Monatshefte für Chemie 137, 185–190 (2006)
DOI 10.1007/s00706-005-0414-8

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

The Oxidation of Hexahydrotriazines

Roland Dorninger[1], **Kurt Klepp**[2], **Reinhard Rametsteiner**[1],
Rudolf Schiffer[1], **Harald Schmidt**[1,*], and **Clemens Schwarzinger**[1]

[1] Institute for Chemical Technology of Organic Materials, Johannes Kepler University Linz, A-4040 Linz, Austria
[2] Institute of Inorganic Chemistry, Johannes Kepler University Linz, A-4040 Linz, Austria

Received July 25, 2005; accepted (revised) October 4, 2005

Summary. *N*-Alkyl-2,4-dioxohexahydro-1,3,5-triazines oxidize readily with oxygen to the corresponding cyanuric acid derivates. The oxidation of 1,3,5-trimethyl-2,4-dioxohexahydro-1,3,5-triazine resulted in a stable form of hydroperoxide. During the oxidation of 1,3,5-trimethyl- 6-phenyl-2,4-dioxohexahydro-1,3,5-triazine this hydroperoxide could not be identified, however, the result was the stable reaction product bis-[6-phenyl-1,3,5-trimethyl-2,4-dioxohexahydro-1,3,5-triazin]peroxide.

Keywords. Cyanuric acid; Hexahydrotriazines; Hydroperoxides; Oxidation; Peroxides.

Introduction

N-Alkyl-2,4-dioxohexahydro-1,3,5-triazines are interesting solvents for the fluid–fluid- extraction of aromatics from aromatics containing hydrocarbon mixtures.

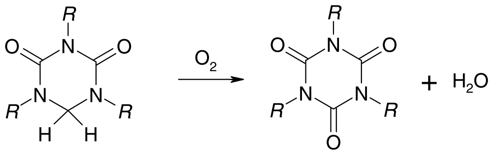
Besides good selectivity and capacity their high resistance to hydrolysis is of importance [1]. During stability investigations we observed the easy oxidation of these compounds by air oxygen. There have been neither reports about the autoxidation of hexahydrotriazines with oxygen nor any reports about their hydroperoxides or peroxides.

Results and Discussion

The oxidation of 2,4-dioxohexahydro-1,3,5-triazine (**1a**) to cyanuric acid (**1b**) is successful only with strong oxidizing agents such as hydrogen peroxide or potassium peroxydisulfate [2]. However, we found now that the *N*-alkyl compounds **2a**–**5a** oxidize surprisingly easily with oxygen to the corresponding cyanuric acid derivates **2b**–**5b**. Since little can be found in scientific literature about the oxidation of hexahydrotriazines, we examined the reaction of **2a** with air using

---

* Corresponding author. E-mail: harald.schmidt@jku.at



1a, **1b** *R* = H-; **2a**, **2b** *R* = Methyl-; **3a**, **3b** *R* = Ethyl-; **4a**, **4b** *R* = Allyl-; **5a**, **5b** *R* = Benzyl-

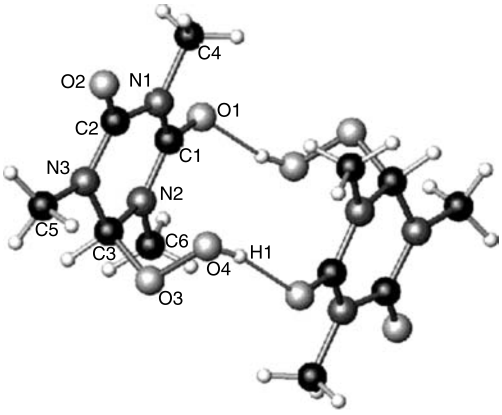
Scheme 1

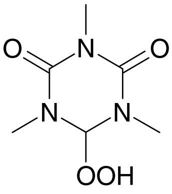
Table 1. Conversion based on oxygen consumption, rate constant, and composition of the reaction solution at different temperatures and an initial concentration of 1 mol/dm^3 **2a**

Temperature/°C	Conversion/%	Rate constant/s^{-1}	Composition/mol dm^{-3}	
			2c	**2b**
70	73	1.76×10^{-4}	0.364	0.374
80	90	5.24×10^{-4}	0.411	0.511
90	90	6.22×10^{-4}	0.178	0.748
100	90	7.35×10^{-4}	0.107	0.824

chlorobenzene as solvent. Within the temperature range of 70–100°C a spontaneous absorption of oxygen of up to a volume of 90% occurred after an induction period of only a few minutes. Oxygen consumption was observed by using a gas burette and the composition of the solution was determined at the end of the reaction by means of HPLC, HPLC-MS, and ^{13}C NMR. The kinetic data of oxidation of **2a** and composition of the reaction solution at the end of the reaction are illustrated in Table 1.

As indicated in Table 1, high concentrations of hydroperoxide **2c** occur at lower temperatures and disintegration to trimethylcyanuric acid (**2b**) begins with increasing temperature. Conversions of this magnitude are not typical for autoxidations. An activation energy of only 18.4 kJ/mol confirmed the ready





2c

Fig. 1. Result of an X-ray structure analysis of 1,3,5-trimethyl-2,4-dioxo-6-hydroperoxohexahydro-1,3,5- triazine (**2c**)

Table 2. Positional and equivalent isotropic displacement parameters for 1,3,5-trimethyl-2,4-dioxo-6-hydroperoxohexahydro-1,3,5-triazine (**2c**), monoclinic, s.g. $P2_1/c$ (no. 14), $a = 8.494(2)$, $b = 8.985(2)$, $c = 11.372(5)$ Å, $\beta = 94.61(2)°$, $Z = 4$

Atom	x	y	z	B_{eq}[a]
N(1)	0.7189(2)	0.0984(2)	0.6345(2)	3.14(4)
N(2)	0.9731(2)	0.1856(2)	0.6205(2)	3.01(4)
N(3)	0.7583(2)	0.3513(2)	0.6036(2)	3.05(4)
C(1)	0.8797(3)	0.0708(3)	0.6448(2)	2.93(4)
C(2)	0.6543(3)	0.2389(3)	0.6172(2)	3.31(5)
C(3)	0.9167(2)	0.3248(3)	0.5762(2)	2.97(4)
C(4)	0.6131(3)	−0.0255(3)	0.6582(3)	5.07(6)
C(5)	0.6964(3)	1.0012(3)	0.0765(2)	4.32(6)
C(6)	1.1452(3)	0.1662(3)	0.6279(2)	4.15(5)
O(1)	0.9304(2)	−0.0522(2)	0.6745(2)	3.99(4)
O(2)	0.5127(2)	0.2599(2)	0.6169(2)	4.91(4)
O(3)	0.9344(2)	0.3412(2)	0.4526(1)	3.66(3)
O(4)	0.8334(2)	0.2317(2)	0.3904(1)	4.06(4)
H(1)	0.895(3)	0.166(3)	0.369(2)	5.6(6)*
H(2)	0.986(2)	0.088(2)	0.112(2)	3.0(5)*
H5a	0.218	0.070	0.909	5.5(6)*
H5b	0.337	0.005	0.009	6.7(7)*
H5c	0.394	0.036	0.878	6.9(8)*
H4a	0.365	0.114	0.387	8.2(9)*
H4b	0.493	0.992	0.368	9(1)*
H4c	0.369	0.037	0.259	8.2(9)*
H6a	0.179	0.079	0.677	10(1)*
H6b	0.201	0.253	0.664	12(1)*
H6c	0.172	0.126	0.559	9.1(9)*

[a] $B_{eq} = \frac{8\pi^2}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a_i a_j}$

* Hydrogen atoms were treated as riding atoms and refined isotropically

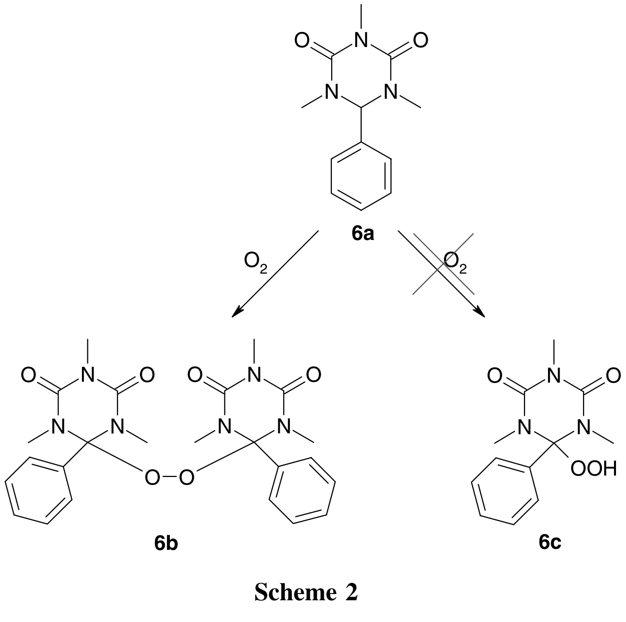
oxidation of **2a**. The isolated 1,3,5-trimethyl-2,4-dioxo-6-hydroperoxohexahydro-1,3,5-triazine (**2c**) crystallized from chlorobenzene as monocline crystals and proved itself exceptionally stable. The X-ray structure analysis (Fig. 1, Table 2) of this compound confirms its structure. As in other 2,4-dioxohexahydro-1,3,5-triazines [3–5], the triazine ring shows a weak boat configuration in **2c**. The molecules are connected in pairs by two almost linear hydrogen bonds, C–O–O–H· · ·O=C. In the crystal structure these pairs are stacked as hexagonal packages.

Compounds **3a** and **4a** were oxidized with oxygen under similar conditions. The alkylated cyanuric acids 3b and 4b were also verified in addition to the respective hydroperoxides **3c** and **4c**. Moreover, a considerable attack on the alkyl group followed, leading to N-dealkylation as well as to numerous less significant oxidation products. Of particular interest was that conversions of only about 30% were reached, followed by no further oxygen consumption. The oxidation of **5a** under analogous conditions leads to a large number of oxidation products. In addition to benzaldehyde and benzoic acid, tribenzylcyanuric acid (**5b**) was verified, which can be explained as a result of N-dealkylation and further oxidation. The corresponding hydroperoxide could not to be identified.

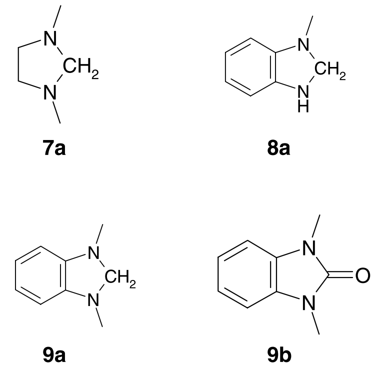
Due to the ready oxidation of **2a** it could be expected that a hexahydrotriazine substituted in position 6 could also be easily oxidized with oxygen. All the more surprising was the observation that there was no oxygen consumption at 100°C in the case of 6-phenyl-1,3,5-trimethyl-2,4-dioxohexahydro-1,3,5-triazine (**6a**). Only after addition of azobisisobutyronitrile as a radical starter, very rapid oxygen consumption followed, which however broke off at a conversion of about 35%. At first we assumed that this breaking off was due to the possible rearrangement and splitting of **6c** into phenol and trimethylcyanuric acid (**2b**). However, neither phenol as possible inhibitor of oxidation nor **2b** could be found in the reaction mixture.

During the oxidation in chlorobenzene as the solvent a white precipitate was observed. The analysis of this reaction product showed a negative hydroperoxide test with lead tetraacetate and a positive peroxide test with potassium iodide solution. In the ^{1}H NMR spectrum of the reaction product the proton in position 6 of the educt **6a** is not present and the proton of the HOO- group clearly visible in the compound **2c**, is also not present. From the ^{13}C NMR spectrum no characteristic structures to discriminate between the compounds **6a** and **6c** can be recognized. By means of ESI-MS (Na- and/or K-ionization) a molecular weight of 496 Da could be determined corresponding to that of the peroxide **6b**, and finally the data of an elementary analysis confirmed the presence of **6b**. The findings in short: The compound in question is not hydroperoxide **6a** but peroxide **6c**.

Within the framework of these experiments, the oxidation of a CH_2-group having the structure >N–CH_2–N< was of interest. Therefore oxidation of 1,3-dimethylimidazolidine (**7a**), 1-methyl-2,3-dihydro-benzimidazole (**8a**), and 1,3-dimethyl-2,3-dihydrobenzimidazole (**9a**) with oxygen was attempted as well as the identification of the reaction products. Within the temperature range from



Scheme 2



7a **8a** **9a** **9b**

Scheme 3

25 to 100°C using chlorobenzene as the solvent no oxygen consumption by **7a** and **8a** was observed; in contrast however, **9a** was very easily oxidized with oxygen to yield 1,3-dimethyl-2-oxo-2,3-dihydrobenzimidazole (**9b**). Even at 25°C oxygen consumption up to a conversion of 90% occurred spontaneously without an induction period. The corresponding hydroperoxide or peroxide could not be identified.

The water resulting from the oxidation does not lead to the hydrolysis of this compound in the case of **9b** because it is very stable with respect to water. Compound **7a** differs because slight amounts of water lead to hydrolysis resulting in methylamine, which inhibits autoxidation. Compound **8a** is also hydrolysis stable, but the remaining NH-group acts as an inhibitor. This observation is in concordance with investigations done by *Drago* and *Riley* [8], who have obtained 1-methyl-5-peroxi-2-pyrrolidone from the oxidation of 1-methyl-2-pyrrolidone with oxygen. However, they did not observe oxygen consumption during oxidation of 2-pyrrolidone.

Experimental

Preparation of 2,4-dioxohexahydro-1,3,5-triazine (**1a**) is described in Ref. [1] and the alkylation of **1a** in Ref. [2]. 6-Phenyl-2,4-dioxohexahydro-1,3,5-triazine was produced by condensation of benzaldehyde with urea at 100°C and subsequent elimination of ammonia at 180°C. The alkylation to the 6-phenyl-1,3,5-trimethyl-2,4-dioxohexahydro-1,3,5-triazine (**6a**) takes place as described in Ref. [2]. The synthesis of *N*,*N*′-dimethylimidazolidine (**7a**) is described in Ref. [6] and the synthesis of *N*,*N*′-dimethylbenzimidazoline (**9a**) in Ref. [7], *N*-methylbenzimidazoline (**8a**) is a resulting by-product. The measurements of the ^{1}H and ^{13}C NMR were taken with a Bruker AC-200 NMR spectrometer and the IR spectra using a Paragon 1000 FT/IR spectrometer (Perkin Elmer). The mass spectra were measured using the ThermoFinnigan LCQ Deca XP plus ion trap MS.

X-Ray Structure Determination

The intensity data collection was performed at 294(1) K on a single crystal with the dimensions $0.3 \times 0.3 \times 0.125\,\mathrm{mm}^3$ using graphite monochromated MoKα-radiation ($\lambda = 0.71073$ Å). The crystal structure was solved in $P2_1/c$ by direct methods (SIR92) and refined to a conventional R of 0.042 ($Rw = 0.042$, GoF = 0.57) for 1428 reflections (cutoff $3\sigma(I)$ and 126 refined variables. Further details on the structure determination and refinement have been deposited with the Cambridge Crystallographic Data Centre under CCDC 283669. The physical and spectroscopic data of compounds **2**, **3**, **4**, and **5** are published in Ref. [2].

General Procedure

A solution of 0.78 g **2a** (5 mmol) in 5 cm^3 chlorbenzene was prepared and stirred at 70°C in a microreactor. In all experiments quantitative O_2 consumption was observed by using a gas burette. The solution was directly analyzed by HPLC.

Trimethylcyanuric Acid (**2b**)

Mp 173–174°C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 3.35$ (pp, 1,3,5-N-*CH₃*) ppm.

1,3,5-Trimethyl-2,4-dioxo-6-hydroperoxo-hexahydro-1,3,5-triazine (**2c**, $C_6H_{11}N_3O_4$)

Mp 130°C (dec); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 11.6$ (s, CH–OO*H*) 5.94 (s, C*H*–OOH), 3.01 (s, 3-N–C*H₃*), 2.87 (s, 2-N–C*H₃*) ppm.

6-Phenyl-1,3,5-trimethyl-2,4-dioxohexahydro-1,3,5-triazine (**6**, $C_{12}H_{15}N_3O_2$)

Mp 120°C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.21$–7.45 (m, *phenyl*), 5.14 (s, 6-C–*H*), 3.27 (s, 3-N–C*H₃*), 2.87 (s, 1,5-N–*CH₃*) ppm.

Bis-[6-phenyl-1,3,5-trimethyl-2,4-dioxohexahydro-1,3,5-triazin]peroxide (**6c**, $C_{24}H_{28}N_6O_6$)

^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.25$–7.45 (m, *phenyl*), 3.42 (s, 3-N–C*H₃*), 2.69 (s, 1,5-N–C*H₃*) ppm; MS (ESI, positive mode): Na-adduct: $m/z = 519$ (MNa^+), 1015 ($2MNa^+$); K-adduct: 535 (MK^+), 1031 ($2MK^+$); elemental analysis: calcd C 58.05, H 5.68, N 16.92, O 19.35; found C 57.9, H 5.8, N 16.8%.

References

[1] Beckhaus W, Kießling W, Schmidt H, Voigt D (1988) Chem Techn **40**: 423
[2] Jernei M, Schmidt H, Stähr M (1996) Chem Techn **48**: 257
[3] Klepp KO, Schmidt H (2002) Z Kristallogr NCS **217**: 567
[4] Klepp KO, Schmidt H (2003) Z Kristallogr NCS **218**: 1
[5] Klepp KO, Schmidt H (2003) Z Kristallogr NCS **218**: 539
[6] Clark-Lewis JW, Edgar JA, Shannon JS, Thompson MJ (1964) Australian J Chem **17**: 877
[7] Eltsov AV (1967) Zh Org Khim **3**: 119
[8] Drago RS, Riley R (1990) J Am Chem Soc **112**: 215