ALKOXYCARBONYLATION OF ALCOHOLS AND PHENOLS BY NITROSOFORMATES

Jaromir MINDL[a1], Ales HALAMA[a2] and Zdenek CERNOSEK[b]

[a] *Department of Organic Chemistry, University of Pardubice, 532 10 Pardubice, Czech Republic; e-mail: [1] mindl@hlb.upce.cz, [2] halama@hlb.upce.cz*

[b] *Department of General and Inorganic Chemistry, University of Pardubice, 532 10 Pardubice, Czech Republic; e-mail: cernosek@hlb.upce.cz*

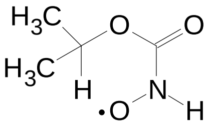
Received March 18, 1996
Accepted April 16, 1996

Unstable neutral radicals [ROCONHO$^\bullet$] **2** and nitrosoformates **3** are formed by oxidation of *N*-hydroxycarbamates with lead dioxide. In the presence of alcohols or phenols and water they solvolyzed to mixtures of symmetrical **4** and asymmetrical **5** carbonates. The content of asymmetrical carbonates **5** increases with increasing reactivity of the nitrosoformates **3** formed, temperature, the content of water in the reaction mixture, and with decreasing reactivity of alcohol. The reactivities of individual alcohols have been evaluated with the help of competitive alcoholysis. The new method of alcohol or phenol alkoxylation has been verified experimentally by preparing six asymmetrical carbonates which were obtained in 34 to 47% yields.

Key words: Lead dioxide, hydroxycarbamates oxidation; Carbonates, preparation by alkoxycarbonylation; Alcohols, alkoxycarbonylation; Phenols, alkoxycarbonylation.

The reaction of iodine or silver oxide with *N*-hydroxycarbamates (ROCONHOH) **1** in aqueous alcohols produces[1] mixtures of *O*- or *N*-alkoxycarbonyl derivatives of *N*-hydroxycarbamates [ROCONHOCOOR, $(ROCO)_2NOH$)]. Later it was found that tetraalkylammonium periodates oxidize *N*-hydroxycarbamates **1** to unstable nitrosoformates **3**. These compounds were used in situ as dienophiles for Diels–Alder cyclization to give esters of 3,6-dihydro-2*H*-1,2-oxazine-2-carboxylic acid[2] or similar polycyclic compounds[3]. As a matter of fact, we wanted to prepare 3-benzyloxycarbonyl-2-oxa-3-azabicyclo[2.2.1]hept-5-ene by cycloaddition of cyclopentadiene with benzyl nitrosoformate **3h** according to Kirby et al.[3], however, by a modified procedure using the safer oxidation agent. With respect to almost the same oxidation potential (+1.6 V, ref.[4]) and accessibility of the compound, we chose lead dioxide. Analysis of products of our experiment revealed cycloadduct but in a mixture with dibenzyl carbonate **4h** (procedure *A*). The presence of carbonate **4h** among the products made us to study the acylation activity of nitrosoformates and to verify the preparative value of this activity.

The reaction of lead dioxide with *N*-hydroxycarbamates is exothermic and produces dinitrogen oxide and carbon monoxide (procedure *B*). The formation of gases was observed even in the presence of alcohols or phenols in the reaction mixture. Oxidation course of isopropyl *N*-hydroxycarbamate **1d** was monitored by ESR analysis (procedure *B*). The observed spectrum (Fig. 1) is characterized by three resolved asymmetrical bands formed by superposition of twelve bands, which was confirmed by computer simulation. The found values of hyperfine splitting (HFS) can be assigned to the interaction of unpaired electrons of nitrogen atom with the nuclear spins of two nonequivalent hydrogen atoms in the structure of the radical. The obtained HFS constants: a_N = 8.7 gauss, a_{N-H} = 3.4 gauss, a_{C-H} = 1.5 gauss. The bands were of the Gaussian type with the half-band with ΔH_{pp} = 4.35 gauss with 30% ratio of Lorentian type. The mean value of *g* tensor is $\langle \boldsymbol{g} \rangle$ = 2.008. Gutch and Watters[5] found a radical with similar values of the above given constants in the oxidation of ethyl *N*-hydroxycarbamate with cerium(IV) sulfate in aqueous sulfuric acid. The presence of two nonequivalent protons in the molecule studied can be explained by the structure of cyclic electrically neutral radical **2d**.



2d

Diisopropyl carbonate **4d** was the final product of the oxidation of carbamate **1d** in dichloromethane. Carbamate **1d** was oxidized to **4d** in isopropanol, as well.

Oxidation of **1d** in methanol produced a mixture of carbonate **4d** and isopropyl methyl carbonate **5ad**. Under the given conditions it can be generalized that oxidation of hydroxycarbonates **1** by lead dioxide in dichloromethane produces neutral radical **2** which subsequently forms nitrosoformate **3** (Eq. (*A*)).

$$\underset{\mathbf{1}}{R^1OCONH{-}OH} \xrightarrow[(PbO_2)]{-H^+,\ -e} \underset{\mathbf{2}}{R^1OCONH{-}O^\bullet} \xrightarrow[(PbO_2)]{-e,\ -H^+} \underset{\mathbf{3}}{R^1OCON{=}O} + H_2O \qquad (A)$$

$$2\ \underset{\mathbf{3}}{R^1OCON{=}O} \xrightarrow[(H_2O)]{-N_2O,\ -CO_2} \underset{\mathbf{4}}{R^1OCOOR^1} \xleftarrow{-N_2O} \underset{\mathbf{3}}{ROCON{=}O} + R^1OH \qquad (B)$$

R^1	$R^1OCONHOH$	$R^1OCON{=}O$	R^1OCOOR^1
Me	**1a**	**3a**	**4a**
Et	**1b**	**3b**	**4b**
i-Pr	**1d**	**3d**	**4d**
Ph	**1g**	**3g**	**4g**
$PhCH_2$	**1h**	**3h**	**4h**

The symmetrical carbonate **4** is formed by another subsequent reaction of nitrosoformate **3** with the present water or alcohol containing the same alkyl group as formate **3** (Eq. (*B*)).

An analogous oxidation of nitrosoformate **3** in R^2OH alcohol containing a different alkyl group produces a mixture of symmetrical **4** and asymmetrical **5** carbonate (Eq. (*C*)).

$$\underset{\mathbf{3}}{R^1OCON{=}O} + R^2OH \xrightarrow[(H_2O)]{-N_2O,\ -CO_2} \underset{\mathbf{4}}{R^1OCOOR^1} + \underset{\mathbf{5}}{R^1OCOOR^2} \qquad (C)$$

R^1	R^2						
	Me	Et	Pr	i-Pr	Bu	*s*-Bu	Ph
Me	–	**5ab**	**5ac**	**5ad**	**5ae**	**5af**	**5ag**
Et	**5ab**	–	**5bc**	**5bd**	**5be**	**5bf**	**5bg**
i-Pr	**5ad**	**5bd**	**5cd**	–	**5de**	**5df**	**5dg**
Ph	**5ag**	**5bg**	**5cg**	**5dg**	**5eg**	**5fg**	–

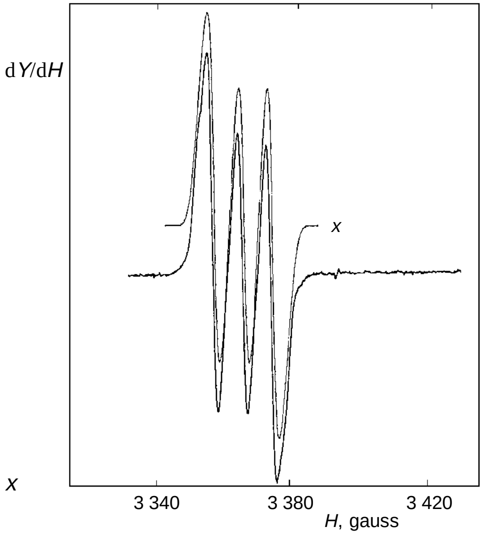


FIG. 1
ESR spectrum of [i-PrOCONHO$^\bullet$] (**2d**), curve *x* represents simulated spectrum of Gaussian type

As the ESR analysis of the reaction mixture confirmed the presence of the only radical (type **2**), we do not suppose a homolytic decomposition of intermediates **3** to carbonates **4** but a nucleophilic reaction with water formed in the previous oxidation. Analysis of the products of oxidation of isopropyl *N*-hydroxycarbamate **1b** with methanolic solution of sodium azide (procedure *C*) did not confirm formation of any other products. The similar experiment indicating S_N1 mechanism of solvolysis was carried out by Olivier and Waters[6] who studied autoacylation of phenylacetohydroxamic acid. Table I gives the results of reaction mixture compositions according procedure *D*.

The ratio of symmetrical carbamate **5** to the mixture of carbonate **4** and **5** depends on the type of groups (R^1 and R^2) in both reaction components and on temperature. For evaluation of the effect of alkyl groups, we used the values of the steric constants E_s as the dominant parameter in the Taft two-parameter equation[7]. As it can be seen in Fig. 2 the above mentioned ratio **5**/(**4** + **5**) (%) in the mixtures increases with decreasing reactivity of alcohol. On the other hand, for a given alcohol this ratio increases with increasing reactivity of nitrosoformate **3**.

The oxidation of methyl *N*-hydroxycarbamate **1a** with lead dioxide in the presence of alcohols was carried out at 40 and –10 °C. As it follows from Fig. 2 (curves *1* and *4*) the **5**/(**4** + **5**) (%) ratio also increases with increasing reaction temperature.

TABLE I
The ratio of carbonates **4** and **5** in reaction mixture at 40 °C

$$R^1OCONO + R^2OH \longrightarrow R^1OCOOR^1 + R^1OCOOR^2 + \ldots$$

R^1	R^2	**4**	%	**5**	%	R^1	R^2	**4**	%	**5**	%
Me	Me	**4a**	92.1		–	Et	Bu	**4b**	51.2	**5be**	29.6
Me	Et	**4a**	70.0	**5ab**	14.3	Et	i-Pr	**4d**	25.9	**5bd**	46.3
Me	Et	**4a**	71.5	**5ab**	4.3[a]	Et	*s*-Bu	**4b**	2.0	**5bf**	47.7
Me	Pr	**4a**	55.2	**5ac**	37.2	i-Pr	Me	**4d**	84.2	**5ad**	7.1
Me	Pr	**4a**	67.9	**5ac**	9.7[a]	i-Pr	Et	**4d**	66.3	**5bd**	9.4
Me	Bu	**4a**	51.5	**5ae**	39.6	i-Pr	Pr	**4d**	62.5	**5cd**	12.0
Me	Bu	**4a**	65.0	**5ae**	8.1[a]	i-Pr	Bu	**4d**	51.9	**5de**	14.1
Me	i-Pr	**4a**	14.6	**5ad**	77.7	i-Pr	i-Pr	**4d**	76.5		–
Me	i-Pr	**4a**	52.3	**5ad**	14.3[a]	i-Pr	*s*-Bu	**4d**	45.6	**5df**	21.3
Et	Me	**4b**	66.3	**5ab**	25.1	Ph	Et	**4g**	34.2	**5bg**	16.8
Et	Et	**4b**	90.2		–	Ph	Bu	**4g**	41.7	**5eg**	7.5
Et	Pr	**4b**	49.7	**5bc**	26.2	Ph	Ph	**4g**	49.0		–

[a] The reaction mixture was kept at –10 °C in a thermostat.

In order to establish the quantitative relationship between structure of the reacting alcohols and their reactivity towards nitrosoformates **3**, we carried out series of competitive alcoholyses using equimolar mixtures of various alcohols R^2OH and R^3OH (procedure *E*). Under the given starting conditions $[R^2OH] = [R^3OH] >> [\mathbf{3}]$ (e.g. 50 : 50 : 1), the ratio of the corresponding reaction rates k_2/k_3 was evaluated from the found carbonate concentration ratios $[R^1OCOOR^2]/[R^1OCOOR^3]$. The ratios of carbonates **5** were determined by chromatography and used for calculating the relative reactivities related to methanol, $r^{R}_{Me} = k_{ROH}/k_{MeOH} = [R^1OCOOR]/[R^1OCOOMe]$. The values of r^{R}_{Me} were determined either directly or by a combined way in the cases where the difference between reactivities of the alcohols compared was too big (see Table II). In the reactions of nitrosoformate **3** with alcohols, the relative reactivities r^{R}_{Me} of the individual alcohols decrease in the order: MeOH > EtOH > PrOH > BuOH > i-PrOH > *s*-BuOH, which corresponds to the E_s values[7]. The evaluation of log r^{R}_{Me} values of reactions of phenyl nitrosoformate **3g** with various alcohols using the Taft two-parameter equation gave both corresponding reaction constants (ρ, δ):

$$\log r^{R}_{Me} = \rho^{*}\sigma^{*} + \delta E_S = 8.5\ \sigma^{*} + 0.8\ E_s ; \quad r = 0.999\ .$$

Figure 3 shows the content of carbonates **5ab**, **4b** and **4a** formed by the reaction of ethyl nitrosoformate **3b** with aqueous methanol. The occurrence of the dominant ethyl

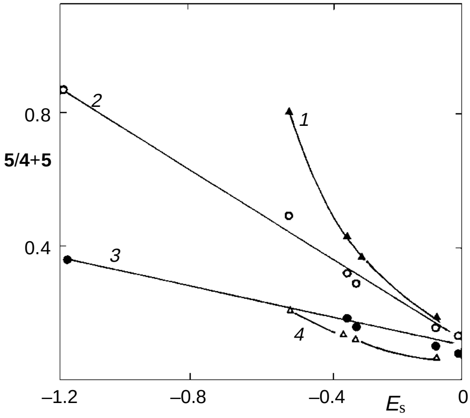


FIG. 2

Relationship between **5**/(**4** + **5**) ratio (amounts of compound in %) in the carbonate mixture and the Taft steric constants E_s of alkyl groups in reacting alcohol and nitrosoformate. Alcoholyses of methyl nitrosoformate **3a** at 40 °C (*1*) and –10 °C (*4*), respectively, ethyl nitrosoformate **3b** at 40 °C (*2*), isopropyl formate **3d** at 40 °C (*3*)

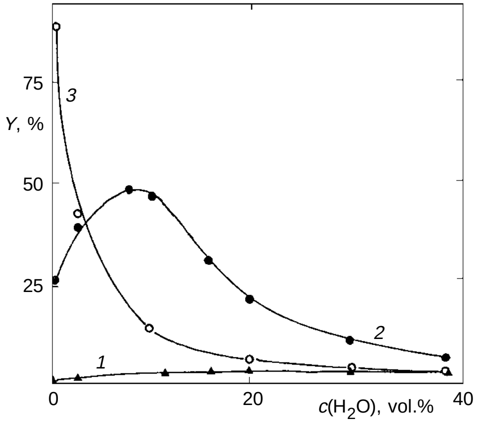
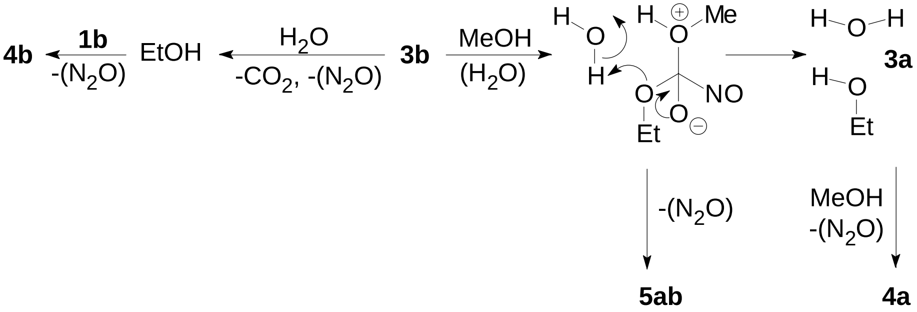


FIG. 3

Dependence of yield (*Y*, %) of carbonates **4a** (*1*), **4b** (*2*), and **5ab** (*3*) formed in the oxidation of ethyl *N*-hydroxycarbamate **1b** in aqueous methanol upon the amount of water present methyl carbonate **5ab** decreases owing to the competitive kinetically controlled hydrolysis to ethanol. The alcohol reacts subsequently with another molecule forming diethyl carbonate **4b**. This compound was found in the reaction mixture without the addition of water. Its content increases distinctly even after small addition of water into methanol but, after continued addition of water, it decreases again. We did not observe the formation of dimethyl carbonate **4a** in the reaction mixture without the water added from outside. The formation of **4a** can correspond the presence of water in tetrahedral intermediate of nitrosoformate **3b** with methanol.



(*D*)

Table II

Relative ratio of products **5** obtained in reaction mixture from nitrosoformates **3** and equimolar mixture of alcohols R^1OH and R^2OH

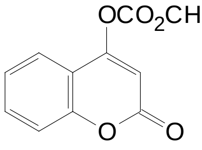
$$R^1OCONO + R^2OH \xrightarrow{k_2} R^1OCOOR^2 + \ldots$$

$$R^1OCONO + R^3OH \xrightarrow{k_3} R^1OCOOR^3 + \ldots$$

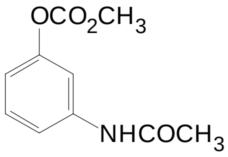
R^1	R^2	R^3	k_2/k_3	$\log r_{R^3}^{R^2}$	R^1	R^2	R^3	k_2/k_3	$\log r_{R^3}^{R^2}$
Et	Pr	Me	0.095	–1.022	Ph	Bu	Me	0.133	–0.876
	Bu	Pr	0.464	–0.334		i-Pr	Bu	0.262	–0.582
	Bu	Me	–	–1.356[a]		i-Pr	Me	–	–1.458[a]
	Pr	i-Pr	0.105	–0.978		Et	Me	0.466	–0.331
	i-Pr	Me	–	–2.000[a]		*s*-Bu	i-Pr	0.215	–0.667
Ph	Pr	Me	0.179	–0.748		*s*-Bu	Me	–	–2.125[a]

[a] Calculated from: $\log r_{Me}^{R^2} = \log r_{R^3}^{R^2} + \log r_{Me}^{R^3}$.

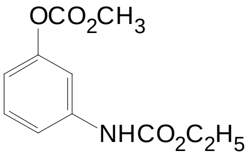
On the basis of our previous experiments concerning the study of conditions of alkoxycarbonylation of alcohols, we chose methyl *N*-hydroxycarbamate **1a** as the starting reagent for the preparation of six asymmetrical carbonates **5ai–5an**. As it follows from Table III the yields of those compounds are relatively low (34–47%). Spectroscopic characteristics of the new compounds are given in Table IV.



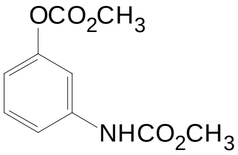
5ai



5aj



5ak



5al

$C_7H_{15}OCO_2CH_3$

5am

$C_9H_{19}OCO_2CH_3$

5an

EXPERIMENTAL

Melting points were measured on a Koffler instrument and are not corrected. IR spectra were measured on an IR 75 Spectrometer (Zeiss), ^{1}H and ^{13}C NMR spectra on a Bruker AMX-360 apparatus in deuteriochloroform, ESR spectra on ESR 221 ZWG, GC was performed on a Carlo–Erba chromatograph, model GV, and GC-MS on a Fison–Mega 5160 apparatus with the mass detector QMD-100 using Carboxen 1000 60/80 mesh and Se52 – Chromosorb A 60/80 mesh columns. HPLC was carried out on an instrument produced by Laboratorni pristroje, Prague using C18 columns and 50% aqueous methanol. The lead content was measured by the FSDDP method on a polarographic analyzer EP-10.

Chemicals

Lead dioxide was prepared from lead tetraacetate according to Brauer[8]. 3-Benzyloxycarbonyl-2-oxa-3-azabicyclo[2.2.1]hept-5-ene was prepared by reported procedure[3]. Methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, (±)-2-butanol (commercial products, Lachema Brno) were pre-dried with calcium oxide, refluxed with 2% sodium metal and distilled before use. 1-Heptanol and 1-nonanol, phenol, 4-hydroxycoumarine, and 3-acetylaminophenol were commercial products (Aldrich). Methyl and ethyl 3-hydroxyphenylcarbamates (products of CHZ-Synthesia Semtin) were crystallized from toluene (m.p. 93–94 °C and 92–93 °C, respectively).

N-Hydroxycarbamates **1** were prepared according to a general procedure[2]. Their physical data were in accordance with those given in literature: **1a** (ref.[2]), **1b** (ref.[9]), **1g** (ref.[10]), **1h** (ref.[2]), isopropyl *N*-hydroxycarbonate **1d**: m.p. 26–27 °C. IR spectrum (film): ν (C=O) 1 750 cm^{-1}. ^{1}H NMR spectrum

($CDCl_3$): 1.25 d, 6 H, $J = 7$ (2 × CH_3); 4.95–5.09 m, 1 H (CH); 7.25 s, 2 H (HO/NH). ^{13}C NMR spectrum ($CDCl_3$): 21.8 (CH_3), 70.2 (CH), 159.3 (COO).

Carbonates **4a–4h**, **5ab–5fg** as chromatographic standards were prepared by the pyridine method[11]. Physical data of other individual esters prepared agree with those given in literature: **4a**, **5ae**, **5ad**, **5be**, **5bc**, **5bd**, **5cd** (ref.[12]), **5ab** (ref.[11]), **5ac** (ref.[13]), **5ag**, **5bg**, **5cg**, **5eg**, **5dg** (ref.[14]), **5fg** (ref.[15]), **5bf** (ref.[16]), **4d** (ref.[17]), **4b**, (Aldrich), **4h** (ref.[18]).

Synthesis of Carbonates **5ai–5an**

To a solution of hydroxy compound (0.025 mol) in dichloromethane (15 ml) cooled to –10 °C, freshly prepared lead dioxide (10 g) was added with intense stirring, and then methyl *N*-hydroxycarbamate (**1a**; 4.4 g) dissolved in dichloromethane (25 ml) was added during 30 min. The reaction mixture was stirred until it reached room temperature and then for another half an hour until the evolution of gases stopped. After treating with 5 ml water, the solid was separated by centrifuging. The solution was shaken twice with 5 ml 5% sodium hydroxide, then with water, dried, and the product was isolated by vacuum fraction or crystallization from methanol.

TABLE III
Analytical data for the carbonates ROCOOMe **5ai–5an**

No.	R	M.p., °C Yield, %	Formula M.w.	Calculated/Found	
				% C	% H
5ai	2-oxo-1-benzopyran-4-yl	98–99	$C_{11}H_8O_5$	60.00	3.66
		45	220.1	59.78	3.68
5aj	3-acetylaminophenyl	115–116	$C_{10}H_{11}NO_4$	57.41	5.30[a]
		47	209.2	57.20	5.32
5ak	3-ethoxykarbonylaminophenyl	86–87	$C_{11}H_{13}NO_5$	55.23	5.48[a]
		42	239.2	55.37	5.41
5al	3-methoxycarbonylaminophenyl	105–106	$C_{10}H_{11}NO_5$	53.33	4.93[a]
		45	225.2	53.23	5.08
5am	heptyl	[b]	$C_9H_{18}O_3$	57.42	9.57
		34	188.1	57.15	9.75
5an	nonyl	[b]	$C_{11}H_{22}O_3$	65.31	10.89
		39	202.1	65.03	10.67

[a] % N calculated/found: **5aj** 6.70/6.95, **5ak** 5.86/6.05, **5al** 6.22/6.25. [b] B.p. (°C/268 Pa), n_D^{20}: **5am** 69.0–71.0, 1.4155; **5an** 85.0–88.0, 1.4242.

TABLE IV
Spectroscopic data of carbonates **5ai–5an**

No.	IR, cm^{-1} ν(C=O)	NMR, ppm	
5ai	1 765 1 702	^{1}H:	3.98 s, 3 H (CH$_3$O); 6.63 s, 1 H (H-3); 7.29 m, 1 H (H-6); 7.31 m, 1 H (H-8); 7.56 dt, 1 H, *J* = 7.9, ^4J = 1.4 (H-7); 7.69 dd, 1 H, ^3J = 7.9, ^4J = 1.4 (H-5)
		^{13}C:	56.1 (CH$_3$O), 103.2 (C-2), 114.7 (C-5a), 116.7 (C-8), 122 (C-5), 124.3 (C-6), 132.8 (C-7), 150.9 (O**C**OOCH$_3$), 153.3 (C-8a), 158.1 (C-4), 161.2 (C-2)
5aj	1 776 1 681	^{1}H:	2.05 s, 3 H (**C**H$_3$CONH); 3.87 s, 3 H (CH$_3$OCOO); 6.85 td 1 H, ^3J = 8.0, ^4J = 2.0 (H-4); 7.18 m, 1 H (H-6); 7.22 m, 1 H (H-5); 7.53 t, 1 H, ^4J = 2.0 (H-2); 8.17 bb, 1 H (NH)
		^{13}C:	24.2 (**C**H$_3$CONH), 55.4 (**C**H$_3$OCOO), 112.8 (C-2), 116.3 (C-4), 117.2 (C-6), 129.5 (C-5), 139.2 (C-3), 151.1 (C-1), 154.4 (O**C**OOCH$_3$), 168.9 (CH$_3$**C**ONH)
5ak	1 743 1 620	^{1}H:	1.21 t, 3 H (C**H**$_3$CH$_2$O); 3.81 s, 3 H CH$_3$OCOO); 4.14 q, 2 H, ^3J = 7.1 (CH$_3$C**H**$_2$O); 6.79 m, 1 H (H-4); 7.10 m, 1 H (H-6); 7.17 t, 1 H, ^3J = 7.9 (H-5); 7.41 bb, 1 H (H-2); 7.52 bb, 1 H (NH)
		^{13}C:	14.0 (**C**H$_3$CH$_2$O), 55.0 (CH$_3$O), 60.8 (CH$_3$**C**H$_2$O), 111.1 (C-2), 115.0 (C-4), 115.8 (C-6), 129.1 (C-5), 139.3 (C-3), 151.1 (C-1), 153.4 (NHCOO), 154.0 (CH$_3$O**C**OO)
5al	1 730 1 608	^{1}H:	3.73 s, 3 H (C**H**$_3$OCONH); 3.87 s, 3 H (CH$_3$OCOO); 6.83 m, 1 H (H-4); 6.97 bb, 1 H (NH); 7.13 m, 1 H (H-6); 7.24 t, 1 H, ^3J = 8.1 (H-5); 7.36 bb, 1 H (H-2)
		^{13}C:	52.3 (**C**H$_3$OCONH), 55.36 (**C**H$_3$OCOO), 111.5 (C-2), 115.6 (C-4), 115.9 (C-6), 129.6 (C-5), 139.1 (C-3), 151.4 (C-1), 153.8 (NHCOO), 154.1 (OCOO)
5am	1 731	^{1}H:	0.87 t, 3 H (H-7); 1.20–1.40 m, 8 H (H-8–H-3); 1.65 m, 2 H (H-2); 3.76 s, 3 H (CH$_3$O); 4.12 t, 2 H (H-1)
		^{13}C:	13.9 (C-7), 22.5 (C-6), 25.6 (C-5), 28.6 (C-4), 28.8 (C-3), 31.6 (C-2), 54.5 (CH$_3$O), 68.2 (C-1), 155.8 (CH$_3$O**C**OO)
5an	1 735	^{1}H:	0.86 t, 3 H, ^3J = 6.7 (H-9); 1.20–1.40 m, 12 H (H-3–H-8); 1.65 m, 2 H (H-2); 3.76 s, 3 H (CH$_3$O); 4.12 t, 2 H, ^3J = 7.9 (H-1)
		^{13}C	13.9 (C-9), 22.5 (C-8), 25.6 (C-7), 28.6 (C-6), 29.1 (C-5 + C-4), 29.3 (C-3), 31.7 (C-2), 54.4 (CH$_3$O), 68.1 (C-1), 155.8 (CH$_3$O**C**OO)

Mass Balance Experiments

Procedure A. Benzyl *N*-hydroxycarbamate (**1h**; 0.5 g, 3 mmol) solution in dichloromethane (5 ml) was added to a suspension of lead dioxide (0.8 g) in cyclopentadiene (0.2 g) and dichloromethane (3 ml) at 0 °C with stirring for 20 min. The mixture was then kept at the room temperature for 30 min. The solid portion was removed by centrifuging and the solution was analyzed by HPLC.

Procedure B. Lead dioxide (1.2 g, 5 mmol) was mixed with a solution of isopropyl *N*-hydroxycarbamate (**1d**; 0.6 g) in dichloromethane (10 ml). After 2 min of spontaneous reaction, the evolution of gaseous oxides ceased, and the sample was transferred into a cell and its ESR spectrum was measured. Another sample was mixed with methanol and after 10 min it was analyzed by GC-MS method. The original mixture was also analyzed by chromatography after 10 min. The same experiment was carried out in 1-propanol. The content of dissolved Pb^{2+} in the reaction mixture determined by polarography was 0.87 g (4.2 mmol). Having repeated this experiment under nitrogen during 40 min, we obtained 95 ml gaseous products. Gaseous phase: IR spectrum (ν_{max}, cm^{-1}): 2 349 (CO_2), 2 224 (NN), 1 349 (CO_2), 1 286 (NO), 667 (CO_2). Gaseous products were compared with the authentic dinitrogen oxide and carbon dioxide by means of GC.

Procedure C. Lead dioxide (1.2 g, 5 mmol) was added to a solution of isopropyl *N*-hydroxycarbamate (**1d**; 0.5 g, 5 mmol) in methanol (5 ml) and after 3 min a mixture of sodium azide (0.32 g, 5 mmol) and methanol (5 ml) was added thereto. The reaction mixture was kept at 40 °C with stirring for another 15 min and then analyzed by HPLC and GC.

Procedure D. In a flask equipped with a reflux condenser, a stirrer, and a gas burette, a solution of *N*-hydroxycarbamate (0.025 mol) in alcohol (or aqueous alcohol) (0.25 mol) was added into stirred suspension of lead dioxide (1.2 g, 5 mmol) in dichloromethane (5 ml) at 40 °C during 10 min. The mixture was kept at this temperature until the evolution of gases stopped. The solid phase was separated by centrifuging and the solution was analyzed by chromatography. A similar procedure was used for the chromatographic comparison at –10 °C.

Procedure E. *N*-Hydroxycarbamate (2.5 mmol) was dissolved in a solution containing two chosen alcohols (0.125 mol of each) and lead dioxide (0.6 g) was added thereto in one portion with stirring at 40 °C. Ten minutes later, an inorganic portion was removed on centrifuge and the solution was analyzed chromatographically.

REFERENCES

1. Boyland E., Nery R.: J. Chem. Soc., C *1966*, 354.
2. Defoin A., Fritz A., Schmidlin C., Streith J.: Helv. Chim. Acta *70*, 565 (1987).
3. Kirby W., McGuigan H., Mackinnon J. W. M., McLean D., Sharma R. P.: J. Chem. Soc., Perkin Trans. 1 *1985*, 1437.
4. Kotrly S., Sucha L.: *Chemicke rovnovahy v analyticke chemii*, p. 226. SNTL, Praha 1988.
5. Gutch C. J. W., Watters W. A.: J. Chem. Soc., C *1965*, 7518.
6. Oliver T. R., Waters W. A.: J. Chem. Soc., B *1971*, 677.
7. Shorter J.: Q. Rev., Chem. Soc. *24*, 433 (1970).
8. Brauer G.: *Handbuch der präparativen anorganischen Chemie*, p. 672. Enke Verlag, Stuttgart 1962.
9. Major R. T., Dursch A. G., Hess H. J.: J. Org. Chem. *24*, 431 (1959).
10. Kohlrausch K. W. F., Sabathy R.: Monatsh. Chem. *72*, 308 (1939).
11. Douglass I. B., Marascia F. J.: J. Am. Chem. Soc. *77*, 1899 (1955).
12. Douglass I. B., Warner G. H.: J. Am. Chem. Soc. *78*, 6070 (1956).
13. Morel G.: Bull. Chem. Soc. Fr. *21*, 819 (1916).

14. Kawashima M.: Japan. Kokai 5319090 (1983); Chem. Abstr. *120*, 189900 (1993).
15. Bowman N. S., Rexford D. R.: J. Org. Chem. *19,* 1219 (1954).
16. Khapuntsev I. I., Pastuschenko E. V., Terentiev A. B.: Izv. Akad. Nauk SSSR, Ser. Khim. *1984*, 1890.
17. Palommaa M. H., Salmi E. J., Suoja K.: Chem. Ber. *72,* 316 (1939).
18. Bowden S. T.: J. Chem. Soc. *1939*, 31.