N-(ALKOXYCARBONYLMETHYL)DIAZENE-N'-OXIDES AND SOME OF THEIR CONVERSIONS

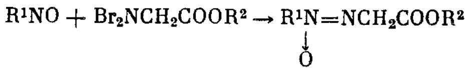
O. A. Luk'yanov, Yu. B. Salamonov, A. G. Bass,
Yu. A. Strelenko, and N. F. Karpenko

UDC 542.91:547.231:547.545:
547.466.22'141

Upon reaction of aliphatic and aromatic nitroso compounds with esters of N,N-dibromoglycine N-substituted N'-(alkoxycarbonylmethyl)diazene-N-oxides are formed. The ethyl ester of (2-phenyldiazene-2-oxido)acetic acid in concentrated H_2SO_4 is transformed into a mixture of the monophenylhydrazide and monophenylhydrazone of monoethyl oxalate and in a solution of gaseous HCl in acetic acid into the phenylhydrazone of the acyl chloride of monoethyl oxalate.

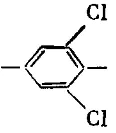
In the literature there is described the only representative of the N-(alkoxycarbonyl)-diazene-N'-oxides, $Me(CH_2)_3CH{=}CH{-}N(O){=}NCHMeCOOMe$, obtained by esterification of an unstable acid isolated from vegetable raw material [1].

We have proposed a general method of synthesis of this class of compounds, which consists of reaction of aliphatic or aromatic nitroso compounds with esters of N,N-dibromoglycine [2]



$$R^1NO + Br_2NCH_2COOR^2 \rightarrow R^1\underset{\underset{O}{\downarrow}}{N}{=}NCH_2COOR^2$$

(Ia—c) (IIa, b) (IIIa—c)

$R^1 = Ph$ (Ia), (IIIa, d); $R^1 = Me_2C(NO_2)$ (Ib), (IIIb,e); $R^1 = Cl—$ 

— (Ic), (IIIc).

$R^2 = Et$ (IIa), (IIIa—c); $R^2 = CMe_3$ (IIb), (IIId,e)

Compound (IIa), described in [2], was generated in situ from the ethyl ester of glycine or prepared separately by treatment of the latter with dibromoisocyanurate (DBI). Compound (IIb) was analogously obtained.

The structure of compounds (III), which decompose upon attempted distillation, was determined by a combination of spectral methods, elemental analysis, and chemical conversions.

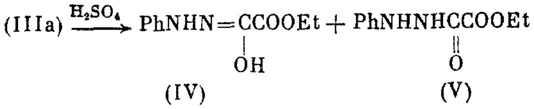
In the ^{14}N NMR spectrum of (IIIa) there is a fairly narrow ($\Delta\nu_{1/2}$ = 150 Hz) line due to the "oxidized" N atom with $\delta = -46.6$ ppm. In the ^{14}N NMR spectrum of (IIIb) two signals are present for the NO_2 group ($\delta = 0.8$ ppm) and the "oxidized" N atom ($\delta = -40.7$ ppm) with approximately equal width ($\Delta\nu_{1/2}$ = 75 Hz).

Upon treatment with organic (Et_2NH) or inorganic (NH_3, aqueous solutions of alkali and Na_2CO_3) bases compounds (III) decompose. Compounds (IIIa-c) and (IIId, e) differ in their reactions with acids. The action of strong acids (HCl, CF_3COOH) leads to decomposition of (IIIc, d), while (IIIa-c) are stable to organic (AcOH, CF_3COOH) or dilute mineral acids. Thus, (IIIa) was isolated in analytically pure form by TLC on silica gel with eluent containing traces of AcOH. It is necessary to note that TLC under these conditions, but in the absence of AcOH, is accompanied by decomposition of (III).

In concentrated H_2SO_4 compound (IIIa) is transformed into a mixture of hydrazone (IV) and hydrazide (V) described in [3] with significant (~90%) predominance of (IV)

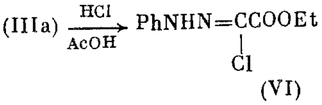
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 352-356, February, 1990. Original article submitted February 20, 1989.

0568-5230/90/3902-0294$12.50



$$(\text{IIIa}) \xrightarrow{H_2SO_4} \underset{(\text{IV})}{\text{PhNHN}{=}\underset{\overset{|}{OH}}{C}\text{COOEt}} + \underset{(\text{V})}{\text{PhNHNH}\underset{\overset{\|}{O}}{C}\text{COOEt}}$$

Under the action of a solution of gaseous HCl in AcOH, (IIIa) is converted to the chlorohydrazone (VI)



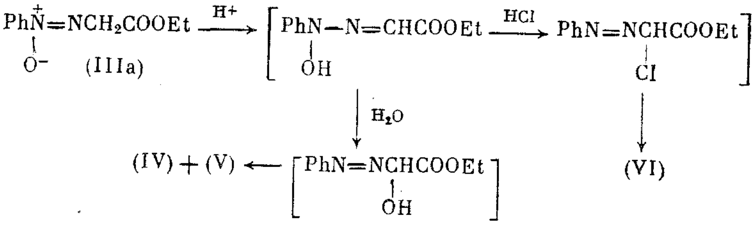
$$(\text{IIIa}) \xrightarrow[AcOH]{HCl} \underset{(\text{VI})}{\text{PhNHN}{=}\underset{\overset{|}{Cl}}{C}\text{COOEt}}$$

The structures of (IV)-(VI) were proved by spectral and analytical data and for (VI) also by comparison with product from an independent synthesis [4]. In the ^{15}N NMR spectrum of (VI) two signals are observed: for Ph—N moieties ($\delta = -229.7$ ppm, $^1J_{N\text{-}H} = 97.2$ Hz) and $C{=}N$ ($\delta = -48.7$ ppm, $^2J_{N\text{-}N\text{-}H} = 2.6$ Hz).

In the ^{15}N NMR spectrum of a mixture of (IV) and (V) three signals are observed: an intense line from the N atom of the PhN fragment (IV, $\delta = -243.2$ ppm, $^1J_{N\text{-}H} = 103.6$ Hz) and two low-intensity lines from the N atom (V, respectively $\delta = -245.9$ ppm, $^1J_{N\text{-}H} = 98.0$ Hz and $\delta = -291.1$ ppm, $^1J_{N\text{-}H} = 88.7$ Hz).

The mass spectra of (IV)-(VI) contain molecular ion peaks and the main direction of fragmentation under electron collision is cleavage of HCOOEt, which leads to the stable fragment ion PhN_2CX^+ (X = Cl, m/z 152; 154; X = OH, m/z 134). There is a known tendency of aromatic diazene oxides to undergo the Wallach rearrangement under the action of concentrated acids [5], which starting from (IIIa) should lead to the hypothetical product 4-$HOC_6H_4N{=}NCH_2COOEt$. However, in our case this does not occur. This conclusion was based on the fact that in the mass spectra of (IV)-(VI) peaks for the corresponding fragments are completely absent.

A possible mechanism for conversion of (IIIa) in concentrated acid is expressed by the following scheme



Reaction of nitroso compounds with (II) in individual cases is apparently accompanied by bromination of the forming (III). Thus, from reaction of (IIa) with 2,4-dinitronitrosobenzene (Id) it was possible to isolate a substance which gives a positive test for halogen. The IR spectrum of this compound contains absorption bands for the diazene oxide fragment (1490, 1280 cm^{-1}) and in the PMR spectrum only signals for the protons of the aromatic ring and ethoxy group are observed.

EXPERIMENTAL

PMR spectra were taken on a Tesla BS-467 instrument with working frequency of 60 MHz and on a Bruker AM-300 instrument with working frequency of 300 MHz in solutions in $CDCl_3$, $(CD_3)_2CO$, or $(CD_3)_2SO$ relative to HMDS. ^{13}C NMR spectra (75.5 MHz), ^{14}N (27.7 MHz), and ^{15}N (30.42 MHz) were recorded on a Bruker AM-300 instrument. For recording of ^{15}N NMR spectra an INEPT pulse sequence was used [6]. Chemical shifts in the ^{14}N and ^{15}N NMR spectra (δ, ppm relative to external standard $MeNO_2$) are given without correction for diamagnetic susceptibility. IR spectra were obtained on UR-20 and Specord IR instruments, using KBr pellets for crystalline substances and neat smears for liquids. Mass spectra were taken on MS-30 and CH-6 instruments.

For chromatography on columns and TLC Silpearl silica gel was used (for TLC, with Luminofor). Melting points were determined on a Koffler table. Compounds (Ia-d) were syn-

TABLE 1. IR and PMR Spectral Data of the Obtained Compounds

Substance	Yield, %	PMR spectrum (δ, ppm from HMDS)				IR spectrum, ν, cm^{-1}
		Solvent	R^1	CH_2	R^2	
(IIIa)	100	$CHCl_3$	8.13m (*o*-H, 2H) 7,38 m (*m*-*p*-H, 3H)	4,23 s	4,14 q (OCH$_2$) 1,21 (CH$_3$)	2980, 2930, 1740, 1485, 1440, 1395, 1365, 1320, 1250, 1190, 1020, 770, 680
(IIIb)	85	CCl_4	2,10 (2CH$_3$)	4,33 s	4,15 q (OCH$_2$) 1,27 t (GH$_3$)	–
(IIIc)	99	CCl_4	7,44 m (Ar, 2H)	4,42 s	4,19 q (OCH$_2$) 1,25 t (CH$_3$)	2975, 2930, 1735, 1555, 1480, 1430, 1380, 1360, 1320, 1250, 1190, 1125, 1020, 850, 815
(IIId)	75	CCl_4	8,20 m (*o*-H, 2H) 7,45 m (*m*-, *p*-H, 3H)	4,45 s	1,30 s (3CH$_3$)	2980, 2935, 1740, 1485, 1445, 1395, 1370, 1320, 1230, 1155, 690
(IIIe)	79	CCl_4	2.08 s (2CH$_3$)	4,58 s	1,46 s (3CH$_3$)	2980, 2930, 1730, 1645, 1570, 1510, 1455, 1400, 1375, 1245, 1155, 830
(IV) + + (V)	100	Acetone-d	9.95 m (NH) 7,55–6,22 m (Ph)	–	4,22 q (OCH$_2$) 1,22 t (CH$_3$)	–
(VI)	92	DMSO-d_6	10,4 s (NH) 7,4 m (Ph, *o*-H) 7.3m (Ph, *m*-H) 6,95 m (Ph, *p*-H)	–	4,26 q (OCH$_2$) 1,27 t (CH$_3$)	–

TABLE 2. ^{13}C NMR Spectral Data of the Obtained Compounds

Compound	Ph	—N—$\underline{C}$—COO	C=O	OCH_2	CH_3
(IIIa)	*p* 137,61 *m* 128,34 *o* 121,71 *i* 146,3	53.6	167,2	60,8	13,7
(IV)	*p* 119,7 *m* 129,2 *o* 113,0 *i* 148,6	157,8	160,7	62,7	14,1
(V)	*p* 120,8 *m* 129,2 *o* 113,8 *i* 148,3	163,8	166,8	61,3	14,0
(VI)	*p* 122,7 *m* 129,3 *o* 114,9 *i* 143,0	114,1	159,8	62,4	14,2

thesized by methods of [7-10], glycine esters by methods of [11, 12], and DBI according to [12]. IR and PMR spectral data for the obtained products are shown in Table 1 and ^{13}C NMR data in Table 2.

Ethyl Ester of N,N-Dibromoglycine (IIa). A weighed amount of glycine ethyl ester was dissolved in abs. CH_2Cl_2, then 1.1 moles of DBI was added, the mixture was stirred for 30-40 min, filtered, evaporated, and then a red liquid with Br_2 odor (IIa) was obtained in quantitative yield, which decomposes with foaming upon keeping in air at ~20°C. Analogously compound (IIb) was synthesized.

General Method for Obtaining Esters of 2-Substituted (Diazene-2-oxido)acetic Acids (III). A solution of equimolar amounts of (I) and (II) in abs. CH_2Cl_2 was stirred for 30-40 min at ~20°C until the characteristic dark-red color was established (as shown by TLC), which was caused by Br_2 evolving in the reaction. The reaction mixture was then evaporated and (III) was obtained, which in the majority of cases (according to PMR data) did not require additional purification. (IIIa). Found, %: C 57.86; H 5.76; N 13.48. $C_{10}H_{12}N_2O_3$. Calculated, %: C 57.69; H 5.77; N 13.46.

Mixture of Monophenylhydrazone of Oxalic Acid Monoethyl Ester (IV) and Monophenylhydrazide of Oxalic Acid Monoethyl Ester (V). To 30 ml of concentrated H_2SO_4 with stirring and cooling 2.2 g of (IIIa) was added dropwise. After days at 6-8°C the mixture was poured onto ice, extracted with CH_2Cl_2, and dried above $MgSO_4$. After solvent removal 2.2 g (100%) of yellow-grey crystals was obtained, which were washed with CCl_4 and recrystallized from abs. alcohol. There were isolated light-yellow crystals of (IV) and (V) with mp of 116-118°C (see [4]). Found, %: C 57.76; H 5.98; N 13.17. $C_{10}H_{12}N_2O_3$. Calculated, %: C 57.69; H 5.77; N 13.46.

Phenylhydrazone of Acyl Chloride of Oxalic Acid Ethyl Ester (VI). 2.3 g of (IIIa) were dissolved in 30 ml of ice-cold AcOH, then for 1 h dry gaseous HCl was passed through, and the mixture was evaporated. There was obtained 2.3 g (92%) of dark-red oil which quickly crystallized into a light-brown powder with mp of 86-87°C (from abs. alcohol). There is no melting point depression with a known sample [5].

LITERATURE CITED

1. W. J. McGahken and M. P. Kunstmann, J. Am. Chem. Soc., 91, 2808 (1969).
2. W. Traube and H. Gockel, Ber., 56b, 384 (1923).
3. W. Bulow, Liebigs Ann. Chem., 236, 197 (1886).
4. A. Favrel, C. R. Acad. Sci., 134, 1312 (1902).
5. O. Wallach and L. Belli, Ber., 13, 525 (1880).
6. G. A. Morris and R. Freeman, J. Am. Chem. Soc., 101, 760 (1979).
7. Synthesis of Organic Preparations [in Russian] (1953), p. 354.
8. I. Guben, Methods of Organic Chemistry [in Russian], Book 1, Vol. 4, (1949), p. 107.
9. H. Borsche, Ber., 56, 1498 (1923).
10. R. R. Holmes and R. P. Bayer, J. Am. Chem. Soc., 82, 3454 (1960).
11. I. Guben, Methods of Organic Chemistry [in Russian], Book 1, Vol. 4, (1949), p. 919.
12. E. Taschner and A. Chimak, Liebigs Ann. Chem., 646, 134 (1961).
13. W. Gottardi, Monatsch. Chem., 98, 507 (1967).