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Chemistry of Nitrosoimines. VI.[1] Attempted Syntheses of Some[1] Resonance Stabilized Nitrosoimines and Their UV Spectra

Kin-ya Akiba, Satoru Matsunami, Chikahiko Eguchi, and Naoki Inamoto
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113

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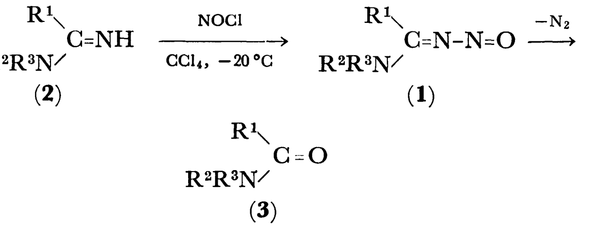
1,1,3,3-Tetrasubstituted 2-nitrosoguanidines, the attempted syntheses and UV spectra of which are reported, are unstable, and decomposed into the corresponding ureas and nitrogen, only 2-nitroso-1,1,3,3-tetraphenylguanidine (**1f**) being obtained as a pure compound. The reaction of **1f** with phenyl isocyanate gave pentaphenylguanidine, probably through 1,4-cycloaddition.

N-Nitrosoaldimines were suggested as being intermediates to explain the formation of aldehydes during the course of reaction of alkylidenetriphenylphosphoranes with nitric oxide.[2] Thoman and Hunsberger reported the syntheses of sterically hindered *N*-nitrosoketimines and showed basic characters of *N*-nitrosoimines for the first time.[3]

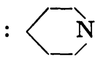
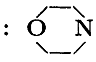
We report herewith on the attempted syntheses of resonance stabilized *N*-nitrosoimines such as 1,1,3,3-tetrasubstituted 2-nitrosoguanidines, their UV spectra, decomposition rates of one of them in a few solvents and some reactions of 2-nitroso-1,1,3,3-tetraphenylguanidine (**1f**).

1,1,3,3-Tetrasubstituted guanidines (**2a**—**f**) and *S*-benzyl-*N*-ethyl-*N*-phenylisothiourea (**2g**) were nitrosated with nitrosyl chloride in carbon tetrachloride in the presence of anhydrous sodium acetate at *ca.* −20 °C according to the reported procedure.[3] Upon the mixing of two reagents, a yellow to orange red color appeared in the solution according to the structure of the product.

All the nitrosoimines (**1a**—**e**,**g**) except 2-nitroso-1,1,3,3-tetraphenylguanidine (**1f**) decomposed to the corresponding carbonyl compounds, *i.e.*, ureas (**3a**—**e**) and thiolcarbamate (**3g**), during the course of reaction and isolation.



Scheme 1.

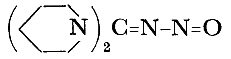
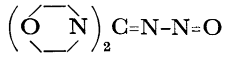
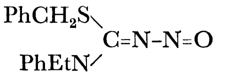
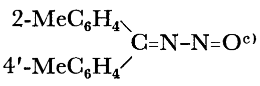
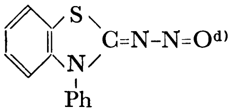
	R¹	R²	R³	Yield (%)
a :	Me_2N	Me	Me	53
b :	Et_2N	Et	Et	11*
e :		$(CH_2)_5$		65
d :		$(CH_2)_2O(CH_2)_2$		57
e :	PhMeN	Me	Ph	61
f :	Ph_2N	Ph	Ph	91
g :	$PhCH_2S$	Et	Ph	86

* The low yield is due to isolation procedure, during which the reaction mixture was kept at low pressure for a long time to evaporate the solvent before distillation.

Ths isolated yields of carbonyl compounds (**3**) are shown in Scheme 1.

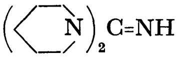
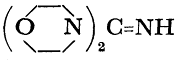
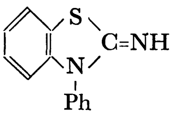
Nitrosation of **2a**—**d** and **2g** was attempted at lower temperatures (−60 to −70 °C) in dichloromethane.

Table 1. Absorption spectra of nitrosoimines (**1**)

	Nitrosoimine	Solvent	λ_{max} (nm)[a] π→π*	n→π*
1a	$(Me_2N)_2C=N-N=O$	CH_2Cl_2	277 (sh)	[b]
1b	$(Et_2N)_2C=N-N=O$	CH_2Cl_2	277	458
1c		CH_2Cl_2	276	462
1d		CH_2Cl_2	276	473
1e	$(PhMeN)_2C=N-N=O$	$CHCl_3$	289 (sh)	488
1f	$(Ph_2N)_2C=N-N=O$	$CHCl_3$	330 (9550)	519 (183)
1g	 $PhCH_2S(PhEtN)C=N-N=O$	CH_2Cl_2	330 (sh)	504
1h	$(4\text{-}ClC_6H_4)_2C=N-N=O$[c]	CCl_4	306 (8770)	522, 596 (107) (107)
1i	 $(2\text{-}MeC_6H_4)(4'\text{-}MeC_6H_4)C=N-N=O$[c]	EtOH	310	523, 585
1j		$CHCl_3$	354 (11800)	506 (62)

a) Numerical values in parentheses show molar extinction coefficients. b) Decomposition too rapid for measurement. c) Ref. 3. d) Ref. 4a.

Table 2. UV spectra of guanidines (**2**)

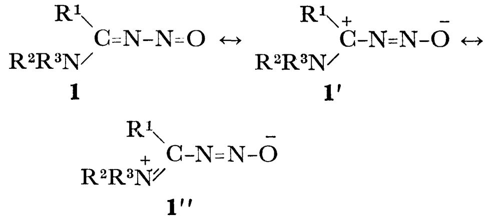
	Guanidine	Solvent	λ_{max} (nm)	ε
2b	$(Et_2N)_2C=NH$	EtOH	225	9.5×10^3
2c		EtOH	224	7.0×10^3
2d		EtOH	224	1.1×10^4
2e	$(PhMeN)_2C=NH$	EtOH	231 250	1.5×10^4 1.2×10^4
2f	$(Ph_2N)_2C=NH$	EtOH	265 (broad)	2.3×10^4
2j		$CHCl_3$	281 288	5.3×10^3 5.9×10^3

The color of the resulting *N*-nitrosoimines (**1**) was deeper and more intense, yellow orange to red brown.

UV spectra of nitrosoimines are shown in Table 1 together with those of three reference compounds (**1h**—**j**).

Nitrosoimines have two characteristic bands (π-π^* and n-π^*). The π-π^* bands are shifted to longer wavelengths than those of the corresponding imines by 50—70 nm (Table 2).

These π-π^* bands can be attributed to neither the separate imino nor nitroso groups,[4] and are probably due to the nitrosoimino group with a large contribution of canonical structures **1'** and **1''**.



1 **1'** **1''**

The π-π^* band shifts further toward a longer wavelength with substitution by a phenyl on the nitrogen (**1e**, **f**, **g**). The effect is common to the parent imines (**2**), but larger in the case of nitrosoimines (**1**).

It might be of interest to note that n-π^* bands of **1a**—**d** are shifted toward longer wavelengths while their π-π^* bands remain constant.

The n-π^* bands of **1** are expected to consist of two components at least, *viz.*, $_{N(C=N)}$n-π^* and $_{N(N=O)}$n-π^*. This was found in the case of nitrosoketimines (**1h**, **i**),[3] but not in our case (Table 1).

UV spectra and rates of decomposition of bis(morpholino)-*N*-nitrosomethyleneimine (**1d**) were measured in four solvents. The results are shown in Table 3. The blue shift of the n-π^* band is very large (473 nm in CH_2Cl_2 and 418 nm in H_2O). Three peaks appear as n-π^* bands in alcohols but the reason is not clear.

Table 3. Solvent effect on absorption spectra and decomposition rates of bis(morpholino)-*N*-nitrosomethyleneimine (**1d**)

Solvent	λ_{max} (nm) $\pi\rightarrow\pi^*$	λ_{max} (nm) n$\rightarrow\pi^*$	k (s^{-1}) (13.5 °C)
CH_2Cl_2	276	473	3.5×10^{-3}
EtOH	276 (sh)	404, (sh) 423.5, 443	2.8×10^{-4}
MeOH	274.5	404, (sh) 425.5, 441	4.0×10^{-4}
H_2O	268.5	418	1.5×10^{-5}

1d is fairly stable in water at room temperature, though the yellowish green color of **1d** fades rapidly with evolution of gas (N_2) at 90 °C. The rates of decomposition were followed by the decrease in π-π^* absorption. Plots of absorption intensity *vs.* time indicates that the rate of decomposition follows first-order kinetics and decreases with the increase in polarity of the solvents (Table 3).

This is consistent with the unimolecular decomposition mechanism in which a non-polar four-membered ring is assumed to be a transition state starting from a polar ground state.

$\mathbf{1} \leftrightarrow \mathbf{1'} \rightarrow$ … $\rightarrow \mathbf{3} + N_2$

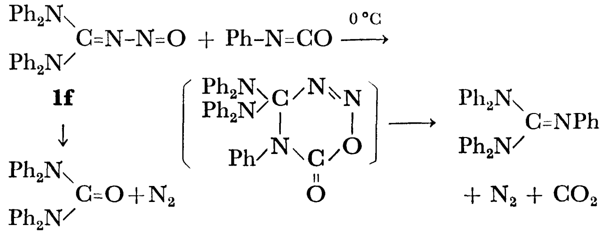
Thoman and Hunsberger also observed that the rate of decomposition of *N*-nitroso-2,4'-dimethyldiphenylmethyleneimine (**1i**) in cyclohexane indicates a first-order mechanism, followed by the rate of evolution of nitrogen.[3]

Guanidines are stable against hydrolysis, so there is no need to consider hydrolysis in contrast to the case of *N*-nitrosoketimines.

If nitrosoimines have a considerable polar character in ground state, they are expected to undergo 1,4-cycloaddition with appropriate dienophiles.

Attempts to react 2-nitroso-1,1,3,3-tetraphenylguanidine (**1f**) with ethyl vinyl ether and maleic anhydride in chloroform at 0 °C for a month were unsuccessful, tetraphenylurea being recovered quantitatively (thermal decomposition product).

Reaction of **1f** with phenyl isocyanate under the same conditions gave pentaphenylguanidine in 38% yield together with 43% of tetraphenylurea as shown below.



1f

1,1,3,3-Tetramethyl-2-phenylguanidine reacted with *p*-toluenesulfonyl isocyanate to give 1,2-cycloaddition product.[5] 1,4-Cycloaddition mechanism might be preferred in the reaction.

Experimental

Materials. *(a) Guanidines*: Commercial 1,1,3,3-tetramethylguanidine (**2a**) was distilled before use (bp 160—161 °C). 1,1,3,3-Tetraethylguanidine (**2b**) was prepared from diethylcyanamide and diethylamine (bp 92 °C/13 mmHg).[6,7] Bis(piperidino)methyleneimine (**2c**) was prepared from piperidine and cyanogen bromide (bp 110—116 °C/0.15—0.2 mmHg).[7] Bis(morpholino)methyleneimine (**2d**) was prepared by the same method (mp 87—93 °C).[7] 1,3-Dimethyl-1,3-diphenylguanidine (**2e**) was prepared as follows: *N*-methylaniline hydrochloride (21.6 g) and *N*-methyl-*N*-phenylcyanamide (20 g) were heated in a sealed tube at 180—190 °C for 2 hr. The resulting mass was dissolved in ethanol. Sodium hydroxide was added to the solution until the pH of the solution became 11. The resulting NaCl was filtered off and ethanol was evaporated. The residue was extracted with benzene, and the residual liquid was distilled under reduced pressure after evaporation of benzene. Bp 124.5—127 °C/0.15 mmHg,[8] yield 51%. The yield decreased when the sealed tube was heated longer (4 or 6 hr) and it was necessary to adjust the pH of the solution to around 11. 1,1,3,3-Tetraphenylguanidine (**2f**) was prepared from diphenylcyanamide[9] (34 g) and diphenylamine hydrochloride (36 g) which were heated in a sealed tube at 175 °C for 6 hr. The resulting mass was extracted with aq. hydrochloric acid and the aq. solution was made alkaline with NaOH.

The resulting precipitates were filtered and recrystallized from ligroin, mp 132.0—132.5 °C, yield 32%.[10] Larger scale preparations gave lower yields (5—20%).

(b) Ureas and Thiolcarbamate: Ureas and thiolcarbamate were prepared from the corresponding secondary amines and phosgene according to methods given in literature; tetramethylurea (**3a**: bp 170.5—173.0 °C),[11] tetraethylurea (**3b**: 61—62 °C/6 mmHg),[12] bispiperidinoketone (**3c**: mp 39—42 °C),[13] bismorpholinoketone (**3d**: mp 139—141 °C)[13] *sym*-dimethyldiphenylurea (**3e**: mp 120—122 °C),[14] tetraphenylurea (**3f**: mp 179.5—180.0 °C),[14] and benzyl *N*-ethyl-*N*-phenylthiolcarbamate (**3g**: mp 46.2—47.0 °C).[15]

General Procedure of Nitrosation. (a) A solution of nitrosyl chloride (4.9 g, 75 mmol) in carbon tetrachloride (50 ml) was cooled under stirring to *ca.* −20 °C in a dry ice-acetone bath with anhydrous sodium acetate (14.8 g, 145 mmol). A cold solution of guanidine (50 mmol) in carbon tetrachloride (20 mmol) was then added dropwise for 20 min, the internal temperature being kept below −10 °C. The mixture was stirred for 20 min at −10 °C, and washed with cold 10% potassium hydrogen carbonate (150 ml) and then with ice-water (150 ml). The dried solution (with anhydrous magnesium sulfate) was evaporated under reduced pressure and the residue was distilled or recrystallized. Ureas thus produced were identified by a comparison with authentic samples.

(b) For UV measurement, dichloromethane was used as a solvent, and nitrosation was performed at *ca.* −70 °C, the dried solution being then used for the measurement. For the kinetic study of decomposition of **1d**, dichloromethane was evaporated below 0 °C, and the resulting yellow slurry was dissolved in an appropriate solvent.

(c) 1,1,3,3-Tetraphenylguanidine (**2f**) was nitrosated according to procedure (a). A red solid appeared during nitrosation which was quickly filtered off after addition of cold 10% potassium hydrogen carbonate. The filtered solid was dried in a vacuum desiccator over P_2O_5. The red solid (**1f**) was then recrystallized from chloroform–ether–petroleum ether at *ca.* −60 °C. Mp 80 °C (dec.); $\lambda_{max}^{CHCl_3}$ 330 (ε 9550) and 519 nm (183); yield, 81—92%.

The compound **1f** is stable in solid state at −20 °C but decomposes fairly rapidly in chloroform at room temperature. Decomposition was not detected when it was left to stand for a day in chloroform at −60 to −70 °C.

Found: C, 76.30; H, 5.43; N, 14.65%. Calcd for $C_{25}H_{20}N_4O$: C, 76.51; H, 5.14; N, 14.28%.

*Thermal Decomposition of 2-Nitroso-1,1,3,3-tetraphenylguanidine (**1f**).* A solution of **1f** (0.9 g, 2.3 mmol) in chloroform (20 ml) was left to stand at 0 °C for a month. The residue, after evaporation of chloroform, was chromatographed on silica gel, and tetraphenylurea (0.762 g, 2.1 mmol, 91%) was eluted with dichloromethane.

*Reaction of **1f** with Phenyl Isocyanate.* Phenyl isocyanate (1.83 g, 15.3 mmol) and **1f** (3.0 g, 7.7 mmol) were dissolved in chloroform (25 ml) and the solution was left to stand at 0 °C for a month. Ethanol (5 ml) was added to convert the residual phenyl isocyanate into the urethane, and the solvent was evaporated. The residue was chromatographed on silica gel to elute urethane and tetraphenylurea (1.19 g, 3.3 mmol, 43%) with dichloromethane. The residual component was eluted with ethanol and again chromatographed on alumina to elute pentaphenylguanidine (1.26 g, 2.9 mmol, 38%), mp 180.0—180.5 °C, $\nu_{C=N}$ 1625 cm^{-1}; $M^+(437)$.

Found: C, 84.77; H, 5.90; N, 9.85%. Calcd for $C_{31}H_{25}N_3$: C, 84.71; H, 5.73; N, 9.56%.

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