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Abstract

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SYNTHESIS AND CLEAVAGE OF DIMERS OF -CHLORO- -NITROSOCARBONYL COMPOUNDS

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The literature describes the addition of nitrosyl chloride only to two α,β-unsaturated carbonyl compounds—acrolein and phenyl vinyl ketone—which, on treatment with amyl nitrite in the presence of hydrochloric acid, give the corresponding β-chloro-α-isonitrosocarbonyl compounds (^{1,2}).

In studying the addition of NOCl to α,β-unsaturated carbonyl compounds having a methyl group in the α-position to the carbonyl, we established that this reaction can be used for the synthesis of hitherto unknown dimers of β-chloro-α-nitroso aldehydes and ketones (I)–(VI):

$$\mathrm{R'-CH=C(CH_3)-COR \xrightarrow{NOCl} (R'-CHCl-C(CH_3)(NO)-COR)_2}$$

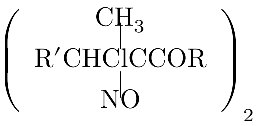
(I)–(VI)

$$\text{(I) } R=CH_3,\ R'=H;\quad \text{(II) } R=C_6H_5,\ R'=H;\quad \text{(III) } R=R'=CH_3;$$
$$\text{(IV) } R=R'=H;\quad \text{(V) } R=H,\ R'=CH_3;\quad \text{(VI) } R-R'=-(CH_2)_3-$$

Although the literature contains almost no data on establishing the mechanism of addition of NOCl to simple olefins, there is an opinion that in this case the reaction is one of electrophilic addition (see, for example, (^{3})). α,β-Unsaturated carbonyl compounds, which have at the double carbon–carbon bond a strong electron-acceptor group that hinders electrophilic addition, nevertheless react with nitrosyl chloride more readily than the corresponding unsaturated hydrocarbons. This compels the supposition that in the present case a nucleophilic addition reaction occurs. As is known, halogenation of α,β-unsaturated aldehydes and ketones also has a nucleophilic character (^{4}).

Table 1

Dimers of β-chloro-α-nitrosocarbonyl compounds



$$\left(\begin{array}{c} CH_3 \\ | \\ R'CHClCCOR \\ | \\ NO \end{array} \right)_2$$

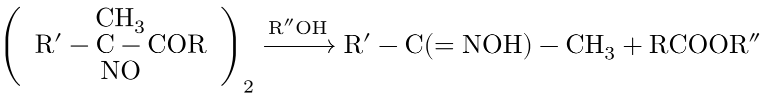
Formula No.	R	R	Yield, %	M.p. (with de-comp.), °C	Cl, % found	Cl, % calcu-lated	N, % found	N, % calcu-lated
I	CH	H	53.5	90	23.8723.99	23.70	9.519.55	9.36
II	C H	H	69	101–102	16.5816.60	16.75	6.376.60	6.62
III	CH	CH	52	78	21.4721.66	21.67	8.808.93	8.56
IV	H	H	36	74–75	26.0026.05	26.16	10.5010.61	10.33
V	H	CH	28	58	23.7623.64	23.70	9.529.62	9.36
VI	–(CH)–	–(CH)–	66.5	90.5	20.2919.99	20.19	7.897.76	7.98

The dimers of β-chloro-α-nitroso aldehydes and ketones obtained by us (see Table 1) are colorless crystalline compounds, sparingly soluble in the cold in ordinary organic solvents. On heating they dissolve in alcohols, halogen derivatives, and hydrocarbons.

with the formation of blue or blue-green solutions (compound (VI)—only in benzene). Heating is accompanied by decomposition of the products, which in most cases makes recrystallization impossible.

In the IR spectra of dimers (I)–(VI), and also of the dimer of 2-nitroso-2-methylbutan-3-one (VII) obtained by us, along with a strong absorption band of the carbonyl group, a band is observed in the region 1275–1285 cm^{-1}—the most intense band in the spectrum. This observation is in agreement with the few data available in the literature on the spectra of dimers of tertiary nitroso compounds ($^{5-7}$).

We have established that dimers (I)–(V), as well as the dimer of 2-nitroso-2-methylbutan-3-one (VII), on heating (dimers of chloronitroso aldehydes even at ordinary temperature) in alcoholic solution undergo cleavage at the carbon-carbon bond with formation of ketone oximes and esters:



$$\left(R' - \overset{CH_3}{\underset{NO}{C}} - COR \right)_2 \xrightarrow{R''OH} R' - C(=NOH) - CH_3 + RCOOR''$$

Since dimer (VI) is poorly soluble in alcohols, its cleavage was carried out in a mixture of methanol and benzene. The methyl ester of δ-chloro-ε-oximinoenanthic acid formed was not isolated in pure form, but was converted by the action of diethylamine into the methyl ester of δ-diethylamino-ε-oximinoenanthic acid:

$$\text{(Dimer VI)} \xrightarrow[C_6H_6]{CH_3OH} CH_3C(=NOH)CHCl(CH_2)_3COOCH_3 \xrightarrow{(C_2H_5)_2NH} CH_3C(=NOH)CH[N(C_2H_5)_2]\,(CH_2)_3C$$

Cleavage of dimers of α-nitrosocarbonyl compounds had not previously been observed by anyone. However, this reaction is close to the cleavage processes occurring during nitrosation of certain ketones having, in the α-position to the carbonyl, a tertiary carbon atom (see the literature in the review on nitrosation ([8])). It should nevertheless be noted that cleavage during nitrosation of ketones occurs when the reaction is carried out in the presence of a strong base (sodium ethylate). The proposed reaction mechanism is quite analogous to the mechanism of alkaline cleavage of β-diketones ([9]). If nitrosation is carried out in an acidic medium, cleavage proceeds in low yield or is not observed at all ([10–12]).

It may be assumed that the cleavage of the dimers of α-nitrosocarbonyl compounds obtained by us in alcoholic medium proceeds according to the following scheme:

$$(R' - C(CH_3)(NO) - C(=O) - R)_2 \rightleftarrows R' - C(CH_3)(NO) - C(=O) - R \xrightarrow{R''OH} \text{[cyclic intermediate]} \longrightarrow R' -$$

Carrying out the cleavage of dimers (I), (III), and (IV) in alcoholic solution in the presence of ammonia, secondary amines, or potassium acetate, we found that, as a result of substitution of chlorine by the corresponding residue, α-amino- or α-acetoxy-substituted ketone oximes are formed.

Table 2 presents the conditions and products of cleavage of dimeric nitrosocarbonyl compounds. The properties of the known compounds corresponded to the literature data.

Table 2

Products of the cleavage of dimers of α-nitrosocarbonyl compounds

Dimer	Cleavage conditions	Cleavage product	Yield, %	B.p., °C (p, mm)	d_4^{20}	n_D^{20}	N, % found	N, % calc.	Source
(I)	CH OH, 70°, 15 min	CH C(=NOH)CH Cl*	71	54.5–55(3)	1.2088	1.4815	–**	–	(14)
	C H OH, NH , 15°, 40 h	N[CH C(=NOH)CH]	55	m.p. 174	–	–	24.08 24.05	24.33	(15)
	C H OH, (C H) NH, 15°, 40 h	CH C(=NOH)CH N(C H)	45	m.p. 48	–	–	18.92 19.43	18.43	(16)
	CH OH, CH COOK, 70°, 1 h	CH C(=NOH)CH OCOCH	55	95–96 (3)	1.1226	1.4463	10.50 10.63	10.68	(17)
(II)	1. CH OH, 70°, 2 h, 2. NH	N[CH C(=NOH)CH]	30	m.p. 174	–	–	–	–	(15)
(III)	CH OH, 70°, 15 min	CH C(=NOH)CHCl—CH	69	50–51(2.5)	1.1421	1.4734	11.63 11.75	11.52	(18)
	CH OH, CH COOK, 70°, 1 h	CH C(=NOH)CH(OCOCH)CH	48	89–90 (3)	1.0953	1.4548	9.55 9.60	9.65	(18)
(IV)	CH OH, 60°, 10 min	CH C(=NOH)CH Cl	62	76.5–77(16)	1.2093	1.4827	–	–	(14)
	CH OH, (CH) NH, 20°, 10 min	CH C(=NOH)CH N(CH)	81	m.p. 98–98.5	–	–	24.00 24.16	24.12	(16)

Dimer	Cleavage conditions	Cleavage product	Yield, %	B.p., °C (p, mm)	d_4^{20}	n_D^{20}	N, % found	N, % calc.	Source
	CH OH, (C H) NH, 20°, 10 min	CH C(=NOH)CH N(C H)	74	m.p. 49	–	–	–	–	(16)
(V)	CH OH, 60°, 10 min	CH C(=NOH)CHClCH	64	64–65(5)	1.1414	1.4730	–	–	(18)
(VI)	1. C H , CH OH, 75°, 2 h2. (C H) NH	$CH_3C(=NOH)CH[N(C_2H_5)_2](CH_2)_3COOCH_3$	48	m.p. 68–69			11.32***	11.47 11.40	–
(VII)	CH OH, 70°, 6 h	CH C(NOH)CH *	47	134–135(754)m.p. 60.5	–	–	–	–	(19)

* A nearly theoretical amount of methyl acetate was also found.
** Found %: Cl 32.78, 32.89; calculated %: 32.97.
*** Found %: C 59.23, 59.08; H 10.10, 10.03; calculated %: C 58.99, H 9.90.

Experimental Section

Methyl and phenyl isopropenyl ketones were obtained by pyrolysis of the hydrochlorides of the corresponding Mannich bases; tiglic aldehyde and 3-methylpenten-2-one-4 by crotonic condensation of acetaldehyde with propionic aldehyde and methyl ethyl ketone, respectively; 2-methylcyclohexen-2-one-1 from 1-methylcyclohexene-1 according to the procedure used for the synthesis of 2-methylcyclopenten-2-one-1 ((13)); methacrolein was distilled before the experiment. The constants of all starting compounds agreed with the literature data.

Preparation of dimers of β-chloro-α-nitrosocarbonyl compounds

To a solution of an unsaturated ketone or aldehyde in absolute ether (200-300 ml per mole of carbonyl compound), cooled with ice and salt (or, in the preparation of dimers (IV)–(VI), with a mixture of solid carbon dioxide and acetone to −40°), an equimolar amount of nitrosyl chloride was added. After several hours all the NOCl had reacted, as could be judged from the change in the color of the solution from red-brown to blue or blue-green. The precipitated dimer was filtered off and washed well with cold ether. By freezing the filtrate at −50−−60°, an additional quantity of dimer can be obtained.

Dimer of 2-nitroso-2-methylbutanone-3 (VII) was obtained according to procedure (12) by nitrosation of methyl isopropyl ketone with isoamyl nitrite in the presence of acetyl chloride in 21% yield. M.p. 101–102° (dec.) in agreement with the literature data.

Cleavage of dimers of α-nitrosocarbonyl compounds in methanol

Dimers (I), (III), and (VII) were heated in methyl alcohol (8-10 ml per 1 g of dimer) until the blue color of the solution, which appears at the beginning of heating, disappeared. After distillation of the methanol (the distillate in some cases was analyzed for methyl acetate by gas-liquid chromatography), the corresponding oxime was isolated by distillation.

Dimers of chloronitroso aldehydes (IV) and (V) cleave in methyl alcohol with spontaneous heating. The solution was then heated for 10 min on a water bath and further treated as described above.

Cleavage in the presence of secondary amines

A dimer of a nitroso aldehyde or ketone was added to a 20-25% alcoholic solution of the amine (threefold excess). In the case of nitroso aldehydes, external cooling is necessary, since otherwise the reaction may proceed very violently. The mixture was stirred until the precipitate had completely dissolved. After distillation of the alcohol and excess amine, the residue was treated with ether. The precipitated salts were alkalized with the calculated amount of saturated potassium hydroxide solution. The solution was extracted with ether, and the extract was combined with the main solution. After removal of the ether, the residue was recrystallized from benzene (dimethylaminoacetone oxime) or frozen out from petroleum ether (diethylaminoacetone oxime).

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