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ZIRCONIUM ASSISTED REGIOSELECTIVE ACYLATION OF DIENES WITH SATURATED OR UNSATURATED ESTERS TO LEAD TO β,γ-UNSATURATED CARBONYL COMPOUNDS

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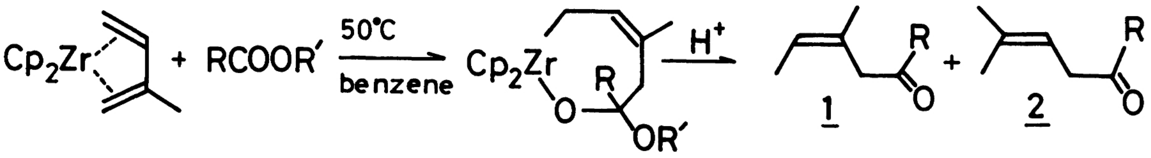
Regioselective formylation or acylation of isoprene at the C_1 atom was realized by reaction of Cp_2Zr(isoprene) with saturated esters followed by protonolysis with acetic acid. The corresponding reaction with various alkyl acrylates resulted in the formation of allyl vinyl ketones.

Highly regioselective addition of ketones and nitriles to isoprene at the C_1 atom has been achieved using a ziconium-isoprene complex, Cp_2Zr(isoprene), as reported previously.[1)] We report here regioselective reactions of saturated or unsaturated esters with Cp_2Zr(isoprene) to give β,γ-unsaturated carbonyl compounds. The reaction of ethyl esters with Cp_2Zr(isoprene) underwent successfully at 50°C for 2 h in benzene and treatment of the product with acetic acid gave (Z)-



(1)

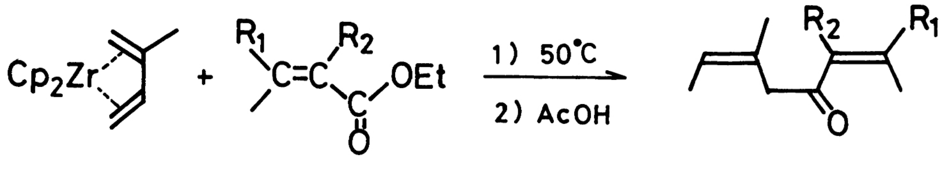
Table 1. Distribution of the Products in the Acylation of Cp_2Zr(isoprene) with Esters

Esters	1(%)	2(%)	Total yield/%
HCO_2Et	99	0	96
CH_3CO_2Et	92	8	96
$i\text{-}C_3H_7CO_2Et$	98	2	98
$CH_2=CHCO_2CH_3$	99	0	96
$CH_3CH=CHCO_2CH_3$	94	6	90
$CH_2=C(CH_3)CO_2CH_3$	92	8	85
$(CH_3)_2C=CHCO_2C_2H_5$	98	2	91

β,γ-unsaturated ketones 1 as confirmed by NOE method (eq. 1). Typical examples are given in Table 1. A practical advantage of this reaction lies in the highly regioselective formylation or acylation of isoprene on hindered site(at C_1 atom) leading to high yields of the product. Thus, a natural product, dihydrotagetone, was prepared by acylation with ethyl isovalerate followed by protonolysis. An oxametallacycle depicted in eq. 1 was postulated as an intermediate because the product obtained from ethyl acetate gave $CH_2DCH=C(CH_3)CH_2COCH_3$ exclusively (93 %) by treatment with CH_3COOD as evidenced by the mass and the ^1H-NMR spectrum. The IR spectrum of the intermediate showed no absorption assignable to the C=O stretching vibration in the region 1450~1800 cm^{-1}. On protonolysis, cleavage of the acetal linkage generates the carbonyl group. Four absorption peaks observed in 1060~1190 cm^{-1} are assignable to the C-O-C vibration of the acetal. Thus, thermal decomposition of the metal acetal linkage to the ketone was completely supressed when zirconium was used as the metal. This behavior contrasts strinkingly with that of the corresponding Grignard reagents which generally provide tertiary alcohols. Recently, similar acylation of early transition metal aryl compounds was reported by Y. Fujiwara for the reaction of PhYbI with ethyl acetate which gave acetophenone in 82 % yield.$^{2)}$

N,N-Dialkylacetamide and acetic anhydride react just as esters do. For example, N,N-dimethylacetamide reacts readily with Cp_2Zr(isoprene) at 50°C and the orange color of the solution changed to colorless. Treatment of the product with acetic acid gave 4-methyl-4-hexen-2-one in 92 % regioselectivity in 90 % yield. Acetic anhydride provided the same compound in 99 % regioselectivity in a quantitative yield.

The present method is widely applicable and provides a promising route to allyl vinyl ketones by reaction with α,β-unsaturated esters(eq. 2 and Table 1). The regioselectivity was high, irrespective of the presence of alkyl substitutents on the alkyl acrylates. The structure of the resulting products was established by the ^1H-NMR, mass and IR spectra and elemental analysis.



(2)

References

1) H. Yasuda, Y. Kajihara, K. Mashima, K. Nagasuna, and A. Nakamura, Chem. Lett., 1981, 671.
2) T. Fukagawa, Y. Fujiwara, K. Yokoo, and H. Taniguchi, Chem. Lett., 1981, 1771.

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