Table 5. *Relative intensities of the peaks due to $C_7H_{15}^+$, $C_4H_9^+$ and $C_4H_7^+$ ions in the $CI(H_2O)$ spectra of isomeric* n-*heptyl bromides*

| *m/e* | 1–$C_7H_{15}Br$ | 2–$C_7H_{15}Br$ | 3–$C_7H_{15}Br$ | 4–$C_7H_{15}Br$ |
|---|---|---|---|---|
| $C_7H_{15}^+$ | 77 | 86 | 84 | 88 |
| $C_4H_9^+$ | 22 | 13 | 15 | 12 |
| $C_4H_7^+$ | 1.4 | 1.2 | 0.7 | 0.5 |

pared to the secondary isomers. It seems that the heptyl ions formed have identical structures. It might be recalled that the intensity of the heptyl ion in the EI spectrum of 1-heptyl bromide amounts to only 5% of the intensity of this ion in the EI spectra of the secondary bromides. Furthermore the $C_4H_8Br^+$ ion is practically absent in CI(< 0.3%), whereas it is rather intense in the EI spectrum.

3.7. *Conclusions.* The $CI(H_2O)$ spectra of the alkyl halides $C_nH_{2n+1}X$ are characterized by the preponderance of the parent alkyl ions $C_nH_{2n+1}^+$ for the lower members of the series, and by the high proportion of parent alkyl ions together with certain alkyl fragments for the higher members of the series; the position and the nature of the halide functional group exert very little effect.

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## REFERENCES

[1] *R. Houriet & T. Gäumann,* Helv. *59,* 107 (1976).
[2] *A. Fiaux, B. Wirz & T. Gäumann,* Helv. *57,* 525 (1974).
[3] *A. Fiaux, B. Wirz & T. Gäumann,* Helv. *57,* 708 (1974).
[4] *J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl & F. H. Field,* Nat. Std. Data Ser., Nat. Bur. Std. No. 26 (1969).
[5] a) *J. L. Franklin,* J. chem. Physics *21,* 2029 (1953); b) *M. S. B. Munson & F. H. Field,* J. Amer. chem. Soc. *88,* 2621 (1966).
[6] *F. H. Field,* J. Amer. chem. Soc. *92,* 2672 (1970).
[7] *F. H. Field,* J. Amer. chem. Soc. *91,* 2827 (1969).
[8] *R. Liardon & T. Gäumann,* Helv. *54,* 1968 (1971).

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# 11. Asymmetric Alkenes Hydroesterification by Palladium Complexes Containing (—)-DIOP. Double Bond Migration and Formation of Isomeric Esters

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(18. XI. 75)

*Summary.* The formation of isomeric esters in the title reaction takes place through different mechanisms; one of them does not imply formation of isomerized substrate.

The asymmetric synthesis of esters through palladium catalyzed hydrocarboxylation of alkenes using (—)-2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-

dioxolane (DIOP) [1] as chiral ligand has been briefly reported by us [2]. In the presence of the above ligand and depending on the substrate, however, the formation of isomeric esters is greater [3] than when using $(PPh_3)_2PdCl_2$ as the catalyst precursor [4] [5].

It has been recently demonstrated [6–8] that the formation of isomerized substrate is not necessary to the formation of isomeric aldehydes in the cobalt catalyzed hydroformylation under high carbon-monoxide partial-pressure; in this case an isomerisation of the substrate-catalyst-complex has been postulated.

Similar conclusions have been reached for palladium promoted reactions [9] [10].

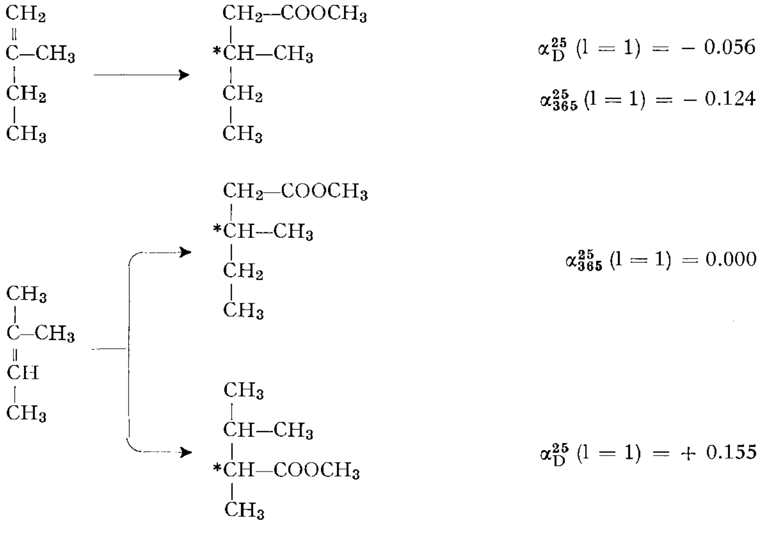
To verify whether isomerisation of the substrate of the substrate-catalyst-complex can be present also in the palladium catalyzed hydroesterification, we have carried out the hydroesterification of 2-methyl-2-butene and of 2-methyl-1-butene (*Scheme*) by using a $PdCl_2$ to DIOP molar ratio of 1:2 and methanol as the solvent at 100°C.

Methyl 3-methylpentanoate arising from 2-methyl-2-butene shows no optical activity, whereas the same ester obtained from 2-methyl-1-butene has a small but definite optical rotation. Both these facts indicate that a mechanism exists which does not imply free 2-methyl-1-butene as the intermediate for the formation of methyl 3-methyl pentanoate from 2-methyl-2-butene.

For methyl 2,3-dimethylbutanoate, which forms together with methyl 3-methylpentanoate in the hydroesterification of 2-methyl-2-butene, a small asymmetric induction (~ 0.6%) has been observed.

As the asymmetric induction in the asymmetric hydroesterification of both substrates is very low, we have carried out the asymmetric hydroesterification of α-ethylstyrene and of (*Z*)- and (*E*)-2-phenyl-2-butene, where products having higher optical purity and higher specific rotations are expected [1]. For these substrates $(DIOP)\cdot PdCl_2$ [3] was used as the catalyst precursor with benzene as the solvent and

*Scheme*

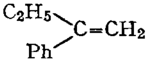
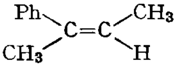
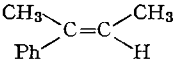


using methanol containing HCl (0.27 N) as the hydrogen donor. The results obtained are shown in the Table.

As expected, the difference in the optical activities of methyl 3-phenylpentanoate obtained from the three different substrates are much larger. Though the mechanism of isomerisation during hydroesterifications as yet has not been investigated and traces of α-ethylstyrene have been detected in the reaction mixture of (*Z*)- and (*E*)-2-phenyl-2-butene, it is possible to conclude that the isomerisation of the substrate is not an essential requisite for the formation of isomeric esters, which arise from carboxylation of carbon atoms not engaged in the double bond of the starting substrate.

Although alternative explanations can be given for the observed phenomenon, we feel, on the basis of similar effects found in the cobalt catalyzed hydroformylation reaction [6–8] that to some extent, isomerisation of the substrate-catalyst-complex takes place and it is immediately followed by hydroesterification, without the release of isomerized substrate from the catalytic complex.

*Optical activity of methyl 3-phenylpentanoate recovered from asymmetric hydroesterification of different substrates*

| Substrate | $\frac{\text{methyl 3-phenylpentanoate}}{\text{total ester products}} \cdot 100$ | $\alpha_D^{25}$ (l = 1) |
|---|---|---|
|  | 98 | + 8.06 |
|  | 50 | + 10.10 |
|  | 70 | + 10.47 |

The mechanistic implications of the above results, concerning the origin of the asymmetric induction in the palladium catalyzed hydroesterification in the presence of (–)-DIOP as asymmetric ligand will be discussed in a forthcoming paper.

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## REFERENCES

[1] *H. B. Kagan & T. P. Dang*, J. Amer. chem. Soc. *94*, 6429 (1972).
[2] *C. Botteghi, G. Consiglio & P. Pino*, Chimia *27*, 477 (1973).
[3] *G. Consiglio & M. Marchetti*, Chimia, in press.
[4] *K. Bittler, N. V. Kutepov, D. Neubauer & H. Reis*, Angew. Chem. *80*, 352 (1968).
[5] *G. Consiglio & P. Pino*, Gazz. chim. ital., in press.
[6] *D. A. von Bézard, G. Consiglio & P. Pino*, Chimia *28*, 610 (1974).
[7] *A. Stefani, G. Consiglio, C. Botteghi & P. Pino*, in preparation.
[8] *F. Piacenti, M. Bianchi & P. Frediani*, Adv. Chemistry Series *132*, 283 (1974) and references therein.
[9] *P. M. Henry*, J. Amer. chem. Soc. *94*, 7305 (1972).
[10] *R. F. Heck*, J. Amer. chem. Soc. *93*, 6893 (1971).