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Preliminary communication

CATALYTIC OXIDATIVE COUPLING OF DIOLS BY $Ru_3(CO)_{12}$

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Summary

$Ru_3(CO)_{12}$ acts as a homogeneous catalyst precursor for the transformation of α,ω-diols to polyesters and lactones.

Recently we reported [1] the following novel oxidative coupling of alcohols to esters:

$$2RCH_2OH + 2A \xrightarrow[145^\circ C]{Ru_3(CO)_{12}} RCO_2CH_2R + 2AH_2$$

The catalyst is $Ru_3(CO)_{12}$ (0.3% mol); the reaction requires a hydrogen acceptor (A), such as tolane, chalcone or maleic anhydride. We have now obtained the following information about this reaction:

(a) Carboxylic acids are not intermediates.
(b) Aldehydes are intermediates; however, a Tishchenko type reaction i.e. $2RCHO \rightarrow RCO_2CH_2R$ was experimentally ruled out.
(c) The participants in the intermolecular coupling stage are alcohols and aldehydes.
(d) Oxygen is not involved; the reaction is carried out under argon or nitrogen.
(e) The reaction is general in that various types of alcohols were readily converted into esters.
(f) The relative reaction rates with $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ as catalysts are 1/100/10.
(g) Mononuclear organometallic complexes, known for their catalytic H-transfer activity [2—5], are inactive in the reaction.

We have now found that $Ru_3(CO)_{12}$ catalyzes polymerization and lactonization of α,ω-diols. The polymerization is unique since such a direct transforma-

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tion of diols to polyesters circumvents the use of carboxylic acids, or any of its activated forms. Moreover, new polyesters with structurally equivalent alcohols-carboxylic acid moieties can be made. Noteworthy also is the formation of lactones from 1,4-butanediol and 1,5-pentanediol.

A series of α,ω-diols were treated with catalytic quantities of $Ru_3(CO)_2$ in the presence of tolane in diglyme at 145°C (Table 1); in all cases the tolane is quantitatively reduced to stilbenes with concomitant disappearance of the diols (GC). 1,4-Butanediol yields quantitatively and selectively butyrolactone, identified by comparison with an authentic sample. The NMR spectrum exhibits only signals originating from butyrolactone, thus ruling out polymerization.

TABLE 1

RATE AND SPECTRAL DATA

α,ω-Diol	Initial rate[a] (mmol· h^{-1})	ν(CO) (cm^{-1})[b]	NMR, δ (ppm)[c]
1,10	1.9	1741	4.05(t,1); 2.26(t,1); 1.61(m,7).
1,6	1.6	1734	4.06(t,1); 2.3(t,1); 1.65(m,3).
1,5	3.0	1732	4.26(t,1.5); 4.07(t,1.0); 2.49(t,1.5); 2.32(t,1.0); 1.78(m,
1,4	3.1	1774	4.18(t,1); 2.32(m,2).
1,3	1.7	1734	[4.35(t); 4.19(t)2.5], 3.88(t,1); [2.66(t); 2.58(t)2.4]; 1.99(quint,1).
1,2	2.1	1752 1713(sh)	4.81(s,1.0); [4.71(s), 4.69(s)1.9]; 4.39(s,4.3); 4.29(s,2.6); 4.17(s,2.7).

[a] The rates were measured with 10.0 ml solution of diol (0.75 *M*), tolane (1.5 *M*) and $Ru_3(CO)_{12}$ (5×10^{-3} *M*) at 140°C; the rates were constant up to 2 h reaction time. [b] Direct measurement of the reaction mixture in diglyme. [c] Measured in $CDCl_3$; the number in brackets are integral ratios.

With the rest of the diols, removal of the solvent and the stilbenes, by repeated extraction with petroleum ether, left a solid residue with polymer-like properties. The NMR and IR spectra of these solids are presented in Table 1, and discussed below.

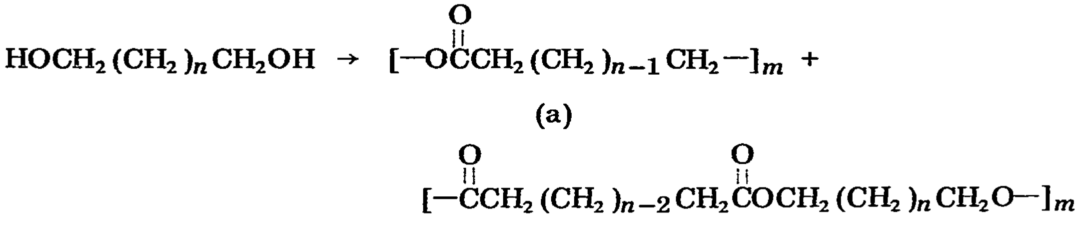
1,10 and 1,6 diols. The IR spectra clearly indicate the presence of an ester function. The two NMR triplets at ca 4.0 and 2.3 ppm, each spin-coupled to the multiplet at 1.6 ppm (spin decoupling), are indicative of the two methylene groups flanking the ester function: $CH_2\mathit{CH_2}OCO\mathit{CH_2}CH_2$.

The composition of the polyester obtained from 1,6-hexanediol was elucidated by analyzing the products arising from trans-esterification of the polymer with methanol:

$$\underset{(1,6)}{\text{Polymer}} \xrightarrow[H^+]{MeOH} HOCH_2(CH_2)_4CO_2Me + MeO_2C(CH_2)_4CO_2Me + HO(CH_2)_6OH$$

Molar ratio: 2.4 1.0 1.0

The nature of the products indicates two general modes of polymerization:



$$HOCH_2(CH_2)_nCH_2OH \rightarrow [-O\overset{O}{\overset{\|}{C}}CH_2(CH_2)_{n-1}CH_2-]_m +$$

(a)

$$[-\overset{O}{\overset{\|}{C}}CH_2(CH_2)_{n-2}CH_2\overset{O}{\overset{\|}{C}}OCH_2(CH_2)_nCH_2O-]_m$$

(b)

Of course polymers having both recurring units ($a + b$) are also possible. While a molar ratio $a/b > 1$ seems reasonable, final analysis must await kinetic experiments.

1,5 and 1,4-diols. These two diols give rise to lactones. However while 1,4-butanediol generates exclusively butyrolactone, 1,5-pentanediol gives rise to a mixture of δ-valerolactone, identified by comparison with an authentic sample, and a polymer. The broad IR bond at 1732 cm^{-1} is compatible with such a mixture. The two sets of triplets in the NMR spectrum are assigned to the CH_2 groups flanking the ester functions; the high-field signals in each set (4.07 and 2.32 ppm) are associated with δ-valerolactone [6]; the second set (4.26 and 2.49 ppm) are assigned to the polymer. It is noteworthy that the reaction rates of the above two diols are the fastest in the series (Table 1).

1,2 and 1,3 diols. Solid polymeric products were obtained from the reaction of the above two diols with $Ru_3(CO)_{12}$ and tolane. Again, the IR spectra of the crude reaction mixtures indicate an ester bond formation, but the NMR spectra are quite complex. With 1,3-propanediol a very weak signal (3.37 ppm, singlet) from a malonate unit ($O_2CCH_2CO_2$) was recorded. At present we cannot assign the three low field triplets (3.88—4.35 ppm). It is conceivable that the active methylene group noted above condenses with a free aldehyde known to be present in solution.

The low and high field NMR signals of the solid crude polymeric product obtained from ethylene glycol (4.81 and 2.70 ppm) are assigned to OCH_2CO_2 and OCH_2CH_2O units respectively. However, in this case formation of lactones is also possible, and these may account for the multiple signal NMR spectrum (Table 1).

The compositions of these two mixtures are being currently studied.

Although the polymers are not yet well defined and their molecular weights were not determined, it is clear, from the evidence presented above, that our new catalytic system is capable of transforming diols to polyesters and lactones. The usefulness of this new type of polymerization and lactonization is being evaluated.

It is important to distinguish between our catalytic system and that described by Descotes et al. [7], $[H_2Ru(PPh_3)_4]$. With the latter catalyst, in the presence of an H-acceptor, alcohols are transformed into aldehydes (ketones) and lactols into lactones, but in no case was intermolecular oxidative coupling of alcohol to ester observed. With diols, only in those cases where lactol formation is geometrically favoured (1,5 and 1,6-diols) were lactones obtained, and with other diols polymeric aldol-type condensation products, arising from di-aldehydes, were obtained [7].

The unique property of our catalytic system is its ability to form an ester linkage intermolecularly. Such behaviour can be attributed to the difference in the properties of the cluster catalytic precursor from those of mononuclear catalysts, which transform alcohols only to the aldehyde stage [2—5].

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