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A NEW TISHCHENKO-TYPE ESTER FORMATION CATALYZED BY RUTHENIUM COMPLEXES

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A self-condensation of aldehydes to yield esters is catalyzed by ruthenium complexes under mild conditions without appreciable side reactions. The reaction is applicable to both aliphatic and aromatic aldehydes, and the ruthenium complexes proved to be particularly active catalysts among other transition metal complexes examined.

The catalytic self-condensation of aldehydes to esters is known as Tishchenko reaction, which is usually catalyzed by aluminum alkoxides.[1,2] Somewhat detailed studies have been made concerning the structural effects of aldehydes and catalysts, cocatalysts and additives as well as crossed ester formations.[2-5] Although metal alkoxides serve as relatively good catalysts, the catalyst efficiency is not quite satisfactory and the reaction sometimes entails the formation of trimeric glycol esters as the result of aldol-condensation.[6] Effect of addition of Lewis acids such as aluminum trichloride, zinc halides, and mercury chloride has been examined and they proved to enhance the reaction rate.[2,4] However, no catalyst based solely on transition metal complexes has been reported to our knowledge.[7] We now report a novel and clean Tischchenko-type ester formation which is free from by-products produced by aldol-condensation and is catalyzed by neutral ruthenium complexes under mild conditions.

$$2\mathrm{RCHO} \xrightarrow[\text{ruthenium complex}]{} \mathrm{RCO_2CH_2R}$$

Table 1 summarizes some typical examples of the ester formation catalyzed by dihydridotetrakis(triphenylphosphine)ruthenium(II), $RuH_2(PPh_3)_4$. The reaction of propionaldehyde to propyl propionate proceeds at room temperature with evolution of heat on addition of $RuH_2(PPh_3)_4$ to the aldehyde. Employment of higher reaction temperature did not significantly enhance the yield of the ester. Careful purification of the aldehyde is required to remove carboxylic acid or water which completely suppresses the ester formation. A small amount of alcohol was formed in the reaction product but no aldol-condensation product was detected. The alcohol was found to be a weak inhibitor while addition of olefin had no significant effect. Addition of an extra amount of triphenylphosphine or 1,2-bis(diphenylphosphino)ethane(dpe) suppressed the reaction, the fact suggesting the requirement

Table 1. Reaction Conditions and Yields or Ester Formation.[a)]

RCHO		$RuH_2(PPh_3)_4$ (Cat.)		Temp.	Time	RCO_2CH_2R		
R	mmol	mmol	RCHO/Cat.	°C	h	Produced	Ester/Cat.	Conv.
			mol.ratio			mmol	mol.ratio	%
CH_2CH_3	68.0	0.051	1333	r.t.	2	13.4	261	46
	68.5	0.250	274	r.t.	2	17.4	70	71
$(CH_2)_2CH_3$	61.2	0.167	366	r.t.	1	19.7	118	65
	59.2	0.256	231	r.t.	2	24.9	97	84
	30.1	0.239	126	r.t.	2	16.5	69	95
	63.8	0.148	431	100	2.5	20.6	139	71
$CH(CH_3)_2$	59.8	0.226	265	r.t.	4.5	21.1	93	76
$(CH_2)_3CH_3$	23.5	0.14	168	85	2	5.08	36	46
$CH_2CH(CH_3)_2$	18.2	0.13	140	85	3	6.17	47	70
$(CH_2)_4CH_3$	16.1	0.20	81	85	3	3.46	17	45
C_6H_5	14.8	0.12	123	r.t.	2	1.69	15	22

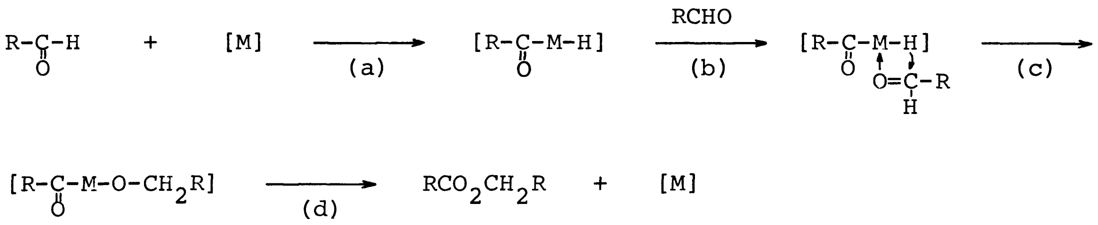
a) Reaction was carried out in a vacuum (10^{-6} atm.) without solvent unless otherwise stated. Reaction conditions were not optimized.

of partial dissociation of PPh_3 from the complex to provide a coordination site for activating the aldehyde. Pyridine also acts as an inhibitor. The higher aliphatic aldehydes as well as aromatic aldehydes are converted into esters in similar manners.

Many transition metal complexes other than ruthenium were also examined, but the ruthenium complexes proved to be specifically active for the ester formation. A rhodium complex, $RhH(PPh_3)_4$, converted butyraldehyde into butyl butyrate but the quantity of the ester produced was slightly over the stoichiometric amount. An iron complex, $FeH_2(N_2)(PPh_3)_2$, showed a weak activity but it mainly gave a polymeric substance presumably formed by aldol condensation. $CoH(N_2)(PPh_3)_3$, $PtEt(acac)(PPh_3)_2$,[8)] $PdMe_2(PMePh_2)_2$[9)] and $PdEt_2(PMePh_2)_2$[9)] produced only minor quantities of esters from aldehydes. Molybdenum complexes including $MoH_4(dpe)_2$, $MoH_4(PMePh_2)_4$, and $Mo(C_2H_4)(dpe)_2$ were either unchanged (the first complex) or decomposed (the last two complexes) on treatment with butyraldehyde and no ester formation was observed. On the other hand, low valent ruthenium complexes such as $RuH_2(PPh_3)_4$, $RuH_2(PPh_3)_3$, $Ru(C_2H_4)(PPh_3)_3$(10) and $RuH(CH{=}CMeCO_2Et)(PPh_3)_3$(11) showed very high activities and $RuH_2(CO)(PPh_3)_3$, $RuHCl(CO)(PPh_3)_3$ and $RuHCl(PPh_3)_3$ showed considerably high activities, whereas $RuCl_2(PPh_3)_3$ and $Ru(CO)_3(PPh_3)_2$ were not effective.

The catalytic formation of esters from aldehydes promoted by the ruthenium complexes is always accompanied by alcohol formation whose amount roughly corresponds to that of catalyst used. It is known that $RuH_2(PPh_3)_4$ catalyzes the transfer of hydrogens from hydrogen donors such as alcohols, aromatic hydrocarbons and dioxane to aldehyde yielding alcohols.12) It is conceivable that one mol of alcohol per mol of ruthenium may be produced by transfer of two hydrido ligands in $RuH_2(PPh_3)_4$ prior to the initiation of the ester forming catalytic cycle.

It is premature to discuss the reaction mechanism in detail, but it must be quite different from the conventional Tischchenko reaction catalyzed by aluminum alkoxide where the transfer of the alkoxo group to the coordinated aldehyde has been established by a mechanistic study.5) We tentatively assume the following reaction scheme involving the oxidative addition of aldehyde to ruthenium.



where [M] stands for a coordinatively unsaturated low valent ruthenium complex. In this scheme the oxidative addition of aldehyde to a ruthenium complex gives an acylhydridoruthenium complex (step a) to which the second molecule of aldehyde coordinates (step b) and accepts the hydrido ligand to afford an acyl-alkoxo complex (step c) which on reductive elimination gives the ester and regenerates the catalytically active unsaturated species (step d) which further carries the catalytic cycle. The formation of the acylruthenimm intermediate is supported by isolation of a σ-diacylruthenium complex, $Ru(COEt)_2(CO)_2(PPh_3)_2$, which was obtained by the reaction of propionaldehyde with $RuH_2(PPh_3)_4$ at 80°C and characterized on the basis of IR and NMR data as well as by chemical reactions such as the formation of methyl ethyl ketone on its treatment with methyl iodide.13) The carbonyl groups in the diacyl complex must have arisen from decarbonylation of the acyl groups. The scheme shown above may be regarded, at least partially, as the reverse process of the ester cleavage reaction catalyzed by low valent transition metal complexes.14)

Further extension of the reaction and the mechanistic study are now in progress.

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References and Note

1) V. E. Tishchenko, J. Russ. Phys. Chem. Soc., 38, 355, 485 (1906).
2) W. C. Child and H. Adkins, J. Am. Chem. Soc., 45, 3013 (1923); ibid., 47, 798 (1925).
3) I. Lin and A. R. Day, J. Am. Chem. Soc., 74, 5133 (1952).
4) K. Kasano and T. Takahashi, Yuki Gosei Kagaku Kyokai Shi, 23, 144 (1965).
5) Y. Ogata, A. Kawasaki, and I. Kishi, Tetrahedron, 23, 825 (1967).
6) F. J. Villani and F. F. Nord, J. Am. Chem. Soc., 68, 1674 (1946); ibid., 69 2605 (1947).
7) Recently self-condensation of aromatic aldehydes to aromatic esters by the use of disodium tetracarbonylferrate(-II) has been reported. However, the feature and the proposed mechanism of this system quite differs from those of the present study: M. Yamashita, Y. Watanabe, T. Mitsudo, and Y. Takegami, Bull. Chem. Soc. Jpn., 49, 3597 (1976).
8) T. Ito, T. Kiriyama, and A. Yamamoto, Bull. Chem. Soc. Jpn., 49, 3250 (1976).
9) T. Ito, H. Tsuchiya, and A. Yamamoto, Bull. Chem. Soc. Jpn., 50, 1319 (1977).
10) S. Komiya and A. Yamamoto, Bull. Chem. Soc. Jpn., 49, 2553 (1976).
11) S. Komiya, T. Ito, M. Cowie, A. Yamamoto, and J. A. Ibers, J. Am. Chem. Soc., 98, 3874 (1976).
12) H. Imai, T. Nishiguchi, and K. Fukuzumi, J. Org. Chem., 41, 665, 2688 (1976).
13) H. Horino, T. Ito and A. Yamamoto, Abstr. No. 2E33, 36th Annual Meeting of the Chemical Society of Japan, Osaka, April 1977.
14) J. Ishizu, T. Yamamoto, and A. Yamamoto, Chem. Lett., 1976, 1091.

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