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α-(4)-Nitrocyclohexyl)-ω-nitropoly(azo-1,4-cyclohexylene *N,N'*-dioxide), an Oligomeric Nitrosoalkane, Exemplifying a Novel Potential Catenation System

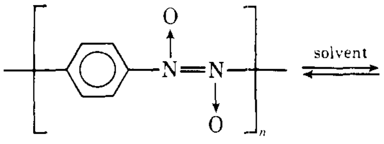
William L. Childress[1] and L. Guy Donaruma*

Department of Chemistry, Institute of Colloid and Surface Science, Clarkson College of Technology, Potsdam, New York 13676. *Received April 18, 1973*

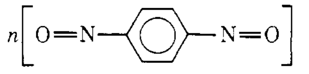
ABSTRACT: Investigations describing the preparation of an oligomeric nitrosoalkane derived from 1,4-dinitrosocyclohexane are reported. The characterization of the oligomer is described. Also, the degradation of this low molecular weight polymer is discussed.

New methods of catenation are of great general interest to polymer chemists, and we wish to report that we have recently completed some initial investigations concerning the use of the nitrosoalkane dimer function to achieve catenation.[1]

It has long been surmised that *p*-dinitrosobenzene and related compounds are polymeric, or at least, oligomeric.[2] However, even though *p*-dinitrosobenzenes may be polymeric (I) in the solid state, in solution they dissociate to form the usual blue or green monomeric species (II) typical of nitrosoalkane or nitrosoaromatic compounds.[3] Molecular weight measurements made on solutions of *p*-dinitrosobenzene indicate that only monomeric species exist in solution. At present, to our knowledge, no one has reported the preparation of oligomeric or polymeric nitrosoalkanes.

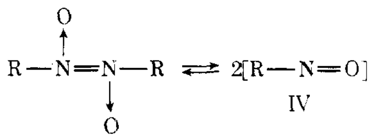


I



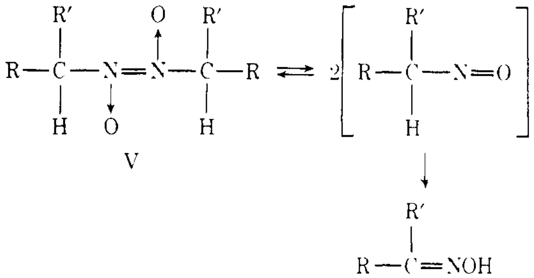
II

When we began these investigations our goal was to prepare a bifunctional nitrosoalkane and to ascertain *via* suitable characterization studies whether or not it was polymeric. To this end, we made use of the available literature to define the stability of the simple nitrosodimer function (III). In the normal solid crystalline state, nitrosodimers (III) tend to be colorless or almost colorless. Upon melting or dissolution in a suitable solvent, blue to green monomeric species (IV) are formed.[3] If the carbon atom bonded to the nitroso group also bears additional substituents which are electronegative, dissociation to IV is more facile[4] and in some cases, only the monomer exists.[5] Steric crowding on or about the nitroso bearing carbon atom also decreases the stability of the dimer.[6] The ability of primary and secondary nitrosoalkanes (V) to isomerize irreversibly to oximes (VI) also is a factor in the stability of both the monomer and the dimer.[7] The isomerization occurs when such nitroso compounds are melted[7] or heated in suitable neutral solvents[7] with varying degrees of facility depending on the structural characteristics of the molecule involved. Also, the isomerization is catalyzed by acids and bases.[7] In addition, polar solvents seem to facilitate the isomerization,[7] and primary nitroso compounds isomerize more readily than secondary nitroso compounds.[7]



$$\mathrm{R{-}\overset{\overset{O}{\uparrow}}{N}{=}\underset{\underset{O}{\downarrow}}{N}{-}R \rightleftharpoons 2[R{-}N{=}O]}$$

III IV



$$\mathrm{R{-}\underset{\underset{H}{|}}{\overset{\overset{R'}{|}}{C}}{-}\overset{\overset{O}{\uparrow}}{N}{=}\underset{\underset{O}{\downarrow}}{N}{-}\underset{\underset{H}{|}}{\overset{\overset{R'}{|}}{C}}{-}R \rightleftharpoons 2\left[R{-}\underset{\underset{H}{|}}{\overset{\overset{R'}{|}}{C}}{-}N{=}O\right] \longrightarrow R{-}\overset{\overset{R'}{|}}{C}{=}NOH}$$

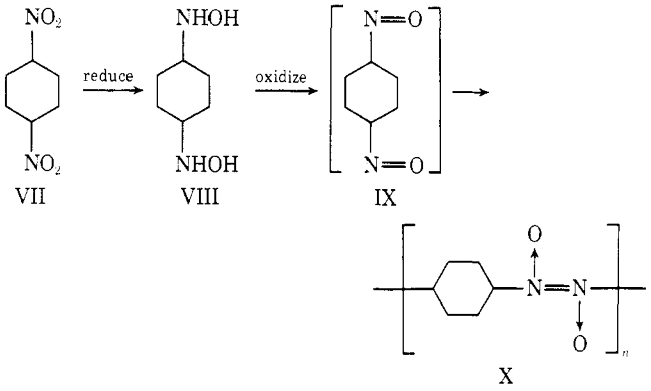
V VI

Only a very few stable bifunctional nitrosoalkanes are known,[8] and in these cases, the nitroso groups are bonded to the rest of the molecule such that dimerization may yield six-membered rings.[8]

Thus, it appeared that in order to prepare a stable polymeric dinitrosoalkane, the following criteria might be important: (1) the nitroso groups should not be directly attached to an aromatic nucleus; (2) electronegative substituents should not be present on the nitroso bearing carbon atoms; (3) the nitroso bearing carbon atoms should not be sterically crowded; (4) the nitroso functions should be secondary rather than primary or tertiary functions since primary functions isomerize more readily and tertiary functions are, relative to this discussion, sterically crowded; (5) acids, bases, and polar solvents should be avoided as much as possible; and (6) the two nitroso functions should not be located in such a fashion that a five- or a six-membered ring might form *via* dimerization.

Results and Discussion

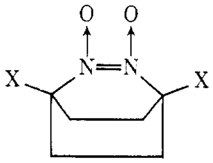
Obviously, in any chemical synthetic sequence, to meet all of the criteria noted above would be difficult, if not impossible. However, by suitable selection of starting materials, it was possible to meet several of the criteria. Therefore, 1,4-dinitrocyclohexane (VII) was chosen as the original precursor, and the following synthetic sequence was envisioned



VII VIII IX

X

It was expected that 1,4-dinitrosocyclohexane would be generated *in situ* and that the final product would be polymeric. The selection was based upon the fact that 1,4-dinitrosocyclohexane (IX) has no nitroso groups bonded to aromatic nuclei, no electronegative or inordinately bulky substituents bonded to the nitroso bearing carbon atom, the nitroso functions are secondary, and it is known that the related compound, dinitrosocyclohexane, forms a stable dimer essentially not isomerized to cyclohexanone oxime in nonpolar solvents and only slowly in polar solvents.[7] However, acids and bases do catalyze the isomerization of dinitrosocyclohexane to cyclohexanone oxime, acids being considerably less effective than bases,[7] and fusion of dinitrosocyclohexane yields cyclohexanone oxime.[7] Furthermore, related bifunctional nitrosoalkanes (XI)

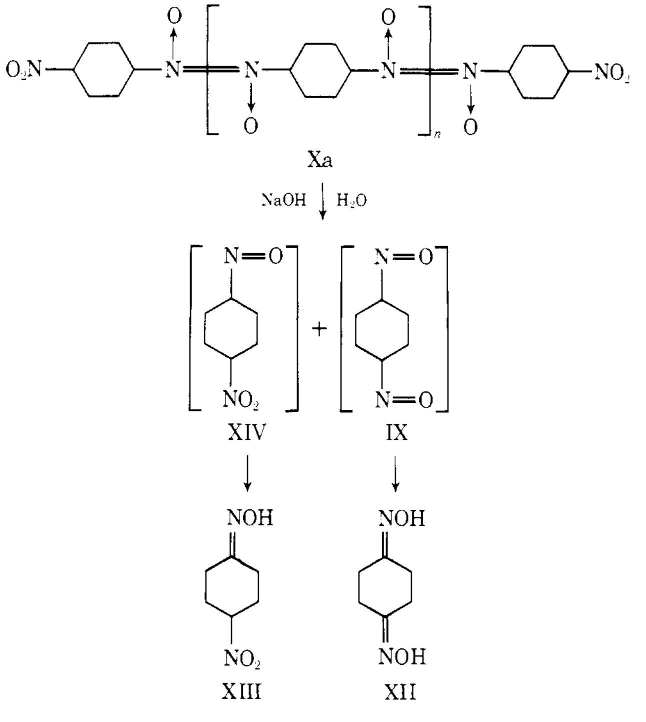


XI, X = Cl or Br

form dimeric six-membered rings.[8] Thus, our anticipated product met a number of the six presumed important criteria outlined above but not all.

Since VIII was intended to be the immediate precursor of the polymer (X) reduction of VII was attempted by low pressure hydrogenation in ethanol in the presence of palladium on charcoal. This system is known to produce the related *N*-cyclohexylhydroxylamine from nitrocyclohexane.[9] However, even though hydrogen uptake was observed, no organic products characteristic of VIII could be found. In fact, only small amounts of oily materials plus ammonia could be isolated, but the final reaction solution did give a positive test with Tollen's reagent which is characteristic of *N*-alkylhydroxylamine derivatives.[10] Assuming that VIII was present but too unstable to be isolated, we oxidized the hydrogenation solution with bromine immediately following the removal of the catalyst. Bromine oxidation of an *N*-alkylhydroxylamine derivative usually produces the corresponding nitroso dimer in fair yields,[7d] but in this case the reaction failed to yield any organic products at all. Therefore, we decided to attempt chemical rather than catalytic reduction of VII to VIII.

Reduction of nitro compounds with zinc in ammonium chloride sometimes yields the corresponding hydroxylamines.[11] When this reduction procedure was applied to VII, again, no product characteristic of VIII could be isolated, but the reaction mixture did give a positive test with Tollen's reagent. Bromine oxidation was again tried on the unworked reaction mixture. In this case, as the bromine was added to the solution, a transient blue color was noted, and a slightly off-white precipitate appeared which when washed and dried melted at 160–165° with decomposition. This product was insoluble in most common organic solvents, but it could be dissolved in and recovered unchanged from concentrated sulfuric acid, dimethyl sulfate, and a 10:1 mixture of trifluoroacetic acid and dimethylformamide. The product had an infrared spectrum which showed a strong absorption band at 1200 cm^{-1} which is indicative of the *trans*-nitroso dimer bond,[12] and when stirred overnight with aqueous sodium hydroxide a homogeneous solution formed which upon acidification gave good yields of 1,4-cyclohexanedione dioxime (XII). Thus, it seemed likely that the product was X or at least related to X. However, the infrared spectrum also showed a small but sharp absorption band at 1550 cm^{-1}, and the product gave a positive blue test.[13] Both of these observations might be interpreted as indicative of the presence of a secondary nitroalkane function. The elemental analysis of the product showed carbon, hydrogen, and nitrogen values significantly lower than those calculated for X, and it seemed likely that it was not in fact X but merely related. The best guess concerning the identity of the product was that it was Xa. If this were true, it should be possible to obtain 4-nitrocyclohexanone oxime (XIII) from the isomerization reaction noted above, and when the isomerization process was repeated, XIII was isolated. Compound XIII proved to



Xa

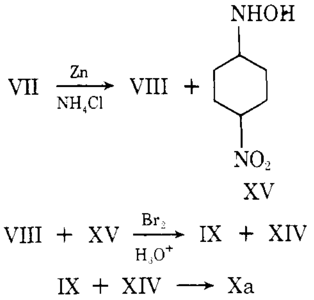
XIV IX

XIII XII

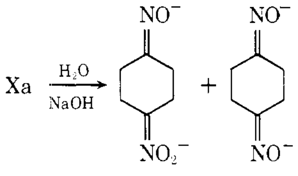
be a new compound and its nuclear magnetic resonance (nmr) spectrum, infrared spectrum, and elemental analyses were consistent with the assigned structure. In addition, XIII was synthesized independently by partial oxidation of XII, and the chemical, spectral, and physical properties of the XIII isolated from the oxidation reaction were identical in all respects with those of XIII obtained from the isomerization reaction.

Probably, Xa was formed as a result of "capping" a growing chain of X by XIV to give end groups characteristic of XIV. Compound XIV, undoubtedly, was present in the reaction mixture due to incomplete reduction of VII.

Scheme I



The degree of polymerization of Xa needed to be determined, but because of the insolubility of Xa in solvents commonly suitable for the usual molecular weight methods, the determination had to be carried out rather indirectly by a form of end-group analysis. Since it already had been established that XII and XIII were the products of the isomerization, the degree of polymerization could be obtained if a way could be found to establish the relative amounts of each oxime produced by the isomerization. It was found that the ultraviolet (uv) absorbances of the anions (XIIa and XIIIa) were additive and noninterfering at 230 nm. Both salts obeyed Beer's law. Working curves prepared and tested using known mixtures of XII and XIII were found to be accurate, and it was now possible to determine the relative amounts of XII and XIII present in the alkaline isomerization mixture and hence in Xa by solving two simultaneous equations as follows



XIIIa XIIa

$$M_aX + M_bY = C$$
$$E_aX + E_bY = A_\lambda$$

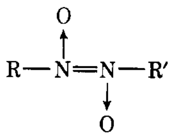
where X = molar concentration of XIIIa, Y = molar concentration of XIIa, M_a = molecular weight of XIIIa, M_b = molecular weight of XIIa, E_a = molar extinction of XIIIa at wavelength λ (ϵ 13,000), E_b = molar extinction of XIIa at wavelength λ (ϵ 6100), A_λ = absorbance of solution at wavelength λ, and C = concentration of Xa (g/l.). Once X and Y were determined, the degree of polymerization (n) was expressed by

$$n = 2Y/X$$

and n was found to be equal to 2.10 corresponding to an average molecular weight of 614.2. It also was interesting to note that using this value for n, the actual elemental analysis for Xa was within the limits of experimental error relative to the calculated analysis.

Compound Xa could be dissolved in concentrated or strong sulfuric acid solutions and recovered by neutralization of the acid solution. The infrared spectra, melting points, and molecular weights of recovered Xa were identical with those recorded prior to solution in sulfuric acid. These observations suggested that protonation was occurring. Therefore, cryoscopic measurements made in sulfuric acid might be utilized to see if such was the case and perhaps to provide an independent check on the molecular weight.

If protonation were taking place, counteranions would be formed which would depress the freezing point of such solutions below that anticipated for the number of particles associated with any given quantity of solute prior to solution. The number of particles (anionic and cationic) derived from interaction of each molecule of solute with the solvent is equal to the observed difference in freezing point between the pure solvent and the solution divided by the product of the molality of the solution and the molal freezing point depression constant (K_f). Also, the product of the observed, cryoscopic molecular weight and the particle number should be equal to the independently observed molecular weight derived from spectroscopy. When cryoscopic measurements were carried out on solutions of Xa in 85% sulfuric acid (K_f = 4.28 ± 0.11) using the traditional Beckmann apparatus, the particle number observed was 3.27 ± 0.23 and the observed molecular weight was 187 ± 13. Thus, it would seem that protonation may have occurred and that the molecular weight observed cryoscopically can be correlated with that observed independently. Therefore, the structure of Xa seems to have been established, and this being the case two other facts are worth mentioning. First, Xa is the first example of a compound possessing a mixed nitroso dimer-type linkage



$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\uparrow}}{N}{=}\underset{\underset{\displaystyle O}{\downarrow}}{N}{-}R'}$$

although an incompletely characterized mixed-nitroso dimer has been previously reported.[14] Second, this is the first unequivocal demonstration that the nitroso dimer-type linkage can be employed to obtain catenation beyond dimerization.

Experimental Section

Cyclohexane-1,4-dione was purchased from The Aldrich Chemical Co. 1,4-Cyclohexanedione dioxime (XII) (mp 201-202°) was prepared using the method of Campbell,[15] and 1,4-dinitrocyclohexane (VII) was prepared according to the procedure of Nielsen.[8] The two stereoisomers of VII (cis, mp 89-90°; trans, mp 174-176°) usually were not separated since the yield of reaction product (Xa) did not seem to be dependent on which isomer was used, and the melting points and infrared spectra of Xa prepared from both isomers were the same. Melting points were taken on a hot stage and are corrected. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer in potassium bromide wafers. Nuclear magnetic resonance spectra were run on a Varian Model A60A spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Cryoscopic measurements were made in reagent grade sulfuric acid diluted to 85% by weight using a commercially available standard Beckmann apparatus cooled by calcium chloride-ice freezing mixtures.

Preparation of the Oligomer (Xa). In a typical experiment, 1.0 g (0.0057 mol) of 1,4-dinitrocyclohexane (VII) (mixture of cis and trans isomers, mp 130-170°) and 1.0 g (0.0187 mol) of ammonium chloride were stirred in 80 ml of 50% aqueous ethanol, and the mixture was heated until all solid material had dissolved. Heating was continued and 1.0 g (0.0153 mol) of zinc dust was added very slowly. The mixture was then stirred and heated at a gentle boil for 30 min. The mixture was filtered, and the filtrate was acidified with 20% aqueous HCl. The acidic solution was stirred, externally cooled with an ice bath, and bromine water (16.1 ml of a solution containing 0.02 g of Br_2/ml) was added dropwise until the bromine color no longer disappeared. By this time, a white precipitate had formed, and the mixture was refrigerated overnight. The mixture was then filtered, the precipitate dried, put in a Soxhlet extractor, and extracted overnight with 95% ethanol. The precipitate was then put into 100 ml of dry benzene, and the mixture was stirred and heated to boiling until approximately half of the benzene had boiled off to remove any water present azeotropically. Filtration of the mixture gave 0.10 g (12.2% based on 1,4-dinitrocyclohexane) of Xa, an off-white solid, mp 160–165° (dec). Increasing or decreasing the reaction time and/or temperature and/or varying the mole ratios of reactants did not change the yields of Xa significantly.

The product (Xa) was insoluble in most common organic solvents tried (acetone, ethanol, benzene, chloroform, ethyl acetate, dimethyl sulfoxide, pyridine, etc.). Compound Xa could be dissolved in dimethyl sulfate and recovered unchanged by dilution with cold methanol. Also, it was soluble in a mixture (10:1) of trifluoroacetic acid–dimethylformamide and could be recovered unchanged by dilution with ice water. The oligomer was easily soluble in sulfuric acid ranging from concentrated to 80% from which it could be recovered by neutralization.

The product also was soluble in aqueous and alcoholic base, but isomerized to oximes in these media.

The "blue" test[13] for the presence of the nitro group was performed by dissolving a small amount of Xa in 1.0 *N* aqueous NaOH. The basic solution was then poured into 2.0 *N* HCl, and a transient blue color, indicative of the presence of the nitro group, was observed. *Anal.* Calcd for $C_{24}H_{40}N_8O_{10}$: C, 48.00; H, 6.67; N, 18.67. Found: C, 48.18; H, 6.66; N, 18.31. **Infrared data:** 3350 cm^{-1} m, 2960 m, 2890 m, 1550 s, 1485 w, 1455 m, 1410 m, 1340 m, 1305 w, 1265 m, 1205 s, 1020 w, 990 w, 920 m, 875 w, 765 w, 735 s (absorption, m = medium, s = strong, w = weak).

Basic Hydrolysis of Xa. Compound Xa (0.25 g) was stirred overnight in 20 ml of 1.0 *N* aqueous NaOH. The solution was then neutralized to pH 6–7 by the dropwise addition of 20% aqueous HCl. A precipitate formed which was removed by filtration and identified by comparative infrared and nmr spectroscopy and mixture melting point determinations as 1,4-cyclohexanedione dioxime (XII).

The filtrate was evaporated to dryness under an air stream, and the residue was extracted with ether. The ether extract was then dried ($MgSO_4$) and evaporated to dryness. The residue was recrystallized from methylene chloride–hexane to give 4-nitrocyclohexanone oxime (XIII), mp 117–119°. *Anal.* Calcd for $C_6H_{10}N_2O_3$: C, 45.57; H, 6.33; N, 17.72. Found: C, 45.77; H, 6.25; N 17.56. **Infrared data:** 3300 cm^{-1} s, 2950 s, 1675 m, 1500 s, 1440 m, 1375 s, 1340 s, 1295 m, 1270 w, 1220 w, 1205 w, 1130 w, 1100 m, 1030 w, 990 s, 945 s, 920 s, 860 m, 850 w, 770 s. **Nmr** (Me_2SO-d_6): δ 5.25 m (1 H), 3.80 pent J = 7.5 Hz (1 H), 2.55 m (4 H), 1.20 m (4 H). **Nmr** (acetone-d_6): δ 4.38 m (1 H), 2.66 pent J = 5 Hz (1H), 1.75 m (8 H). **Uv data (XIIIa):** λ_{max} 230 nm (ϵ_{230} 13,000).

Alternate Route to 4-Nitrocyclohexanone Oxime (XIII). The preparation of 1,4-dinitrocyclohexane (VII) *via* the oxidation of cyclohexane 1,4-dioxime (XII) was set up and carried out.[8] After the crude VII had been filtered off, the filtrate was neutralized to pH 6–7 with solid sodium bicarbonate and extracted three times with 50-ml portions of ether. The ether extracts were combined and dried ($MgSO_4$). The ether solution was then evaporated to dryness, and the residue was recrystallized from methylene chloride–hexane to give a yellow solid, which was identified as 4-nitrocyclohexanone oxime (XIII) by comparative ir and nmr spectroscopy and mixture melting point determinations. The yield of this by-product varied from 1 to 2%.

Determination of Molecular Weight by Ultraviolet Spectroscopy. Solutions of various concentrations of cyclohexane 1,4-dioxime (XII) and 4-nitrocyclohexanone oxime (XIII) in 0.1 *M* NaOH in 15% aqueous ethanol were made up. Ultraviolet spectra were determined for each of the solutions, and absorbance *vs.* concentration curves were established for each compound to determine the extinction coefficient for each. The absorbances of the anions (XIIa and XIIIa) were additive, noninterfering, and obeyed Beer's law. Working curves were prepared and were found to be accurate to within 2% relative error.

Compound Xa was accurately weighed and put into 0.1 *M* NaOH in 15% aqueous ethanol such that the concentration was approximately 0.20 g/l. in oligomer. The mixture was then stirred until solution was complete (several days at room temperature). However, solution could be affected within 2 hr if the mixture was heated to 70–80°. When solution was complete, the spectrum of the solution was taken, and the amount of each oxime, XII and XIII, was determined. From this, the molecular weight of the oligomer was calculated using the equations described above. For the preparation of Xa described above, n = 2.1. In otherwise identical experiments, n was found to vary slightly and values found were 1.8, 2.1, 2.2, 2.8, and 2.9.

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(1) Taken in part from the dissertation submitted by William L. Childress in partial fulfillment of the requirements for the Ph.D. degree.

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