FORMATION OF CARBONATE OR BENZOATE ESTERS VIA NITROSOCARBONYL COMPOUNDS

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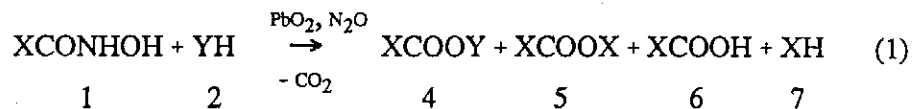
A novel one-vessel oxidation and subsequent solvolysis of hydroxamic acids in the presence of lead(IV) oxide have been explored.

Introduction

Compounds of a hydroxamic acid type are practically inert to neutral protic solvents. The solvolysis velocity is influenced by the presence of acidic, basic or micelar catalysts and/or temperature[1,2]. Other ways of solvolytic reactions have not been reported.

We have now found that the presence of lead(IV) oxide in alcoholic or phenolic solutions of alkyl- resp. aryl N-hydroxycarbamates or benzhydroxamic acid 1 has a dramatic influence on velocity of their solvolyses. From alkyl- or aryl N-hydroxycarbamates 1b - 1h mixtures of the carbonate esters 4, 5 were formed together with other alcohols or phenols 7 in the liquid phase. Dinitrogen monoxide together with carbon dioxide were found among the gaseous products. The solvolytic products of benzhydroxamic acid 1a in methanol were methyl benzoate 4a and benzoic acid 6a together with dinitrogen monoxide. The general reaction may be presented according to Eq. (1)

$$XCONHOH + YH \xrightarrow[- CO_2]{PbO_2, N_2O} XCOOY + XCOOX + XCOOH + XH \quad (1)$$

$$\quad 1 \qquad\quad 2 \qquad\qquad\qquad 4 \qquad\quad 5 \qquad\quad 6 \qquad\quad 7$$

X = Ph, BuO, PhO, $(4-CH_3C_6H_4O)$
Y = MeO, iPrO, BuO, PhO, $(4-CH_3C_6H_4O)$

The ester 4h was not observed in the reaction mixture in the absence of solvent 2. Lead(IV) oxide was practically inactive to all the used solvents 2 under similar reaction conditions. The reaction (1) was slightly exotermic and took place at room temperature. The quantity of lead(IV) oxide is a limiting factor for the formation of products 4 - 7 (see Table I run d). Similarly, the quality of lead(IV) oxide has an influence on the yield of products (see Table I runs d, f). Commercial oxide (Lachema, Brno) gives poorer yields than the oxide freshly prepared according to Ref.[3] (see Table I runs d, f). By comparing the rel. % of

Table I Preparation of esters 4 from hydroxamic acids 1 according to Eq. (1) and balance of all products

Exp.	X	Y	Yield (%) of 4[a]([b]) isolated	Rel. yield GC, (%)[c] 4	5	(6), 7
a	Ph	MeO	(52)[d]	95	-	(5)
b	BuO	PhO	-	15	56	29
c	PhO	BuO	-	36	3	61
d	PhO	PhO	23, (42), (5)[e]	47	-	53
e	PhO	$(4-MeC_6H_4O)$	-	22	51	27
f	$(4-MeC_6H_4O)$	$(4-MeC_6H_4O)$	24, (44)	54	-	46
g	PhO	iPrO	-	0	15	85
h	PhO	-	14[f]	41	-	59

[a] From equimolar mixture of 1 and 2 and two moles of lead(IV) oxide in benzene solution.
[b] With lead(IV) oxide prepared according to Ref.[3].
[c] GC % were determined using standard samples (which were prepared according to Ref.[4]: butyl phenyl carbonate b.p. 102 - 104 °C / 16 mm Hg, n_D^{20} 1.4699, diphenyl carbonate m.p. 79 - 80 °C, dibutyl carbonate b.p. 96 - 97 °C / 16 mm Hg, n_D^{20} 1.4129, phenyl p-tolyl carbonate m.p. 63 - 64 °C, di-p-tolyl carbonate m.p. 113-114 °C, phenyl isopropyl carbonate b.p. 96 - 97 °C / 16 mm Hg, n_D^{20} 1.4795.
[d] In the presence of 30 molar amount of methanol.
[e] In the presence of 0.2 molar amount of lead(IV) oxide.
[f] In the absence of 2, yield of 5h

products 4 - 7 we can see a lowering reactivity of the alcohols or phenols 2 in the order: 4-MeC$_6$H$_4$OH, PhOH, iPrOH.

A classical reaction of methyl benzoate with hydroxylamine gives benzohydroxamic acid and methanol already at room temperature[5]. We have observed the reverse reaction. It is not supposed to be caused by a change of equilibrium in the presence of lead(IV) oxide. We propose that the course of the reaction has two steps. *In-situ* unstable nitrosoformate or nitrosocarbonyl benzene 3 is generated. Compounds of this type were prepared by Gordon[6] using tetraethyl ammonium periodate oxidation of 1 in dichloromethane. The intermediate 3 can undergo a reaction with 2 giving the esters 4 or can reacts with water producing 6 in a competitive process. Alkyl or aryl hydrogencarbonates 6b - 6f can easily be decarboxylated to alcohols or phenols 7, which can react with 3 in competition solvolysis (see Scheme A). We suggest an elimination-addition mechanismus of 3 with above given solvents. Subsequently formed hyponitric acid is spontaneously destroyed to dinitrogen monoxide.

XCONHOH → XCON=O → XCOOY 4

XCON=O → XCOOH → XH

XCOOX 5

Scheme A

An alternative transformation of intermediate 3 could involve its homolytical decomposition into radicals XCO· and NO· which would combine to the same products 4 - 7. In this case we would find nitrogen monoxide and oxalate esters in the reaction mixture which, however, was not the case. A relatively great selectivity of reaction velocity with regard to the structure of alcohols and phenols does correspond neither to a homolytic nor to a heterolytic splitting (see Table I). Other indirect suppost of the suggested addition-elimination mechanism

of intermediate 3 with 2 was given by Gordon[5]. He found that phenyl nitrosoformate undergoes cyclization reactions with dienes leading to phenyloxycarbonyl-dihydrooxazines in which the C-N bond was not changed.

Typical-reaction: Oxidation solvolysis of phenyl N-hydroxycarbamate 1d with phenol

A freshly prepared phenyl N-hydroxycarbamate (2.5 g, 16 mmol) was suspended in benzenic (50 ml) solution of phenol (1.6 g, 16 mmol). The apparatus was connected with a gasometer. Lead(IV) oxide commercial grade (7.6 g, 32 mmol) was added portionwise with constant stirring under nitrogen atmosphere at room temperature during 30 min. The temperature of the mixture increased to 35 °C spontaneously. Then the mixture was refluxed with stirring for another 30 min. until the liberation of gas (380 ml) stopped. A sample of solution was withdrawn for GLC analysis. The heterogeneous mixture was filtered and the solution separated was extracted with aqueous sodium hydroxide, dried (Na_2SO_4) and the solvent was evaporated until dry. Diphenyl carbonate 4d (0.8 g, 23 %0 was crystallized, m.p. 79 - 80 °C (methanol). Mass spectrum (m/z): 214 (M+15%), 169 (21), 142 (24), 141 (54), 115 (7), 93 (10), 77 (100), 65 (83), 51 (64), 39 (81). IR absorption (Nujol), ν_{max}/cm^{-1} 1776 (C = 0), 1252, 1181 (C - O). NMR data δ_H(360.14 MHz: $CDCl_3$: Me_4Si) 7.22 - 7.27 m, 3H(H2, H4, H6), 7.35 - 7.40 m, 2H(H3, H5). δ_c(360.14 MHz: $CDCl_3$: Me_4Si) 150.98 (C 1), 120.86 (C 2, 6), 126.25 (C 4), 129.53 (C 3, 5).

IR dat of gaseous phases, ν_{max}/cm^{-1} 2349 (CO_2), 2224 (NN), 1349 (CO_2), 1286 (NO), 667 (CO_2), 585 (N_2O)

Mass spectrum 1 fraction: 44 (M+100%), 28 (12), 22 (3), 16 (9), 12 (10). 2. fraction: 44 (M+100%), 30 (42), 28 (13), 16 (8), 14 (8). Ratio of fractions was 1 : 2.

The IR and NMR spectra were measured on a Perkin-Elmer and a Bruker AMX-360 apparatus, respectively. The GC-MS was carried out on a Fisons Mega 5160 apparatus with mass detector QMD-100.

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