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Preliminary communication

TRANSITION METAL-CATALYZED SYNTHESIS OF OCTADIENOIC ACIDS FROM DIENES AND 3-BUTENOIC ACIDS

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Summary

A highly regioselective addition of dienes to 3-butenoic acids is reported. Rhodium(I) cationic complexes are exceedingly efficient catalysts.

Although butadiene, isoprene and 1,3-dienes in general have been brought into reaction with both activated and non-activated olefins [1, 2], no report has appeared on reactions with β,γ-unsaturated acids. We have investigated this reaction as part of our studies on the use of chelating systems in transition metal-catalyzed organic syntheses [3], with a view to achieving high catalytic activity and regioselectivity.

Heating butadiene or other dienes and the desired 3-butenoic acid under nitrogen in the presence of catalytic amounts of rhodium(I) complexes resulted in the formation of 3,6-octadienoic acids. In the simplest case the reaction gave I as the major product, accompanied by its isomer II (eq. 1). Triarylphosphines,

$$\begin{aligned}&\mathrm{CH_2{=}CHCH{=}CH_2 + CH_2{=}CHCH_2COOH} \xrightarrow{\text{Rh cat.}}\\&\underset{\text{(I)}}{\mathrm{CH_3CH{=}CHCH_2CH{=}CHCH_2COOH}} + \underset{\text{(II)}}{\mathrm{CH_2{=}CHCH(CH_3)CH{=}CHCH_2COOH}}\end{aligned}\tag{1}$$

preferably triphenylphosphine, were used as ligands. Cationic rhodium complexes turned out to give the best selectivity and the highest catalytic activity.

In most cases solvents were not used but many types of compound are compatible, such as ethers, esters, nitriles, alcohols or carboxylic acids.

In a typical experiment 0.3 mol of 3-butenoic acid and 0.35 mol of butadiene were allowed to react at 120°C for 12 h under N_2 in the presence of 1×10^{-5} mol of $Rh(COD)(PPh_3)_2PF_6$ and 4×10^{-5} mol of PPh_3 (COD = 1,5-cycloocta-

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diene). Conventional work up led to isolation of 0.2 mol of I [4] and II (85/15)as 3-*E* and 3-*Z* isomers in comparable amounts. The double bond at the 6-position in I is mainly *E*. Both isomers are easily hydrogenated on Pd/C to octanoic and 5-methylheptanoic acid, respectively. The yield was 66% based on the butenoic acid. This corresponds to the unusual value of 20000 mol of product per mol of complex, which is unprecedented in the synthesis of unsaturated acids. It is interesting to note that simple olefins react with butadiene in the presence of rhodium complexes [1, 2] but these reactions lead to predominant attack on the internal position of the double bond. In particular when the butenoic methyl ester was used with $RhCl_3$ as catalyst most of the product was a mixture of isomers derived from attack of R (R = $CH_3CH{=}CHCH_2$ or $CH_2{=}CHCH(CH_3)$) on the internal carbon of the double bond as in $CH_2{=}C(R)$-CH_2COOCH_3. When $RhCl(PPh_3)_3$ was used, a complex mixture, containing both linear and branched products, was formed.

We thus attribute the high regioselectivity observed with 3-butenoic acid to the directing effect of the chelating butenoic group in a complex of the type $(CH_3CH{=}CH{=}CH_2)Rh(Cl)OOCCH_2CH{=}CH_2$ (phosphines are omitted for simplicity) where the butenoic double bond must become η^2-coordinated and the butadiene-derived η^3-allyl group must go to the η^1-form and migrate to the terminal butenoic carbon.

The reaction described is not limited to the unsubstituted 3-butenoic acid. Higher homologues, bearing alkyl substituents on the 2, 3 or 4 positions, all react in similar way. In particular the main reaction product from butadiene and 3-butenoic acid still is a 3-butenoic acid and it reacts further, although more slowly, at C(4) to give $R_2CH{=}CHCH_2COOH$ and $R_3CCH{=}CHCOOH$ (R as above).

Higher homologues of butadiene can also react with butenoic acids, thus widening the scope of the reaction remarkably and isoprene gives product III [5] (eq. 2).

$$CH_2{=}C(CH_3)CH{=}CH_2 + CH_2{=}CHCH_2COOH \xrightarrow{\text{Rh cat}} \underset{\text{(III)}}{(CH_3)_2C{=}CHCH_2CH{=}CHCH_2COOH} \qquad (2)$$

Extension to different substrates and other aspects related to catalytic activity of several complexes are currently being investigated. $Ni[P(O\text{-}i\text{-}Pr)_3]_4$ can also be used as catalyst; in preliminary experiments I and II (80/20) were formed together with their 2,6-isomers (mainly *E*). The yield was 96% and the catalytic activity corresponded to 90 mol per mol of complex.

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