

REACTION OF 1,1-DICHLORO-1-NITROALKANES

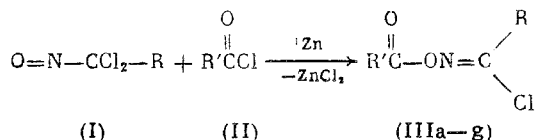
WITH ACID CHLORIDES AND ZINC

T. A. Epishina, V. B. Sokolov,
and I. V. Martynov

UDC 542.91:547.231'131:547.297:546.47

1,1-Dichloro-1-nitrosoalkanes, similar to α-halocarbonyl compounds, react with acid chlorides and zinc to give O-acylated acylhydroximoyl chlorides.

In a continuation of our study of the chemical properties of 1,1-dichloro-1-nitrosoalkanes [1-3], we examined the reaction of nitrosoalkanes (I) with acid chlorides (II) and zinc. A precondition for the study of this reaction is the high reactivity of (I) relative to nucleophilic reagents such as trivalent phosphorus acid derivatives and the capacity of (I) to form phosphorylated oximes upon reaction with phosphorus oxychloride and zinc [4]. The literature data [5] indicate that (I) should react with (II) and zinc similarly to α-halocarbonyl compounds. Indeed, in the presence of an equimolar amount of zinc, (I) reacts exothermally with (II) at 20°C to give O-acylated oximoyl chlorides (III) in 15-49% yield.



R = CH₃, R' = CH₃ (a); R = C₂H₅, R' = CH₃ (b); R = C₂H₅, R' = C₃H₇ (c); R = C₂H₅, R' = *i*-C₃H₇ (d); R = C₃H₇, R' = *i*-C₃H₇ (e); R = CH₂Cl, R' = C₃H₇ (f); R = CH₂Cl, R' = *i*-C₃H₇ (g).

Chlorides (III) are colorless, mobile liquids, whose composition and structure were demonstrated by elemental analysis and PMR and IR spectroscopy. The IR spectra show bands at 1600-1625 (C=N) and 1760-1800 (C=O).

EXPERIMENTAL

The PMR spectra were taken on a Bruker CXP-200 spectrometer in deuteroacetone relative to TMS. The IR spectra were taken on a Specord 75 IR spectrometer.

O-Acetyloximoyl Chloride (IIIa). A sample of 7.85 g (0.05 mole) acetyl chloride and 12.8 g (0.05 mole) 1,1-dichloro-1-nitrosoethane were added with stirring to a suspension of 6.2 g (0.1 mole) zinc dust in 100 ml ether at 20°C. The reaction mixture was stirred until decolorized (2 h) and 50 ml hexane was added. Zinc chloride was separated and the mixture

TABLE 1. Physicochemical Indices of O-Acylated Oximoyl Chlorides (IIIb)-(IIIg)

Compound	Yield, %	Bp, °C (P, mm Hg)	n _D ²⁰	Found, %			Chemical formula	Calculated, %		
				C	H	N		C	H	N
(IIIb)	46.8	75-76 (7)	1.4462	39.85	5.03	9.03	C ₅ H ₈ ClNO ₂	40.15	5.39	9.36
(IIIc)	24.7	96-98 (7)	1.4506	47.08	6.63	7.98	C ₇ H ₁₂ ClNO ₂	47.33	6.81	7.86
(III d)	28.2	88-90 (7)	1.4524	47.60	6.67	7.41	C ₇ H ₁₂ ClNO ₂	47.33	6.81	7.86
(III e)	11.8	90-95 (7)	1.4508	50.65	7.41	7.09	C ₈ H ₁₄ ClNO ₂	50.14	7.36	7.31
(III f)	23.1	78-79 (2)	1.4744	36.68	4.47	6.82	C ₆ H ₉ Cl ₂ NO ₂	36.39	4.58	7.07
(III g)	22.7	77-80 (2)	1.4734	36.52	4.31	7.32	C ₆ H ₉ Cl ₂ NO ₂	36.39	4.58	7.07

Institute of Physiologically Active Compounds, Academy of Sciences of the USSR, Chernogolovka. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 2, pp. 477-478, February, 1990. Original article submitted April 19, 1989.

TABLE 2. Spectral Indices of O-Acylated Oximoyl Chlorides (IIIb)-(IIIg)

Compound	PMR spectrum, δ , ppm (J, Hz)	IR spectrum, ν , cm^{-1}
(IIIb)	1.24 t (3H, $J=7.1$), 2.43 s (3H), 2.52 m (2H)	1785 (C=O), 1625 (C=N)
(IIIc)	1.0 t (3H, $J=7$), 1.26 (3H, $J=7$), 1.75 m (2H), 2.53 m (2H), 2.62 t (2H, $J=7$)	1762 (C=O), 1600 (C=N)
(III d)	1.23 m (9H), 2.5 m (2H), 3.05 m (H)	1785 (C=O), 1610 (C=N)
(III e)	1.02 t (3H, $J=7$), 1.27 d (6H, $J=7.3$), 1.75 m (2H), 2.45 t (2H, $J=7.2$), 3.06 m (H)	1760 (C=O), 1615 (C=N)
(III f)	1.06 t (3H, $J=7.1$), 1.74 m (2H), 2.64 t (2H, $J=7.1$), 4.26 s (2H)	1800 (C=O), 1625 (C=N)
(III g)	1.28 d (6H, $J=7.2$), 3.06 m (H), 4.24 s (2H)	1795 (C=O), 1620 (C=N)

was evaporated. The residue was fractionated to give 2.0 g (15%) (IIIa), bp 85-87°C (20 mm), n_D^{20} 1.4405. Found: C, 35.64; H, 4.35; N, 10.12%. Calculated for $\text{C}_4\text{H}_6\text{ClNO}_2$: C, 35.44; H, 4.46; N, 10.33%. PMR spectrum (δ , ppm): 2.23 s (3H), 2.43 s (3H).

O-Acylated oximoyl chlorides (IIIb)-(IIIg) were obtained by analogy from 0.05 mole 1,1-dichloro-1-nitrosoalkane, 0.05 mole acetyl chloride, and 0.05 mole zinc. The physical indices for these products are given in Tables 1 and 2.

LITERATURE CITED

1. I. V. Martynov, A. N. Ivanov, T. A. Epishina, and V. B. Sokolov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 9, 2158 (1986).
2. V. B. Sokolov, A. N. Ivanov, T. A. Epishina, and I. V. Martynov, *Zh. Obshch. Khim.*, 57, 1211 (1987).
3. I. V. Martynov, A. N. Ivanov, T. A. Epishina, and V. B. Sokolov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 9, 2128 (1988).
4. V. B. Sokolov, T. A. Epishina, and I. V. Martynov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 7, 1691 (1988).
5. V. V. Shchepin, N. Yu. Russkikh, and I. I. Lapkin, *Zh. Org. Khim.*, 23, No. 7, 1454 (1987).

SPECTROSCOPIC STUDY OF THE CONFORMATION OF

1,3,2-DIOXAPHOSPHORINANES WITH A P=S BOND

I. Kh. Shakirov, R. R. Shagidullin,
and R. P. Arshinova

UDC 543.422:541.63:547.1'118

5,5-Dimethyl-2-thio-2-phenoxy- and 5,5-dimethyl-2-thio-2-ethoxy-1,3,2-dioxaphosphorinanes exist in the liquid state and in solution in a three-component equilibrium featuring two chair forms with equatorial orientation of the P=S bond differing in the orientation of the OPh or OEt groups and a chair form with an axial P=S bond. The P=S bond in 4-methyl-2-thio-2-phenoxy-1,3,2-dioxaphosphorinane occupies the equatorial position.

Raman and IR spectroscopy have been used to study the structure of 1,3,2-dioxaphosphorinanes with P^{III} and P^{IV} , including compounds with an exocyclic P=S bond [1-4]. Normal mode calculations have been carried out for some of these compounds, which permit a reliable interpretation of the experimental data. The conformationally sensitive bands in these spectra were found. As a result, correlations were established, which confirm both the solution of the direct spectral problem and the atom-atom potential function calculations. In particular, in contrast to 2-oxo-1,3,2-dioxaphosphorinanes, the skeletal ring vibrations

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 2, pp. 479-482, February, 1990. Original article submitted April 24, 1989.