DECARBONYLATION OF ALIPHATIC α,β-UNSATURATED ALDEHYDES USING THE WILKINSON COMPLEX

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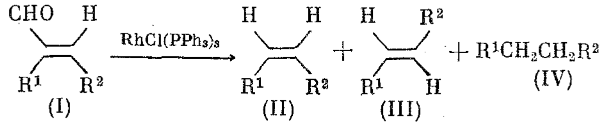
Having available an efficient method for the synthesis of E-α,β-unsaturated aldehydes (I) [1, 2], we studied their possible stereospecific decarbonylation in the presence of the $RhCl(PPh_3)3$ complex [3], the use of which permits achieving under fairly mild conditions the stereospecific decarbonylation of α-ethylcinnamaldehyde (Ic), and also of some α,β-unsaturated aldehydes of the steroid series [4].



$R^1 = C_2H_5$, $R^2 = C_7H_{15}$ (a); $R^1 = C_2H_5$, $R^2 = (CH_2)_9OAc$ (b); $R^1 = C_2H_5$, $R^2 = C_6H_5$ (c).

However, we found that aldehydes (Ia, b) are decarbonylated in the presence of $RhCl(PPh_3)3$ only on long heating at temperatures above 100°C in all of the solvents studied by us and those usually used in this reaction, i.e., under substantially more drastic conditions than aldehyde (Ic). Here we detected in the reaction products a mixture of the Z- (II) and E-olefins (III), the corresponding paraffin (IV), and high-molecular-weight substances. A careful removal of oxygen from the solvent permits lowering the amount of (IV) in the reaction products substantially (Table 1). However, also in this case the reaction practically does not go below 100° and remains nonstereospecific.

In all probability, the nonstereospecific decarbonylation of aliphatic aldehydes (Ia, b) is explained by the drastic conditions required for the reaction to proceed in the studied case, which, in turn, is apparently caused by the lower electrophilicity of the oxygen of the carbonyl group in (Ia, b) when compared with (Ic).

EXPERIMENTAL

The $RhCl(PPh_3)_3$ complex was obtained as described in [3]. Found: C 70.18; H 5.00; Cl 4.09; P 9.72; Rh 10.87%. $C_{54}H_{45}P_3RhCl$. Calculated: C 70.10; H 4.90; Cl 3.82; P 10.05; Rh 11.12%. Cinnamaldehyde is smoothly decarbonylated in the presence of the obtained complex under the conditions described in [5].

Decarbonylation of E-2-Ethyl-2-decen-1-al (Ia). In a dry argon atmosphere, to a solution of 6.1 g (6.6 mmoles) of $RhCl(PPh_3)_3$ in either dry CH_2Cl_2, C_6H_6, MeCN or PhCN was added 1 g (5.5 mmoles) of (Ia) and the mixture was kept for the time indicated in Table 1 at the given temperature. In the case of the temperatures that exceed the boiling point of the corresponding solvent the reaction was run in sealed ampuls in an argon atmosphere. To remove the oxygen the solvent was cooled to −70° in a distillation apparatus, the oxygen was removed by suction, the apparatus was filled with dry argon (the operation was repeated three times), and then the solvent was distilled in an argon atmosphere. Heating of the sample was stopped when the reaction mass became clear and a yellow precipitate appeared. The precipitate was filtered and washed well with alcohol. The combined filtrate was evaporated, analyzed by GLC (2-m-long column packed with 5% of SE-30 deposited on Chromaton N-AW-DMCS), and then chromatographed under pressure on a column packed with silica gel (40/100 μm), using hexane to elute the mixture of C_{11} hydrocarbons. The yield of the hydrocarbon mixture (when based on aldehyde taken for reaction) and its composition, established by GLC (2-m-long column packed with 15% of Carbowax 20 M deposited on Chromaton N-AW-HMDC), are given in Table 1.

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*Deceased.

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TABLE 1. Decarbonylation of E-2-Ethyl-2-decen-1-al (Ia) [(Ia):$RhCl(PPh_3)_3$ ratio = 1:1.26]

Solvent	T., °C	Time, h	Yield and composition of hydrocarbon mixture (IIa):(IIIa):(IVa), %
CH_2Cl_2	60	20	5; recovered 91% (Ia)
CH_2Cl_2	100	10	24(65 : 13 : 22) *
CH_2Cl_2	160	0,7	30(62 : 18 : 20) *
Freed of O_2 CH_2Cl_2	100	10	25(69 : 28 : 3) *
MeCN	160 †	0,7	5 *
PhCN	160	4	20(26 : 17 : 57) *

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*The remainder of the reaction products is a mixture of high-molecular substances, which was not studied closer.

†The reaction practically does not go at lower temperatures in MeCN and PhCN, and also in benzene.

Decarbonylation of E-2-Ethyl-2-dodecen-1-al (Ib). The decarbonylation of (Ib) in O_2-free CH_2Cl_2 at 100°, under the conditions described for (Ia), gave a 22% yield of a (IIb):(IIIb):(IVb) mixture in a 70:28:2 ratio.

CONCLUSIONS

The decarbonylation of α,β-unsaturated α,β-disubstituted aliphatic aldehydes in the presence of the $Rh(PPh_3)_3$ complex proceeds only at temperatures above 100° and is not a stereospecific reaction.

LITERATURE CITED

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