoacetate + catalyst 3.

Reaction of phenanthrene with ethyl diazoacetate has been studied previously and *anti*-ester 21 was described as the major product.[2] The reaction was repeated using 3, Rhpiv and CuCl as catalysts and the resulting mixtures of monoesters analyzed for 21 (Table 2). Conversion of phenanthrene increased in the sequence CuCl < Rhpiv < 3 while at the same time ester 21 almost disappeared from the monoester mixture.

The most hindered aromatic bond tested was the pyrrole $\beta\beta$-bond of zinc tetraphenylporphyrin 22. CuCl

Table 2.

| Catalyst | monoesters (total yield%) | 21/(total monoester) (%) |
|---|---|---|
| 3 | 51 | 7–9 |
| Rhpiv | 38.5 | 20–22 |
| CuCl | 17 | 95–97 |

catalysis was known[24] to give the expected cyclopropanic chlorins 23 after demetalation (*syn/anti* ratio = 0.1). On replacing CuCl by 3, the reaction site shifted to a meso-phenyl group which was homologized to a cycloheptatriene carboxylate 24 (only traces of 23 could be detected; catalysis with Rhpiv did not give appreciable amounts of products).

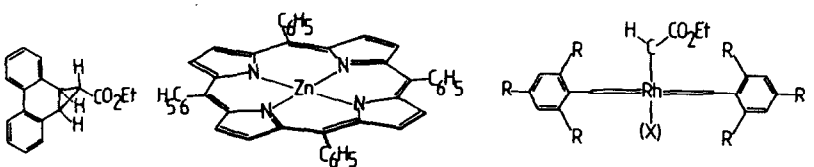
## DISCUSSION

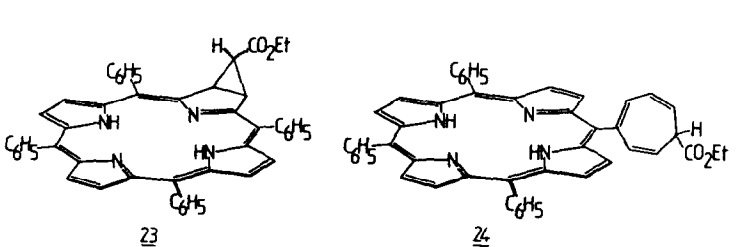
The major difference between metalloporphyrins and other catalysts used for carbene transfer is the rigidity of the macrocyclic ligand. Among metal–nitrogen bonds of metalloporphyrins Rh–N bonds belong to the most stable.[25] We may thus infer that the geometry of the Rh + 4N fragment will not deviate appreciably from a square planar configuration.

Although the precise mechanism of the diazoester–rhodium(III)porphyrins reaction is not yet clearly understood,[8,16] we think that a rhodium–carbene complex A is a reasonable working hypothesis. We do not intend to speculate about the nature of an hypothetical ligand X.

The peripheral substituents are of two types: (a) free rotating ethyl groups in 2 always allow one side of the reactive intermediate to be accessible for an approaching substrate; (b) the meso-phenyl groups (3–5), whose rotation is slow,[18] may be considered as positioned perpendicularly with regard to the porphyrin nucleus; the steric hindrance due to the ortho substituents will be crucial since they point towards the reactive site.[19] One expects interactions in the increasing order H,H ( = 3) < $CH_3$,H ( = 4) ≪ $CH_3$,$CH_3$ (5), the catalyst geometry varying from flat (2) to bowl-shaped (5).

Whatever the precise mechanism of the carbene transfer reaction is, larger peripheral substituents will increase the tendency for all bulky groups (alkene substituents + ester group) to point away from the macrocycle during the course of the reaction and thus



will increase the *syn/anti* ratio. This is exactly what was observed in the case of *cis*-alkenes. On the other hand *trans*-alkenes cannot avoid larger interactions with the macrocyclic ligand: this is confirmed by the relatively lower amounts of cyclopropanes which are formed.

Aromatic substrates showed a more dramatic effect namely partial or total regioselectivity change. Their large size and lateral steric hindrance (rings A and C of phenanthrene, meso-phenyl groups of ZnTPP **22**) hindered partially (phenanthrene) or totally (ZnTPP) the approach of the most reactive bond.

In conclusion, we have confirmed the importance of steric effects for altering the stereochemical course of cyclopropanation of olefins by carbethoxycarbenoids. We have demonstrated that properly designed and readily accessible catalysts like **5** gave *syn*-cyclopropanes as major products (54–87%) with all *cis*-alkenes subjected ot our reaction conditions.

Comparison of data for Rhpiv and **2** show the large steric influence of the porphyrin nucleus when this ligand is complexed with an active metal center. The introduction of bulky peripheral substituents further enhances the resulting selectivity. In this respect it is of importance to point out that our results are consistent with those of Groves[20] who found that metalloporphyrins catalyzed epoxidation of olefinic substrates showed a marked *cis* vs *trans* selectivity.

## EXPERIMENTAL

NMR spectra were recorded on Perkin–Elmer R32 (90 MHz) and Cameca (250 MHz) spectrometers. Visible spectra were measured on a Cary 118 spectrophotometer. Mass spectra were recorded on a Thomson–Houston THN 208 spectrometer. Microanalyses were performed by the Service de Microanalyse de l'Institut de Chimie, Strasbourg. Products were analyzed by glc using a Girdel Serie 30 Chromatograph and (OV 17.5%, 1.5 m, 90–110°). Quantitative separation was performed on Merck silicagel 60. Cyclohexene, 1,3- and 1,4-cyclohexadiene, norbornene, 1-hexene, phenanthrene (Fluka), styrene, ethyl-diazoacetate (Merck) and *cis* - 4 - methyl - 2 - pentene (Aldrich) were of the best commercially available quality. Meso-tetraphenylporphyrin,[11] meso - tetra - o - tolylporphyrin,[11] meso-tetramesitylporphyrin,[11] iodorhodium(III)meso - tetraphenylporphyrin,[8] meso-cyanooctaethylporphyrin[10] were prepared according to literature procedures.

### *Catalysts* **2**, **4** *and* **5**

The literature procedure[8] was followed except that metalation giving **2** and **5** was slow and necessitated a prolonged reflux in 1,2-dichloroethane (respectively 16 and 36 h under $N_2$). Yields: **2** (47%), **4** (48%), **5** (60–93%).

**2**: NMR ($CDCl_3$) $\delta$ 1.8–2.0 (m, 24, $CH_3$), 3.8–4.3 (m, 16, $CH_2$), 10.15 (s, 1, meso), 10.22 (s, 2, meso). MS: *m/e* 787 (5%), 660 (100%, −I). Visible ($CH_2Cl_2$) $\lambda_{max}$ 418 nm ($\epsilon$ 66000), 553 (11000), 589 (18000). Calc. for $C_{37}H_{43}N_5IRh$: N, 8.89. Found: N, 8.89%. No satisfactory results could be obtained for C and H.

**4**: NMR ($CDCl_3$) $\delta$ 1.8–2.1 (m, 12, $CH_3$), 7.5–7.7 (m, 12, meta + para H), 8.0–8.2 (m, 4, ortho H), 8.64–8.68 (m, 8, pyrrole H), MS: *m/e* 898 (3%), 771 (100%, −I). Visible ($CH_2Cl_2$) $\lambda_{max}$ 426 nm ($\epsilon$ 94000), 534 (12000). Calc. for $C_{48}H_{36}N_4IRh$: N, 6.26. Found: N, 6.23%. No satisfactory results could be obtained for C and H.

**5**: NMR ($CDCl_3$) $\delta$ 1.72 (s, 12, ortho $CH_3$), 2.03 (s, 12, ortho $CH_3$), 2.61 (s, 12, para $CH_3$), *ca.* 7.26 (meta H + $CHCl_3$ signal), 8.60 (s, 8, pyrrole H). MS: *m/e* 1010 (1%), 883 (100%, −I). Visible ($CH_2Cl_2$) $\lambda_{max}$ 424 nm ($\epsilon$ 106000), 534 (12000). Calc. for $C_{56}H_{52}N_4IRh$: C, 66.53; H, 5.18; N, 5.49. Found: C, 66.35; H, 5.24; N, 5.36%.

### *Cyclopropanation of alkenes*

The catalyst (**2–5**) (5 mg) was dissolved in the alkene (1 ml) and 1,2-dichloroethane (1 ml) and heated at 60 ± 2°. A mixture of ethyl diazoacetate (0.5 ml) and olefin (3.5 ml) was then added (syringe) over 0.5 h while $N_2$ was collected in a water burette. The solution was kept at 60° for a further 5 min and the theoretical volume of $N_2$ was recovered shortly after the end of addition. The reaction mixture was evaporated (reduced pressure) and the residue diluted with pentane and left at 20°for 12 h. The pentane solution was separated and evaporated. A first GLC analysis was performed at that stage. Separation of the monoester fraction was obtained after chromatography on silica gel (eluent hexane + 2% AcOEt). The monoester mixture was then checked for purity (glc, NMR) and the products identified by comparison of the spectra and chromatographic data (from literature or from samples prepared according to the literature).

*Cyclohexene.* See Ref. 2 for cyclopropanes. The allylic insertion product was separated on silica gel (hplc, hexane/ethyl ether 20:1) and identified as ethyl 2 - cyclohexene - 1 - acetate.[22]

*Cyclohexa-1,4-diene.* See Ref. 2 for cyclopropanes. The insertion product was isolated by preparative glc (Varian Aerograph, OV 17 20%), but suffered dehydrogenation to ethyl phenylacetate. By analogy, we suppose that it is ethyl 2,5 - cyclohexadiene - 1 - acetate.

*Norbornene, 1,3-cyclohexadiene, 1-hexene, styrene.* See Ref. 2 for cyclopropanes.

*Cis* - 4 - *methyl* - 2 - *pentene.* The cyclopropanes were separated by hplc (silica gel, hexane/ethyl ether 20:1) as colorless liquids.

**14**. NMR ($CDCl_3$) 1.01 (d, 3, isopropyl), 1.05 (d, 3, isopropyl), 1.15 (d, 3, $CH_3$), 1.26 (t, 3, ester $CH_3$), 1.0–1.3 (m, 3, ring H), 1.5 (m, 1, isopropyl CH), 4.12 (q, 2, ester $CH_2$). MS: calc for $C_{10}H_{18}O_2$ *m/e* 170.1307; found *m/e* 170.1303.

**15**. NMR ($CDCl_3$) 0.89 (d, 3, isopropyl), 0.97 (d, 3, isopropyl), 1.25 (d, 3, methyl), 1.26 (t, 3, ester $CH_3$), 1.2–1.4 (m, 2, 2 ring H), 1.62 (t, 1, $CH$–$CO_2C_2H_5$, J = 9 Hz), 2.1 (m, 1, isopropyl CH), 4.10 and 4.11 (2q, 2, ester $CH_2$). MS: calc for $C_{10}H_{18}O_2$ *m/e* 170.1307; found *m/e* 170.1303.

*Trans-4-methyl-2-pentene.* Reaction with ethyldiazoacetate in the presence of **3** gave a 45% monoester fraction. The NMR spectrum showed both alkene proton signals and methyl and methylene singlets. From these data we deduced the presence of *ca.* 20% insertion product (into the isopropyl CH bond). The mixture was not further investigated. *Trans* - di - isopropylethylene gave a very low yield of monoesters ( *ca.* 20%) whose NMR spectrum showed the presence of large amounts of allylic insertion product (*ca.* 50%).

### *Aromatic substrates*

*Phenanthrene.* Addition of ethyl diazoacetate (1 ml) over 0.5 h to a solution of phenanthrene (6.24 g) and **3** (10 mg) in $C_6H_5Cl$ (5 ml) at 60° gave a dark reaction mixture which was treated with $CH_3OH$ to crystallize excess phenanthrene. Chromatography (silica gel, 200 g, eluent toluene) gave a monoester fraction (890 mg). The proportion of cyclopropane **21** was measured from the NMR spectrum[2,24] (doublet at 3.17 ppm).

*ZnTPP* **22**. The low solubility of **22** precluded the use of the above procedure. Reverse proportions were thus required and yields were calculated with respect to the porphyrin. ZnTPP (200 mg) and **3** (5 mg) $C_6H_5Cl$ (3 ml) were heated at 60°. Ethyl diazoacetate (0.3 ml) in $C_6H_5Cl$ (3 ml) was added over 10 min and the solution heated for a further 5 min. The crude reaction mixture was chromatographed on a silica gel column (60 g in toluene) with toluene, to give recovered ZnTPP **22** (96 mg) followed by a violet band. Toluene was evaporated and the residue was dissolved in $CH_2Cl_2$ (5 ml), treated with conc HCl (1 ml), neutralized (excess aq. $NH_3$), washed ($H_2O$), and dried ($Na_2SO_4$).

Porphyrin **24** was crystallized from $CH_2Cl_2$-pentane (11 mg), m.p. 191–193° NMR ($CDCl_3$) $\delta$ −2.75 (broad s, 2, NH), 1.43 (t, 3, $CH_3$), 3.36 (t, 1, $CH$–$CO_2C_2H_5$), 4.42 (q, 2, $CH_2$), 5.5–5.8 (m, 2, cycloheptatriene), 6.72 (dd, 1, cycloheptatriene), 7.2–7.4 (m, 2, cycloheptatriene), 7.7–7.8 (m, 9, meta + para), 8.1–8.3 (m, 6, ortho), 8.80 (broad s, 8, pyrroles). MS: *m/e* 700 ($M^+$, 100), 627 (30%, $-CO_2C_2H_5$). Visible ($CH_2Cl_2$) $\lambda_{max}$ 420 ($\epsilon$ 260000), 510 (18400), 550 (8750), 590 (6000), 650 (4000). Calc. for $C_{48}H_{36}N_4O_2$: C, 82.26; H, 5.18; N, 7.99. Found: C, 81.41; H, 5.40; N, 7.36%.

*Catalytic reaction in the presence of Rhpiv or CuCl*

The procedure was identical to that described above except for the amount of catalyst (2 mg Rhpiv; 10 mg CuCl).

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