REACTION OF 1,1-DISUBSTITUTED HYDRAZINES WITH DIBROMOISOCYANURATE IN THE PRESENCE OF NITROSOBENZENE

S. G. Zlotin, O. V. Prokshits, N. F. Karpenko, and O. A. Luk'yanov

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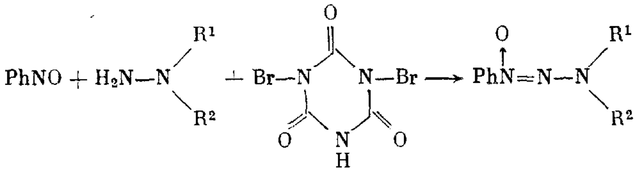
A study was carried out on the reaction of 1,1-disubstituted hydrazines with dibromoisocyanurate in the presence of nitrosobenzene. Depending on the structure of the hydrazine component, the reaction may proceed either to 3,3-disubstituted 2-phenyltriazene 1-oxides or the products of the oxidative dimerization of hydrazine derivatives, namely, 1,1,4,4-tetrasubstituted tetrazenes.

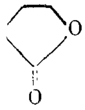
The reaction of 1,1-disubstituted hydrazines with nitrosoarenes in the presence of oxidizing agents, such as HgO [1], $Pb(OAc)_4$ [2], the diethyl ester of azodicarboxylic acid [3], or excess nitroso compound [2,4], leads to 3,3-disubstituted 1-aryltriazene 1-oxides. Each of these reactions has limited application and, with the exception of a variant proposed by Hoesch [2], gives low yields. Reactions involving halogenating agents commonly used for the oxidation of hydrazine derivatives [5,6] may have more common application. In the present work, we studied the reaction of 1,1-disubstituted hydrazines with nitrosobenzene and dibromoisocyanurate (DBI), which is an efficient brominating agents employed for obtaining the diazene N-oxide group [7,8].

We have shown that the reaction of 1,1-disubstituted hydrazines (I)-(III) with nitrosobenzene and DBI leads to the formation of the corresponding 3,3-disubstituted triazene 1-oxides (IV)(VI). These reactions proceed in organic solvents such as CH_2Cl_2, ether, THF, and dioxane–ether at from –40 to –20°C. The yields of (IV)-(VI) range from 57 to 98% and exceed those reported for (V) and (VI) achieved using other oxidizing agents [1,2].



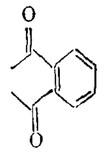
(I)—(III) (IV)—(VI)

$R^1 = CH_3$, $R^2 = CH_2CH_2CN$ (I), (IV); $R^1—R^2 =$



(II), (V);

$R^1—R^2=$



(III), (VI).

We should note that DBI is the first oxidizing agent, which permits the synthesis of triazene 1-oxides using from a variety of hydrazine derivatives such as 1,1-dialkylhydrazines and cyclic N-aminoimides and N-aminourethanes. In this case, 1,1-dialkylhydrazine may undergo this reaction either as the free base or as the hydrochloride salt, which enhances the preparative value of this method.

While the major products of the reaction of nitrosobenzene with (I)-(III) and DBI are the corresponding triazene 1-oxides (IV)-(VI), the oxidation of N-acyl- and N-alkoxycarbonylhydrazines, whose functional groups are not part of a cyclic system, proceeds

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1679-1681, July, 1990. Original article submitted January 29, 1990.

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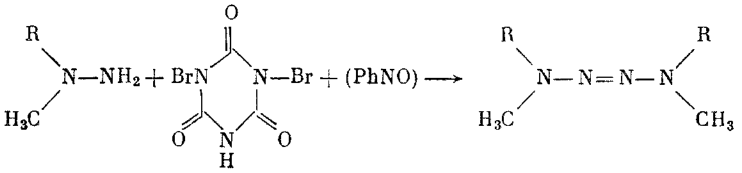
by the action of DBI without the participation of nitroso compounds to give a complex mixture containing tetrazenes (IX) and (X), which are characteristic products of the oxidative dimerization of hydrazine derivatives [5,6]. The yields of (IX) and (X) are 15 and 23%, respectively. The lack of a reaction of nitrosobenzene with the components of the oxidative system was confirmed by the preparation of (IX) and (X) from the corresponding hydrazines, (VII) and (VIII), and DBI without the addition of a nitroso compound.



(VII), (VIII) (IX), (X)

R = $COCH_3$(VII), (IX), CO_2CH_3(VIII), (X).

A possible scheme for the formation of products (IV)-(VI), (IX), and (X) involves the formation of unstable N-halohydrazine derivatives by the action of DBI. Depending on the structure of the hydrazine component, these N-halo derivatives either react with the nitroso compound present in the system or undergo oxidative dimerization. The important role of DBI in the reaction is indicated by the decrease in the yield of (IV) to 20-30% and of (IX) to 10% upon carrying out the reaction in the presence of weaker halogenating agents such as Br_2, N-bromosuccinimide, and tert-butyl hypochlorite.

The structures of the compounds synthesized were established by IR and PMR spectroscopy, mass spectrometry, and elemental analysis. In the case of (V) and (VI), the products were identified by comparison with authentic samples obtained according to Miesel [1] and Hoesch [2]. A study of the mass spectra of products (IV)-(VI), (IX), and (X) showed that all these compounds give molecular ion peaks of varying intensity. The mass spectra of triazene N-oxides (IV)-(VI) have strong peaks for the PhNO fragment ions (m/z 107), whose formation is apparently related to cleavage of the molecular ions at the $N(O)=\wr=N$ bond. This finding indicates that the N-oxide oxygen in the initially synthesized compound and in products (V) and (VI) is located at N^1 of the triazene N-oxide group. The formation of intense peaks for nitrosoarene fragment ions is characteristic for the mass spectral fragmentation of 1-aryltriazene 1-oxides [2], while the cleavage of triazene 2-oxides upon electron impact involves the formation of nitrosoamine radical-cations [9].

EXPERIMENTAL

The IR spectra were taken on a Specord 75 IR spectrometer. The PMR spectra were taken on a Tesla BS-467 spectrometer at 60 MHz with HMDS as the internal standard. The mass spectra were taken on a Varian MAT CH-6 spectrometer with direct sample inlet into the ion source at 70 eV. The accelerating voltage was 1.75 kV and the emission current was 100 μA. Thin-layer chromatography was carried out on Silpearl UV-250. Derivatives (I)-(III), (VII), and (VIII) were obtained according to previous procedures [10-14].

3-Methyl-3-cyanoethyl-1-phenyltriazene 1-Oxide (IV). A sample of 2.3 g (8.08 mmole) DBI was added with stirring to 0.4 g (4.04 mmoles) (I) and 0.5 g (4.67 mmoles) nitrosobenzene in 10 ml THF at −40°C. The mixture was maintained for 5 h with gradual warming to ~20°C. The solvent was distilled off and the product was separated by thin-layer chromatography to give 0.47 g (57%) (IV) as a yellow oil, R_f 0.22 (1:2 hexane–ether as the eluent). Found: C, 59.33; H, 5.99; N, 27.69%. Calculated for $C_{10}H_{12}N_4O$: C, 58.82; H, 5.88; N, 27.45%. IR spectrum (ν, cm^{-1}): 1470 (N(O)=N), 2240 (CN). PMR spectrum in $CDCl_3$ (δ, ppm, J, Hz): 2.69 t (CH_2CN), J = 7), 3.14 s ($N-CH_3$), 3.54 t ($N-CH_2$, J = 7), 7.23-7.47 m (3H, C_2H_5), 7.82-8.09 m (2H, C_6H_5). Mass spectrum, m/z (I, %): M^+ 204(43), 122(42), $PhNO^+$ 107(67), 105(40), 97(61), 93(38), 78(69), 77(19), 68(100), 54(48).

An analogous procedure gave 3-(O,N,N-phenylazoxy)-2-oxazolidinone (V) in 78% yield, mp 101-102°C (from ethanol) (mp 97-99°C [1]), R_f 0.54 (ether). Found: C, 51.82; H, 4.47; N, 20.2%. Calculated for $C_9H_9N_3O_3$: C, 52.17; H, 4.35; N, 20.29%. IR spectrum (ν, cm^{-1}): 1200 (C–O–C), 1480 (N(O)=N), 1790 (C=O). PMR spectrum in acetone-d_6 (δ, ppm): 4.24-4.65 m (NCH_2CH_2O), 7.47-7.67 m (3H, C_6H_5), 7.98-8.13 m (2H, C_6H_5). Mass spectrum, m/z (I, %): M^+ 207(14); $PhNO^+$ 107(60), 105(16), 91(7), 78(10), 77(86), 46(76), 45(100), 44(30).

N-(O,N′,N′-Phenylazoxy)phthalimide (VI) was obtained in 98% yield, mp 162-163°C (162-164°C [2]), R_f 0.45 (1:2 hexane–ether). The spectral indices correspond entirely to those given by Hoesch [2].

1,4-Diacetyl-1,4-dimethyltetrazene (IX) was obtained in 15% yield, mp 149-150°C (1:1 hexane–acetone), R_f 0.58 (ether). Found: C, 41.36; H, 6.91; N, 31.49%. Calculated for $C_6H_{12}N_4O_2$: C, 41.86; H, 6.98; N, 32.56%. IR spectrum (ν, cm^{-1}): 1700 (C=O). PMR spectrum in acetone-d_6 (δ, ppm): 2.27 s ($COCH_3$). Mass spectrum, m/z: M^+ 172.

1,4-Dimethyl-1,4-di(ethoxycarbonyl)tetrazene (X) was obtained in 23% yield, mp 132-133°C (hexane), R_f 0.25 (1:2 hexane-ether). IR spectrum (ν, cm^{-1}): 1140 (C-O-C), 1700 (C=O), PMR spectrum in $CDCl_3$ (δ, ppm, J, Hz): 1.28 t (CH_3, J = 7), 3.38 s (NCH_3), 4.3 q ($COCH_2$, J = 7). Mass spectrum, m/z: M^+ 232.

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HIGH-TEMPERATURE TRANSNITRILATION OF 2-BROMOCAPROIC ACID

Yu. N. Polivin, V. A. Vinokurov, S. V. Makarshin,
R. A. Karakhanov, M. A. Silin, and E. A. Ageev

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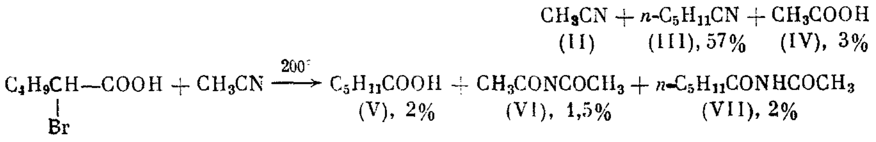
Chromato-mass spectrometry and IR and PMR spectroscopy were used to study the high-temperature reaction of 2-bromocaproic, 2-iodocaproic, and 2-bromo-2-phenylacetic acids with acetonitrile. The formation of anomalous transnitrilation products (capronitrile and benzyl cyanide) is a consequence of the initial conversion of 2-halo-substituted caproic and phenylacetic acids to caproic and phenylacetic acids, respectively.

In previous work [1], we found that the reaction of 2-bromocaproic acid (I) and acetonitrile (II) proceeds with the formation of an anomalous transnitrilation product, namely, capronitrile (III). In order to determine the nature of this interesting phenomenon, we carried out a detailed study of the reaction of (I) and (II) and other related compounds using chromato-mass spectrometry.

We found seven compounds in the reaction mixture:



$$\underset{\mathrm{Br}}{\mathrm{C_4H_9CH}}\mathrm{{-}COOH} + CH_3CN \xrightarrow{200^\circ} \begin{array}{l} \underset{(II)}{CH_3CN} + \underset{(III),\ 57\%}{n\text{-}C_5H_{11}CN} + \underset{(IV),\ 3\%}{CH_3COOH} \\ \underset{(V),\ 2\%}{C_5H_{11}COOH} + \underset{(VI),\ 1,5\%}{CH_3CONCOCH_3} + \underset{(VII),\ 2\%}{n\text{-}C_5H_{11}CONHCOCH_3} \end{array}$$

Institute for Problems in Petroleum and Gas, Academy of Sciences of the USSR, Moscow and I. M. Gubkin Moscow Institute of Petroleum and Gas, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1682-1684, July, 1990. Original article submitted February 3, 1990.