

C-NITROSO COMPOUNDS. PART V.

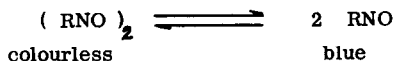
THE PREPARATION OF CIS-AZODIOXY COMPOUNDS (CIS-DIMERIC NITROSO COMPOUNDS). (1)

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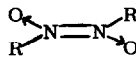
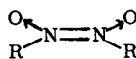
INTRODUCTION.

Nitroso compounds are known to exist in monomeric and dimeric forms, which are in equilibrium in solution:



Solutions of tertiary nitroso-dimers are blue, owing to considerable dissociation. Solutions of primary and secondary nitroso alkanes contain only traces of the monomer at room temperature and are therefore colourless.

Gowenlock et al. (2) have demonstrated the existence of cis-trans isomerism for primary and secondary dimeric nitroso alkanes, which can best be represented by the following structures:



They were able to prepare all possible symmetric primary and secondary  $C_1 - C_4$  cis-dimers and one  $C_5$  cis-dimer (sec. pentyl) by gas-phase photolysis and pyrolysis of alkyl nitrites (3). Cis-dimeric nitrosomethane has also been prepared by decomposition of acetyl peroxide in the presence of an alkyl nitrite (4), and by oxidation of N-methylhydroxylamine with periodate (5). Substituted cis-dimeric nitroso compounds are known with a  $\beta$ -chloro substituent only. These can be isolated from the reaction of nitrosyl chloride with an olefin (6).

This paper describes a photochemical preparation of some cis-dimeric nitroso compounds in good yields from solutions of the trans-dimers in 2-methyl-tetrahydrofuran.

NOMENCLATURE.

Gowenlock and Lütke (7) have stressed the analogy in chemical and physical properties between azo-, azoxy- and dimeric nitroso compounds. To emphasize the similarity also in the nomenclature we suggest the prefix azodioxy- for the latter class of compounds and reserve the prefix nitroso- for monomeric (true) nitroso compounds.

METHOD.

The trans-dimer is dissolved in enough 2-methyl-tetrahydrofuran ( MTHF ) to give a clear glass upon cooling at liquid nitrogen temperature. By irradiation of this glass with a high-pressure mercury lamp in a glass vessel, filled with liquid nitrogen, ( blue ) monomer is generated. When the dimer is completely photodissociated, the temperature of the solution is raised to  $-78^{\circ}$  C in a  $\text{CO}_2$  / acetone mixture, at which temperature the monomer slowly disappears and the cis-dimer precipitates as a white solid, which is dried and stored at  $-25^{\circ}$  C. Its structure follows from the IR- and UV-spectrum and conversion into the trans-dimer upon heating.

RESULTS.

The compounds, which have been prepared by this method are collected in table I. They are unknown in the literature, except cis-azodioxymethane.

TABLE I

<u>Compound</u>	(100 mg <u>trans</u> -dimer in) ml MTHF	<u>Yield (%)</u>	$\lambda_{\text{max}}^{\text{H}_2\text{O}}$ (nm)	$\log \epsilon_{\text{max}}^{\text{H}_2\text{O}}$
<u>cis</u> -azodioxymethane	50	66	265	4.02
<u>cis</u> -azodioxycyclopentane	1	53	270.5	4.06
<u>cis</u> -azodioxycyclohexane	5	87	270.5	4.05
<u>cis</u> - $\alpha$ -azodioxytoluene	10	54	267	n. d. ")
<u>cis</u> - $\alpha$ -azodioxyethylbenzene	3	25	n. d.	n. d.
<u>cis</u> -azodioxy-2,2'-dinitrocyclohexane	15	64	n. d.	n. d.

n. d. ") = not determined, owing to very low solubility.

Negative results were obtained with trans- $\alpha$ -azodioxydiphenylmethane, although blue monomer was generated at the low temperature, and with tertiary nitroso compounds like 2-methyl-2-nitrosopropane.

As a criterion of purity the melting point of the cis-dimer is unreliable because of isomerisation to the trans-dimer upon heating. A more suitable criterion is the molar extinction coefficient at the wavelength of maximal absorption, for which Gowenlock (3) found  $\log \epsilon_{\text{max}} \approx 4.00$ . The absence of the strong IR-absorption band of the trans-dimer at about  $1200 \text{ cm}^{-1}$  is also an indication of high purity. IR-spectra of the cis-compounds in KBr-pellets were furthermore compared with similar data, given by Gowenlock (8) and Ogloblin (6) ( see table II ). By prolonged heating of the KBr-pellets at  $50^{\circ}$  C the spectra of the trans-azodioxy compounds were obtained, except in the case of cis-azodioxymethane.

TABLE II

IR-spectra of some cis-azodioxy compounds (  $\text{RNO} \}_2$  in KBr.

<u>R =</u>	<u>Cis-absorption bands in <math>\text{cm}^{-1}</math></u>						
Methyl	1403	1392	----	1338	----	1058	1022
Cyclopentyl	1437	1404	1365	1320	1293	1050	1023
Cyclohexyl	1444	1404	1360	1326	1290	1047	1024
2-Nitro-cyclohexyl	1422	----	1356	1326	1296	1057	1042
Phenylmethyl	1431	1393	1347	1317	----	1055	1030
1-Phenylmethyl	1428	1413	1348	----	----	1056	1022

DISCUSSION.

The experimental conditions for this new method were determined with nitrosocyclohexane. Glass transmits only light with a wavelength beyond about 310 nm; by using an appropriate filter combination we have proved that the spectral region 320-360 nm ( in which the trans-dimer shows a considerable absorption ) is effective in producing the photodissociation. Prolonged irradiation at  $-196^{\circ}$  C does not affect the yield of the cis-compound, indicating that the monomer is photochemically stable at this temperature.

When after this irradiation the mixture is allowed to come to room temperature, a very small e.s.r. -signal of dicyclohexylnitroxide ( $R_2NO\cdot$ ) is observed (9).

Red light has no influence upon both trans-dimer and monomer at  $-196^{\circ}$  C. The results above and the persistence of the blue colour at  $-196^{\circ}$  C in the dark indicate that the dimer is and remains completely photodissociated at this temperature.

Part of the cis-dimer formed by dimerization at  $-78^{\circ}$  C remains as such in solution at this temperature and can be recovered as the trans-compound after evaporation of the solvent at room temperature. So the yield of the cis-dimer depends on the amount of solvent as demonstrated by the following results:

TABLE III

Influence of the amount of solvent upon the yield of cis-dimer.  
100 mg trans-azodioxycyclohexane in MTHF.

ml MTHF	Yield of <u>cis</u> -dimer (%)
5	87
5	87
15	76
15	71
50	46

MECHANISM.

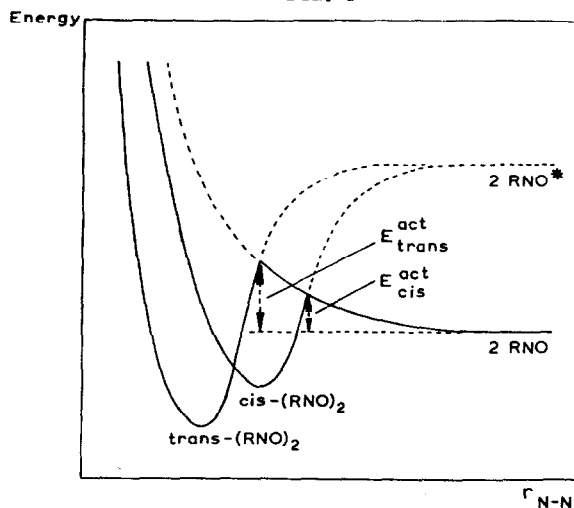
Gowenlock and Luttkie (7) suggested that the cis-dimer is formed after preorientation of the monomer on the wall of the reaction vessel.



However, when we prepared cis-compounds photochemically in a polythene reaction vessel where preorientation is very unlikely, the same yield was obtained as in a glass vessel. A careful UV-spectroscopic investigation of the formation of cis-azodioxycyclohexane revealed that this compound is stable in MTHF at  $-78^{\circ}$  C, as indicated by the constant wavelength of maximum absorption:  $\lambda_{cis}^{max} = 277.5$  nm;  $\lambda_{trans}^{max} = 292$  nm. The filtrate of the reaction product had an intermediate  $\lambda_{max}$ , thus demonstrating the presence of both cis- and trans-dimer. These results can be explained by assuming that the formation of the cis-dimer is kinetically favoured over that of the trans-dimer, although the latter is thermo-

dynamically more stable. This can be rationalized in an energy-diagram, similar to that used by Gowenlock (10) and Lüttke (11) for monomer/trans-dimer equilibria. The relative positions of the curves for cis- and trans-dimers ( figure I ) illustrate that the cis-dimer is thermodynamically less stable and that the N - N -distance is longer in the cis- than in the trans-form, as determined for azodioxymethane ( 1.31 and 1.22 Å resp. ) (12).

FIG. I



$E_{cis}^{act}$  and  $E_{trans}^{act}$  represent the energies of activation for resp. cis- and trans-formation from the ( ground state ) monomer, while  $RNO^*$  stands for the excited fragments arising from a dimer-molecule through N - N cleavage (11). From this figure it follows that  $E_{cis}^{act} < E_{trans}^{act}$ ; this means that apart from entropy factors the formation of the cis-dimer is kinetically favoured.

#### EXPERIMENTAL PART.

MTHF ( Fluka ) was purified by distillation over sodium. A freshly distilled sample was always used.

Trans-azodioxycyclohexane, -cyclopentane and trans-2-azodioxy-2-methyl-propane were prepared according to the method of Emmons (13,14). Trans-azodioxy-2,2'-dinitrocyclohexane was synthesized from cyclohexene and dinitrogen trioxide (15). Trans- $\alpha$ -azodioxytoluene, -ethylbenzene and -diphenylmethane were prepared by photochemical nitrosation of the corresponding hydrocarbons (16); by carrying out this nitrosation at  $-80^{\circ}C$  the cis-dimers of nitrosocyclohexane, -cyclopentane, - $\alpha$ -nitrosotoluene and - $\alpha$ -nitrosoethylbenzene were obtained. Cis-azodioxycyclohexane can also be prepared by irradiation of the trans-compound with UV-light in a solution of benzene and a saturated hydrocarbon ( 1 : 1 mixture ) at or below room temperature. Trans-azodioxymethane was formed by gas-phase photolysis of tertiary butylnitrite (17).

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