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Oxidative Radical Addition to Alkenes: a Convenient Route to γδ-Unsaturated Acids and γ-Lactones

By Gennady I. Nikishin, Maxim G. Vinogradov, and Tat'ana M. Fedorova (N. D. Zelinsky Institute of Organic Chemistry, U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.)

Summary Diethyl malonate and diethyl alkylmalonates react with olefins and manganese(III) or cobalt(III) acetates in the presence of copper(II) acetate to give diethyl alk-2-enylmalonates which produce upon hydrolysis $\gamma\delta$ -unsaturated acids or γ -lactones.

Synthesis of aliphatic acids *via* malonic esters is usually based on two procedures: (i) alkylation of sodium derivatives of malonic ester with alkyl halides¹ or (ii) free-radical addition of the ester to an olefin in the presence of peroxide

initiators.² We report a modification of the latter pathway, which involves the use of transition-metal salts.

Oxidation of malonic acid esters with these salts in the presence of an alk-1-ene leads to alkyl-substituted compounds. For example, diethyl malonate (0.5 mol) reacts with manganese(III) acetate dihydrate (0.025 mol) and hept-1-ene (0.05 mol) at 90° to afford n-heptyl malonate in 50% yield (based on oxidant).

The addition of catalytic amounts of copper(II) acetate completely alters the course of the reaction. In this case,

HCR¹ (CO₂ Et)₂ + M^{III} (OAc)₃
$$\longrightarrow$$
 ·CR¹ (CO₂ Et)₂
+ M^{II} (OAc)₂ + Ac OH
 $R^2CH_2C(R^3) = CH_2 + ·CR^1 (CO_2 Et)_2 \longrightarrow$
 $R^2CH_2 \dot{C} (R^3)CH_2 CR^1 (CO_2 Et)_2 \xrightarrow{CuII(OAc)_2}$
(1)
 $R^2CH = C(R^3)CH_2 CR^1 (CO_2 Et)_2 \xrightarrow{H_2O.OH^2}$
(2)
 $R^2CH = C(R^3)CH_2CH (R^1)CO_2H$
 $R^2CH_2 CO_2$
(3)
 $R^2CH_2 CO_2$

Scheme. $R^1=H$ or Bu^n , $R^2=H$, Bu^n , or $n\text{-}C_8H_{11}$, $R^3=H$ or Me. $M^{111}=Mn^{111}$ or Co^{111} .

diethyl hept-2-enylmalonate was the only isolable product. Other alkenylmalonates were similarly obtained (40-70%). For example, a mixture of diethyl malonate (0.2 mol), isobutene (0·1 mol), manganese(III) acetate (0·1 mol), and copper(II) acetate (0.00075 mol), when shaken in acetic acid (65 ml) at 60°, until the brown colour had disappeared, vielded diethyl methallylmalonate (60%). The formation of the products may be explained as shown in the Scheme.

It was shown earlier³ that α -oxoalkyl radicals, obtained from aliphatic aldehydes and ketones, reacted with olefins in the presence of copper(II) acetate to afford a mixture of $\beta\gamma$ - and $\gamma\delta$ -unsaturated carbonyl compounds arising from the oxidation of intermediate radicals. By contrast, the oxidation of the radical (1) proceeds selectively to give only the isomer (2) (g.l.c. and n.m.r.). Elimination of hydrogen from the δ - rather than from the β -carbon atom in radical (1) is probably related to the polar effect of the CO₂R groups, which prevents the nucleophiles from attracting the β -hydrogen atom.

Hydrolysis of the diesters (2) was carried out in acidic4 or basic⁵ medium. Diesters of the type (2) with an internal double bond were converted on hydrolysis into γδ-unsaturated acids (3). Decomposition of alkenyl-substituted esters (2; $R^2 = H$, $R^3 = Me$) in acidic solution gave the γ -lactone (4).

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⁴ C. M. Stevens and D. S. Tarbell, J. Org. Chem., 1954, 19, 1996.

⁵ V. P. Gol'mov, Zhur. obshchei Khim., 1953, 23, 1162.