Journal of Organometallic Chemistry, 263 (1984) 243–246
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ASYMMETRIC SYNTHESIS BY CHIRAL RUTHENIUM COMPLEXES

X *. ENANTIOFACE DISCRIMINATING ISOMERIZATION OF OLEFINS

UGO MATTEOLI, MARIO BIANCHI, PIERO FREDIANI, GLORIA MENCHI
Istituto di Chimica Organica dell'Università, Via G. Capponi 9, 50121 Firenze (Italy)

CARLO BOTTEGHI and MAURO MARCHETTI
Istituto di Chimica Applicata dell'Università, Via Vienna 2, 07100 Sassari (Italy)

(Received October 17th, 1983)

Summary

Prochiral 3-methyl-5-phenylpent-2-ene has been isomerized in the presence of $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$, both in the presence and in the absence of hydrogen. (*S*)-(+)-1-Phenyl-3-methylpent-1-ene was formed as the consequence of an enantioface differentiating process.

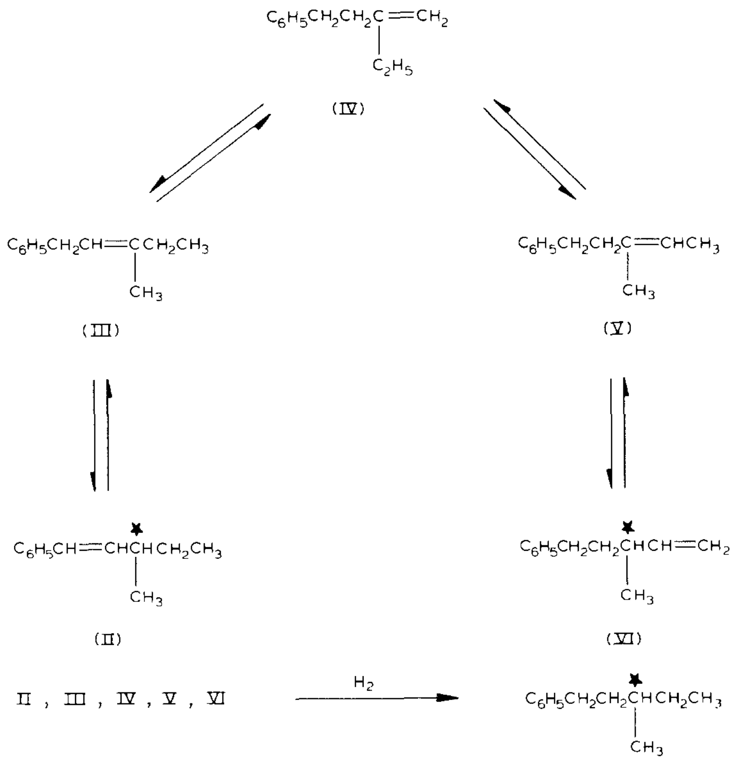
Introduction

In a previous paper we have reported that olefin isomerization is concurrent with its hydrogenation when using $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ [1]. Isomerization may affect considerably the stereoselectivity of the hydrogenation process. The structure of the olefin used up to now in this field has not, however, permitted us to see if the isomerization taking place during the hydrogenation was a stereoselective reaction.

In order to test whether an enantioface discriminating isomerization of an olefin was possible in the presence of the above catalytic system we have chosen as substrate an olefinic system having the 3-methyl-1-phenylpentane (I) framework. Scheme 1 shows the structure of all the isomeric olefins which give I on hydrogenation. Olefins III, IV and V are prochiral and only II and VI are chiral. The amount of VI in an isomerizing mixture of these olefins is small for thermodynamic reasons. Moreover the relation between optical activity and configuration, and between rotatory power and optical purity were known for both I and II [2]. Rotatory powers of these compounds are fairly high and therefore even small asymmetric inductions may be detected.

---

[*] For part IX see ref. 1.



SCHEME 1 (I)

Because of the good isomerizing activity of cluster ruthenium complexes, even in the absence of hydrogen [3–7], we decided to carry out experiments under these conditions.

Results and discussion

The prochiral substrate chosen to provide information about the asymmetric isomerization under hydrogenation conditions is 3-methyl-5-phenylpent-2-ene (V) $[(E)/(Z) = 1]$. Its synthesis has already been described [8]. The isomerization experiment on V has been realized using $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ as catalyst, at 80°C under 130 atm of hydrogen. After 23 h the composition of the reaction mixture was: (*E*)-II 12.5%, (*Z*)-II 0.2%, (*E*)-III 12.4%, IV 2.2%, (*E*)-V 21.8%, (*Z*)-V 10.7% and I 40.2%. Olefin (*E*)-II has been separated from the crude by preparative GLC. Its optical purity (o.p.) was 0.5%.

Another isomerization experiment has been carried out on the same substrate, with the same catalyst, in the absence of hydrogen, at 150°C, which is the minimum temperature at which the reaction takes place. The reaction mixture after 508 h consists of a mixture of isomeric olefins having the following composition: (*E*)-II 10.0%, (*Z*)-II 1.2%, (*E*)-III 14.0%, (*Z*)-III trace, IV 6.2%, (*E*)-V 46.2% and (*Z*)-V 22.4%. The optical rotation shown by the reaction mixture, after removal of the catalyst, is due only to the presence of II. The optical rotation was α_D^{25} + 0.050 ($l = 1$, neat). Olefin II was present as a mixture of the (*E*) and (*Z*) isomers in the ratio

1.2 : 10.0. The maximum optical rotation of (*Z*)-II being unknown we cannot calculate the value of the o.p. of the two isomers of II.

The results of both tests however clearly show that prochiral olefins, as well as functionalized unsaturated compounds [9,10], may give rise to optically active compounds by an enantioface discriminating process in the presence of an appropriate catalyst.

Experimental

Physico-chemical determinations were performed with the following instruments: NMR Perkin–Elmer R32 spectrometer; Perkin–Elmer 241 polarimeter; IR Perkin–Elmer 580B Data System. GLC analyses were performed with a Perkin–Elmer Sigma 1 System.

The products were separated by use of a Perkin–Elmer 251 spinning band distillation column and a Perkin–Elmer F21 preparative scale gas-chromatograph.

Materials

(*S*)-(+)-3-Phenylpentane (I) was synthesized starting from (*S*)-(−)-2-methylbutan-1-ol as described by Piacenti et al. [2]. (*E*)-(*R,S*)-1-Phenyl-3-methylpent-1-ene was prepared from (*R,S*)-2-methylbutan-1-ol according to Piacenti et al. [2]; the presence of about 6% of an isomeric by-product was shown by GLC-mass analysis. This by-product was identified as (*Z*)-1-phenyl-3-methylpent-1-ene since the mixture of (*E*) and (*Z*) olefins (94/6) gave, on ozonolysis followed by $LiAlH_4$ reduction of the ozonide, benzyl alcohol and (*R,S*)-2-methylbutan-1-ol as the only products. (*R,S*)-3-Methyl-5-phenylpent-1-ene was prepared according to Stefani [11]. 2-Ethyl-4-phenylbut-1-ene (IV) was prepared in 50% overall yield from commercial 3-phenylpropanal (Fluka AG) in three steps (addition of ethylmagnesium bromide to this aldehyde to give (*R,S*)-5-phenylpentan-3-ol, $K_2Cr_2O_7$ oxidation of this alcohol to the corresponding ketone, and reaction of this last compound with triphenylmethylenphosphorane [12]): b.p. 59°C (0.2 mmHg); NMR $\delta(CDCl_3, TMS)$ 1.03 (t, 3H, CH_3), 2.03 (q, 2H, CH_2CH_3), 2.33 (m, 2H, CH_2CH_2C), 2.72 (m, 2H, $CH_2C_6H_5$), 4.78 (s, 2H, $CH_2{=}C$), 7.21 (m, 5H, C_6H_5). (*E,Z*)-3-Methyl-5-phenylpent-2-ene (V) was obtained in 50% overall yield through a Wittig reaction [12] between commercial 4-phenylbutan-2-one (Fluka AG) and triphenylethylidenphosphorane. The physical properties and NMR data of this olefin were identical to those reported in the literature [8]. The catalytic precursor $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ was prepared by a known procedure [13]. All solvents were purified and dried by standard procedures. All solvents and reagents were distilled under nitrogen before use.

Isomerization of (E,Z)-3-methyl-5-phenylpent-2-ene (E/Z = 1)

(a) In the presence of hydrogen. A solution of $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ (0.124 g) in the substrate (5 g) was introduced by suction into a 125 ml stainless steel autoclave. Hydrogen, up to 130 atm, was introduced into the autoclave, which was then rocked and heated at 80°C in a thermostatic oil bath for 23 h.

The gas chromatogram (50 m capillary column 0.02″, i.d., packed with Ucon Fluid LB-550-X at 60°C for 1 h and then the temperature increased at a rate of 1°C/min up to 130°C) of a sample of the crude product had seven peaks: A 0.2%, B

40.2%, C 10.7%, D 2.2.%, E 21.8%, F 12.4% and G 12.5%. On the base of retention times determined on authentic samples the peaks were attributed as follows: A(*Z*)-II, BI, C(*Z*)-V, D(*E*)-IV, E(*E*)-V, and G(*E*)-II.

By preparative GLC of the crude product, after it had been separated from the catalyst by distillation under reduced pressure, the compound giving peak B was isolated and it was shown to be 3-methyl-1-phenylpentane by comparison of its NMR spectrum with that of an authentic sample; the product had α_D^{25} +0.157° ($l = 1$, neat), optical purity 1.1% [2] and (*S*) configuration [2].

A portion of the mixture previously collected, and containing the compounds giving peaks C,D,E,F,G (with G 24.5%) and having α_D^{25} +0.040° ($l = 1$, neat) was treated with hydrogen under pressure (120 atm at 20°C) in the presence of Raney nickel, at 60°C for 12 h. (*S*)-(+)-3-Methyl-1-phenylpentane was formed as the only product, having α_D^{25} +0.018° ($l = 1$, neat). The optical purity of the (*E*)-II is therefore 0.5% [2] and its configuration (*S*) [2]. The other portion of the mixture, dissolved in n-pentane, was ozonized at −78°C for 2 h. This solution was then treated with an excess of $LiAlH_4$ at 0°C and then refluxed; after the usual work-up a mixture of alcohols was obtained, whose components were found to be methanol, ethanol, butan-2-ol, 2-methylbutanol, benzyl alcohol, 2-phenylethanol, 1-phenylpentan-3-ol and 1-phenylbutan-3-ol by GLC-mass analysis. The presence of butan-2-ol and 2-phenylethanol indicated that the product giving peak F was III.

(b) Without hydrogen. A solution of $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ (0.111 g) in the substrate (4.5 g) was heated in the autoclave at 150°C for 508 h under nitrogen. The crude product contained (*Z*)-II 1.2%, (*Z*)-V 22.4%, IV 6.2%, (*E*)-V 46.2%, (*E*)-III 14.0%, and (*E*)-II 10.0%. The crude material, separated from the catalyst by distillation at reduced pressure, had α_D^{25} +0.050° ($l = 1$, neat). After hydrogenation of the mixture on Raney nickel under the conditions given above, (*S*)-(+)-3-methyl-1-phenylpentane was collected, having α_D^{25} +0.020° ($l = 1$, neat) and an optical purity of 0.35%.

Acknowledgement

This research was partially supported by C.N.R. Rome.

References

1 M. Bianchi, U. Matteoli, P. Frediani, G. Menchi, F. Piacenti, C. Botteghi and M. Marchetti, J. Organomet. Chem., 252 (1983) 317.
2 F. Piacenti, M. Bianchi and P. Frediani, Adv. Chem. Ser., 132 (1974) 283.
3 M. Valle, D. Osella and G.A. Vaglio, Inorg. Chim. Acta, 20 (1976) 213.
4 G.A. Vaglio, D. Osella and M. Valle, Transition Met. Chem., 2 (1977) 94.
5 P.M. Lausarot, G.A. Vaglio and M. Valle, Transition Met. Chem., 4 (1979) 39
6 G.A. Vaglio and M. Valle, Inorg. Chim. Acta, 30 (1978) 161.
7 J.L. Graft and M.S. Wrighton, Inorg. Chim. Acta, 63 (1982) 63.
8 H.J. Reich, S.K. Shah and F. Chow, J. Am. Chem. Soc., 109 (1979) 6648.
9 C. Botteghi and G.P. Giacomelli, Gazz. Chim. Ital., 106 (1976) 1131.
10 K. Tani, T. Yamagata, S. Otsuka, S. Akutagawa, H. Kumobayashi, T. Taketomi, H. Takaya, A. Miyashita and R. Noyori, J. Chem. Soc., Chem. Commun., (1982) 600.
11 A. Stefani, Helv. Chim. Acta, 56 (1973) 1192.
12 A. Maercker, in Organic Reactions, Wiley, New York, Vol. 14, 1965, p. 270.
13 C. Botteghi, S. Gladiali, M. Bianchi, U. Matteoli, P. Frediani and P.G. Vergamini, J. Organomet. Chem., 140 (1977) 210