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Stereochemistry in the Di- π -methane Rearrangement: Aryl Migration. Exploratory and Mechanistic Organic Photochemistry^{1,2}

Sir,

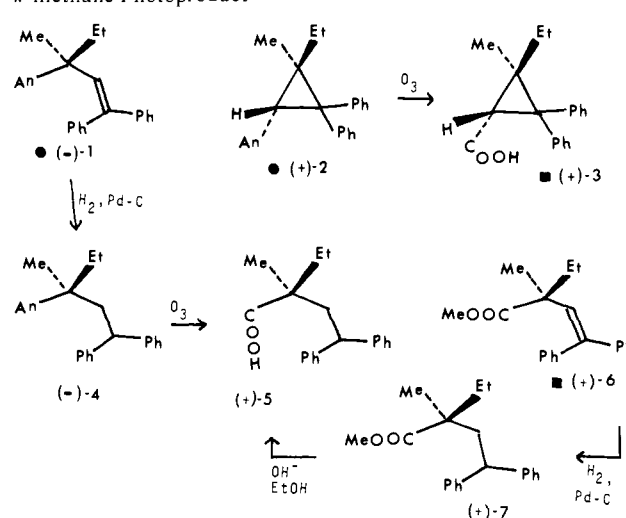
There are three known versions of the di- π -methane rearrangement:³ the divinylmethane variety, the arylvinylmethane type, and the oxa-di- π -methane^{3d,e} variation. These differ in many respects. The last generally uses a triplet reactant while examples of the first two involving both singlets and triplets are known. The first two also differ markedly. The divinylmethane rearrangement requires methane carbon substitution while the arylvinyl type does not, the arylvinylmethane singlets tend to react more slowly than their divinyl counterparts,⁴ and substituent effects are reversed for these two cases.⁴

The reaction stereochemistry has been studied in only two of the three rearrangements. In our development of the di- π -methane rearrangement,^{3a,b,5} we focussed attention on the stereochemistry of the divinylmethane type. At the methane carbon inversion of configuration was found.^{5c} In a parallel oxa-di- π -methane example, Dauben⁶ has noted almost complete loss of stereochemistry. This is in agreement with the results of Schaffner.⁷

We now report on the stereochemistry of the missing example. Thus we have found complete inversion of configuration at the methane carbon for the arylvinylmethane variation.

For our study we selected 3-*p*-methoxyphenyl-3-methyl-1,1-diphenyl-1-pentene (**1**), since the central methyl, ethyl substitution was that employed in our previous case^{5c} and in the study by Dauben.⁶ Also, this reactant and its photoproduct (**2**) could readily be configurationally related to one another using our earlier study^{5c} as a basis. The interrelating scheme

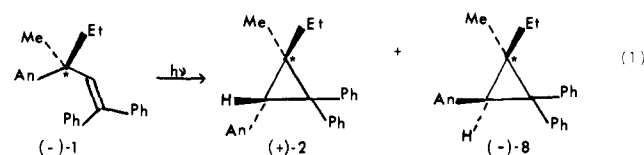
Chart I. Interrelationship of Configurations of Reactant and Di- π -methane Photoproduct^{a,b}



^a Compounds labeled with solid dots are those whose configurations needed to be related. Compounds labeled with solid squares are those whose configurations were known from our earlier study.^{5c} ^b Experimentally (-)-6, (-)-7, and (-)-5 enantiomers were actually interrelated; reverse configurations are depicted for simplicity of presentation. Optically pure, >99.5%, (-)-1 was used.

is depicted in Chart I⁸ for the trans photoproduct **2**. The cis photoproduct configuration was determined in similar fashion.

Experimentally, direct irradiation of (-)-3-*p*-methoxyphenyl-3-methyl-1,1-diphenyl-1-pentene (**1**) led to (+)-*trans*-2-ethyl-2-methyl-3,3-diphenyl-*p*-methoxyphenylcyclopropane (**2**) in addition to the (-)-*cis* isomer. This allows us to formulate the di- π -methane rearrangement stereochemistry as shown in eq 1.



Inspection of eq 1 reveals that for both diastereomers of photoproduct the configuration at carbon-3 (i.e., the methane carbon) of anisylalkene **1** has been inverted.

Since, even at conversions as low as 15%, 12.8% racemization was observed, there was the question whether the entire reaction mechanism was a concerted one.

However, the low stereospecificity was found to be an experimental artifact rather than real, and our findings indicate how careful one must be in avoiding secondary effects in photochemistry.

Thus, we repeated our irradiations with 10 and 5.6% conversions, and we found diminishing racemization of cyclopropane product with decreasing percent conversion. Owing to overlapping ultraviolet absorption spectra of reactant and product, even at 15% conversion, 4.0% of the light was captured by cyclopropane photoproducts **2** and **8**.

As noted in Table I and Figure 1 extrapolation to zero conversion led almost precisely to zero racemization.

Table I. Optical Purity of Photoproduct **2** vs. Percent Conversion^a

Percent conversion	14.2 ± 0.7	10.1 ± 0.5	5.6 ± 0.4	Zero conversion ^b
Percent optical purity of photoproduct 2 ^c	87.2 ± 1.5	91.3 ± 1.6	95.0 ± 2.0	100.1 ± 1.7 ^b

^a Measurements at 5 wavelengths, with rotations vs. λ providing evidence of absence of contaminants. ^b Extrapolated value. ^c Each measurement in Table I is the average of two, independent determinations.

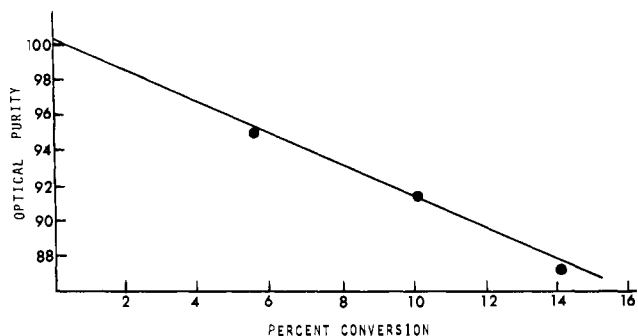
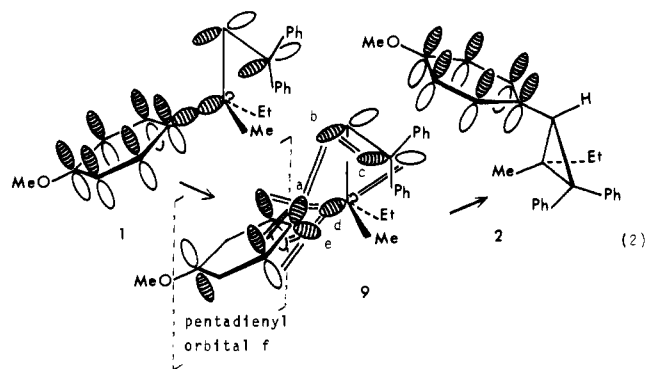


Figure 1. Optical purity of photoproduct **2** vs. percent conversion.

Hence our conclusion is that the reaction proceeds totally stereospecifically within experimental error. This is in agreement with our study of the stereochemistry of the "diene version" of the di- π -methane rearrangement where inversion of the methane carbon configuration was also observed.^{5c} Thus, the hydrocarbon di- π -methane rearrangement contrasts with the oxa-di- π -methane variation.

The rationale that we have used⁵ for inversion of configuration has been the requirement for a Möbius array with six delocalized electrons in the excited state. Presently there is no such simple array of atomic and hybrid orbitals. The truncated set of orbitals, consisting only of those in bonds being formed or dissipated, is given in eq 2. There is still a Möbius array^{5,9}



in the half-reacted species **9** which provides an excited-state-allowed¹⁰ pathway. However, in this case, the nonbonding MO of the pentadienyl moiety left in the originally aromatic ring is one of the six basis orbitals a-f comprising the Möbius array. It has been noted^{10,11} that MOs as well as AOs can be taken as basis orbitals in constructing such cyclic arrays.

Thus eq 2 illustrates use of the Möbius-Hückel treatment where one moiety is complex.

We conclude by noting that arylvinylmethane stereochemistry parallels that of the divinylmethane version rather than the oxa-di- π -methane variety and that singlet vs. triplet factors seem dominant.

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References and Notes

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Reversible Binding of Dioxygen to Ruthenium(II) Porphyrins

Sir,

We are presently concerned with the interaction of dioxygen and carbon monoxide with metalloporphyrin complexes as models for biologically important heme proteins.¹ In the iron(II) systems that have been developed to mimic the reversible oxygenation of myoglobin, oxidation to iron(III), which is brought about by interaction of a second iron(II) moiety with an initially formed Fe^{II}-O₂ species,² is prevented by (1) designing porphyrins of such a geometry (or supporting them on a rigid polymer backbone) so as to physically prevent such an interaction or (2) use of low temperatures (subzero) to retard such an interaction. An alternative approach to these problems using the more substitution-inert ruthenium(II) analogues has, in our hands, yielded significant results.

In this communication we report on reversible O₂ binding in solution under ambient conditions by solutions of ruthenium(II) complexes of *meso*-tetraphenylporphyrin (TPP) and octaethylporphyrin (OEP).

To our knowledge,³ this is the first report of reversible dioxygen binding by a ruthenium(II) species in solution. Hopf and Whitten⁴ have "activated" ruthenium(II) porphyrins to do similar chemistry to that described here by using surfactant complexes in monolayer assemblies; however, we find the "activation" of the porphyrins toward O₂ (and CO) can be accomplished by the use of labile axial ligands, especially acetonitrile.

The complexes Ru(OEP)L₂ and Ru(TPP)L₂ (L = CH₃CN) were synthesized as purple crystals⁵ by photolysis of the corresponding Ru(porphyrin)(CO)(C₂H₅OH) complexes⁶ in acetonitrile under argon over 8–10 h (Hanovia medium pressure 450-W mercury vapor bulb). Dilute solutions (~10⁻⁵ M) of the bisnitrile species are also formed cleanly and rapidly (10 min) by photolysis of the carbonyl complexes using a Rayonet photochemical reactor. Figure 1 shows spectral data for such formation of Ru(OEP)(CH₃CN)₂; a number of isosbestic points are generated. Use of solvents such as dimethylacetamide (DMA), dimethylformamide (DMF), and pyrrole, gives similar in situ spectral changes attributable to formation of the corresponding Ru(OEP)(solvent)₂ species.

Solutions of Ru(OEP)(CH₃CN)₂ in DMA, DMF, or pyrrole absorb 1.0 mol of O₂/Ru reversibly at room temperature and 1-atm pressure.⁷ At constant O₂ pressure, the reactions follow pseudo-first-order behavior: the uptake is almost instantaneous in DMA (*t*_{1/2} ~ 1 min); *t*_{1/2} is ~7 min in pyrrole and ~30 min in DMF. Figure 2 shows the accompanying