Journal of Organometallic Chemistry, 51 (1973) C21–C23
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Stereospecific decarbonylation of acyl(h^5-cyclopentadienyl)carbonyl(triphenylphosphine)iron complexes

THOMAS G. ATTIG, PETER REICH-ROHRWIG and ANDREW WOJCICKI
The McPherson Laboratory, The Ohio State University, Columbus, Ohio 43210 (U.S.A.)

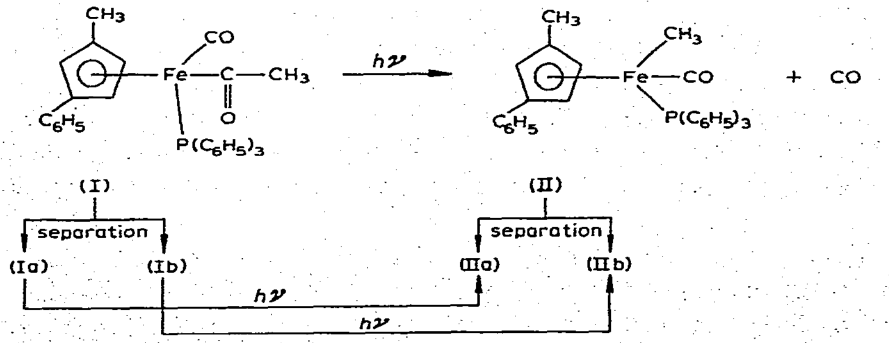
(Received January 26th, 1973)

SUMMARY

Photochemical decarbonylation of (h^5-C_5H_3-1-CH_3-3-C_6H_5)Fe(CO)[P(C_6H_5)$_3$]($COCH_3$) and h^5-C_5H_5Fe(CO)[P(C_6H_5)$_3$][$COCH_2CH(CH_3)C_6H_5$] proceeds with high stereospecificity at iron.

The decarbonylation of transition metal acyl carbonyl complexes is known to proceed with retention of configuration at α carbon of R[1]. We now wish to report the stereochemical outcome of the decarbonylation of two types of metal acyls which possess a chiral metal center.

Treatment of 1-methyl-3-phenylcyclopentadiene with $Fe_2(CO)_9$ affords [(h^5-C_5H_3-1-CH_3-3-C_6H_5)$Fe(CO)_2$]$_2$, which after reduction with Na/Hg in THF and addition of CH_3I yields (h^5-C_5H_3-1-CH_3-3-C_6H_5)$Fe(CO)_2CH_3$. Treatment of the last-mentioned complex with P(C_6H_5)$_3$ affords (I). (I) exists in the form of two diastereomerically-related pairs of enantiomers (*RR–SS* and *RS–SR*), (Ia) and (Ib), which were sep-



scheme 1

arated by a combination of column chromatography and fractional crystallization from benzene–pentane.

The diastereomers (Ia) and (Ib) undergo photochemical decarbonylation (λ = 3500Å) in benzene or THF to give the corresponding alkyls, (IIa) and (IIb). These transformations are shown in Scheme 1. (Ia) and (Ib), as well as (IIa) and (IIb), have readily distinguishable ^{1}H NMR spectra. Hence diastereomeric purity can be conveniently determined by integration of the resonances for corresponding nonequivalent protons. The NMR spectra of a 50/50 mixture of (Ia)/(Ib) and (IIa)/(IIb) in the region τ 5–10 are shown in Figs. 1 and 2, respectively.

After a 95/5 mixture of (Ia)/(Ib) had been irradiated for 5, 15, and 40 min, usual work-up led to isolation of 88/12, 84/16, and 59/41 mixtures of (IIa)/(IIb). The unreacted acyl was recovered as an unchanged 95/5 mixture of the diastereomers. Similarly, photolysis for 5 min of the diastereomerically pure (Ib) afforded an 8/92 mixture of (IIa)/(IIb). The change in the ratio of (IIa)/(IIb) with longer irradiation times is due to epimerization of the alkyl. This was established by photolyzing a 70/30 mixture of (IIa)/(IIb) under the conditions of the decarbonylation. The observed decrease in the diastereomeric ratio as a function of time indicates epimerization subsequent to the elimination of CO. These results therefore demonstrate that the photochemical decarbonylation of (I) follows a highly stereospecific course (> 84% stereoselectivity) which is solvent independent.

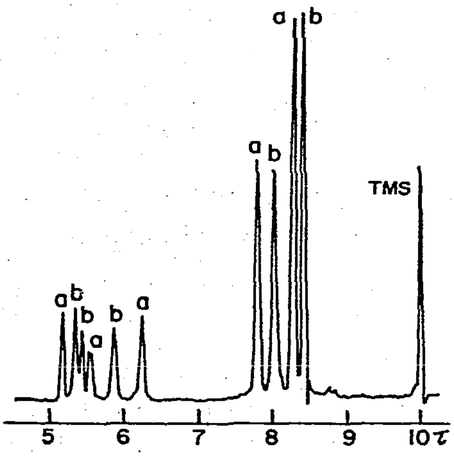


Fig. 1. A 100-MHz NMR spectrum in the τ 5–10 region of a 50/50 mixture of the two diastereomeric pairs of enantiomers (a and b) of (I).

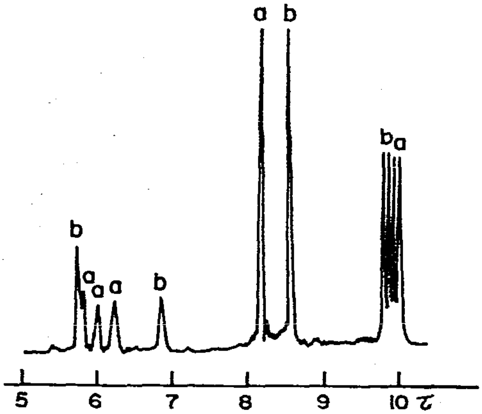


Fig. 2. A 100 MHz NMR spectrum in the τ 5–10 region of a 50/50 mixture of the two diastereomeric pairs of enantiomers (a and b) of (II).

Similar results were obtained for the photochemical decarbonylation of the two diastereomeric pairs of enantiomers of h^5-$C_5H_5Fe(CO)[P(C_6H_5)_3][COCH_2CH(CH_3)C_6H_5]$, (IIIa) and (IIIb). The loss of CO to give h^5-$C_5H_5Fe(CO)[P(C_6H_5)_3][CH_2CH(CH_3)C_6H_5]$, (IVa) and (IVb), is highly stereospecific (> 64% stereoselectivity), but followed by epimerization of the product. This system is, however, complicated by slight and unequal decomposition of (IVa) and (IVb) during chromatography.

Alexander[2] has recently demonstrated that the photochemical decarbonylation of h^5-$C_5H_5Fe(CO)_2(^{13}COCH_3)$ results in elimination of a terminal, not the acyl, CO. Migration of the methyl group onto the vacated site follows. Our results show that such migration occurs stereospecifically, with the metal at least substantially, and possibly completely, retaining its nonplanar configuration.

The synthesis and resolution of a number of chiral transition metal centers have been reported in organometallic chemistry[3,4]. It is noteworthy that (I) and (II) represent the first examples of chiral compounds in which an unsymmetrically substituted cyclopentadienyl ring is *pentahapto*-bonded to an asymmetric metal. This type of complex offers an important advantage in studies concerned with chiral centers. Most of its reactions leave intact the two centers of asymmetry (*i.e.* metal and ring), and therefore preserve presence of diastereomers. Furthermore, the ring is configurationally stable in its attachment to the metal. Therefore, the NMR spectra unambiguously reflect configurational changes at the metal in replacement or modification of any of the other three ligands.

We are presently examining the stereochemistry of other reactions occurring at the M–C bond of (I) and (II) and will report our results later.

ACKNOWLEDGEMENT

We thank the National Science Foundation for support of this research. Awards of a University postdoctoral fellowship (P.R.-R.) and a National Science Foundation Traineeship (T.G.A.) are also acknowledged.

REFERENCES

1 A. Wojcicki, *Advan. Organometal. Chem.*, 11 (1973) in press.
2 J.J. Alexander, personal communication, 1972.
3 H. Brunner, *Angew. Chem. Int. Ed. Engl.*, 10 (1971) 249.
4 A. Davison and D.L. Reger, *J. Amer. Chem. Soc.*, 94 (1972) 9237.