30 min. The mass spectrum of this material showed no diminution of ^{18}O enrichment at the carbonyl position.

Bicyclo[2.2.0]hexane-1-methyl *p*-nitrobenzoate was from previous work; see ref 6.

Rearrangement of Unlabeled Bicyclo[2.2.0]hexane-1-methyl *p*-Nitrobenzoate in ^{18}O-Labeled Aqueous Acetone.—A 100-mg (0.38 mmol) portion of ester (0.076 *M*) was dissolved in 5 ml of ^{18}O-labeled 60% aqueous acetone containing 69 μl of 2,6-lutidine (45% molar excess). The water was 30% enriched in ^{18}O; therefore, the ^{18}O enrichment in the aqueous solvent was 20% after equilibration of acetone and water. This solution was sealed in a Pyrex tube and maintained at 117° for 130 hr (ten half-lives). The tube was then cooled and opened. Its contents were poured into 30 ml of water and extracted with five 10-ml portions of pentane. The combined pentane extracts were washed with two 20-ml portions of saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the pentane by distillation at atmospheric pressure through a 5-in. Vigreux column. The residue was dissolved in a small amount of carbon tetrachloride for vpc injection. 1-Norbornanol was collected from a 5 ft × 0.25 in. 10% TCEP [1,2,3-tris(β-cyanoethoxy)propane] column at 110°. The mass spectrum of this white, crystalline solid was measured and compared with that of a sample of 1-norbornanol containing only natural abundance of ^{18}O. This comparison indicated a 20% enrichment of ^{18}O in the 1-norbornanol from this rearrangement study.

Determination of ^{18}O Enrichment.—An average of ten scans per sample was run and the measurements were repeated 48 hr later. In each case unlabeled and labeled material were scanned, one immediately after the other. The precision of these measurements was ±3% out of 100% for an ^{18}O enrichment of 7.5%; for a 20% enrichment of ^{18}O, the precision was even better (see ref 7).

Registry No.—1 (^{18}O), 18542-77-3; 1 (^{16}O), 18542-78-4.

Photochemical Reaction at ~3500 Å of Nitric Oxide with Cyclohexane and Toluene

John F. W. Keana and Carroll C. Wright

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

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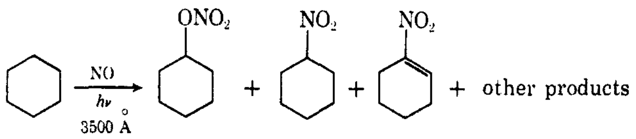
Recently, Piper and Drago[1] have found a new broad, structured absorption band centered at 3700 Å (ϵ 52 ± 1) for nitric oxide when dissolved in various organic solvents such as carbon tetrachloride and acetonitrile. This band is not observed in the gas phase and is attributed to the spin-forbidden transition $^2\pi \rightarrow {}^4\pi$ which becomes less forbidden owing to solvent–molecule interactions in the liquid phase. It occurred to us that irradiation of these solutions with suitable wavelength light might lead to new and useful photoreactions of nitric oxide.

We report here results of a qualitative investigation of the nature of the 3500-Å photoproducts of nitric oxide with cyclohexane and toluene. While nitric oxide has been reported to undergo photosensitized[2] and unphotosensitized short-wavelength photoreactions[3] with alkanes in the gas phase and high-energy radiation-induced reactions[4,5] with alkanes in the liquid phase, the only reaction reported at all similar to ours is that between nitric oxide and benzene under 3130-Å irradiation to give *o*-nitrophenol and 2,4-dinitrophenol.[6]

Results and Discussion

No products were formed upon passing nitric oxide through either solvent without irradiation. In the case of toluene a deep green solution developed over a 1-day period; however, evaporation of the solvent afforded only colorless toluene and no residue.

The product mixture obtained from the photochemical reaction between nitric oxide and liquid cyclohexane after removal of excess solvent was a yellow-green oil having at least eight components by vapor phase chromatography (vpc). The three major peaks were collected and shown to be cyclohexyl nitrate (1), nitrocyclohexane (2), and 1-nitrocyclohexene (3), obtained, respectively, in a ratio of about 6:2:1. Two of the minor peaks showed retention times and peak enhancements corresponding to cyclohexanol and cyclohexanone. A third minor peak showing a retention time corresponding to cyclohexyl nitrite was present in some runs. Adipic acid was found in trace amounts deposited on the wall of the reaction vessel.



1 2 3

It is probable that absorption of 3500-Å light leads to excited nitric oxide which abstracts a hydrogen atom from the solvent to give a cyclohexyl radical. This latter species should combine rapidly with nitric oxide to give nitrosocyclohexane. Subsequent steps leading to the observed products are probably similar to those proposed by Donaruma and Carmody[7] and others[5,8] who have obtained analogous products by reaction of nitric oxide with alkyl radicals or nitrosoalkanes. Since we observed very little cyclohexyl nitrite, it is possible that this material undergoes a further photochemical reaction[9] to give nitric oxide and cyclohexyloxy radical. The latter can combine with nitrogen dioxide present[7] to lead to additional cyclohexyl nitrate. Alternatively, the slow purge of nitric oxide through the system could remove much of the nitrogen dioxide as it is produced, and therefore prevent cyclohexyl nitrite formation. In the *closed system* employed by Donaruma and Carmody[7] cyclohexyl nitrite was presumed to come from buildup of nitrogen dioxide after several hours of reaction.[10]

When toluene was employed as the solvent instead of cyclohexane another complex mixture resulted having at least nine components by vpc. Only one of the major peaks could be conveniently collected. This

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was shown to be benzyl nitrate. Three minor peaks had retention times identical with those of α-nitrotoluene, benzaldehyde and benzyl alcohol. Unfortunately, pure benzyl nitrate partially decomposed on the vpc column to give peaks with retention times identical with those of benzaldehyde and benzyl alcohol. Thus it is unclear whether or not these latter compounds are produced in the photochemical reaction. Small amounts ($<3\%$) of phenolic material,[6] possibly nitrophenols (ir and solubility behavior), could be isolated from the original photolysis mixture by extraction with sodium hydroxide.

The photochemical reaction herein reported constitutes another method for the functionalization of alkyl residues. It must also be kept in mind if nitric oxide is employed to scavenge photochemically generated alkyl radicals in solution.

Experimental Section

Reagent grade toluene was fractionally distilled while reagent grade cyclohexane was fractionally distilled from concentrated sulfuric acid prior to use. Nitric oxide (98.5% pure) was purchased from the Matheson Co. Irradiations were conducted in a RPR-100 Rayonet photochemical apparatus employing the 3500-Å range lamps. Vapor phase chromatographic analyses were performed on a 3% Dow 710 on Chromosorb W column at the temperatures indicated below. Cyclohexyl nitrate,[11] 1-nitrocyclohexene,[12] cyclohexyl nitrite,[13] benzyl nitrate,[14] and α-nitrotoluene[15] were prepared by published procedures. Nitrocyclohexane was obtained from the Aldrich Chemical Co. Products isolated by preparative vpc were identified by comparison of their vpc retention times and nmr and ir spectra with those of authentic samples. Relative yields were estimated by cutting out the vpc trace and weighing it. Detector response was assumed to be identical for all compounds. Yields are reported as percentages of the oily reaction product remaining after evaporation of excess solvent.

General Procedure.—A cylindrical Pyrex vessel equipped with a sintered glass gas inlet tube which extended to the bottom of the vessel was charged with 150 ml of solvent. Nitrogen was bubbled through the solvent for 4 hr and then likewise nitric oxide for 15 min prior to irradiation. While a slow stream of nitric oxide was allowed to bubble through the solvent, the initially colorless solution was irradiated for 20 hr and then nitrogen was passed through the resulting yellow solution for 15 min to remove nitrogen oxides. Excess solvent was removed under reduced pressure and shown by vpc and nmr to be essentially free of photolysis products. The remaining oil was used in the experiments below.

Cyclohexane Product Analysis.—A portion of the 1.81 g of yellow-green oil was analyzed by vpc at a column temperature of 104°. Retention times of 3.2, 5.1, and 9.4 min corresponded to cyclohexyl nitrate (20%), nitrocyclohexane (6%), and 1-nitrocyclohexene (3%), respectively. *Ca.* 25% of the yellow-green oil remained nonvolatile at 150° (0.01 mm).

Toluene Product Analysis.—A portion of the 0.567 g of residual brown oil was analyzed by vpc at a column temperature of 123°. A retention time of 4.6 min corresponded to benzyl nitrate (9%).

Registry No.—Nitric oxide, 10102-43-9; cyclohexane, 110-82-7; toluene, 108-88-3.

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The Reaction of Active Methylene Compounds with Carbon Disulfide in the Presence of Ammonia. III. The Reaction of Cyclopentanone and Cycloheptanone[1a]

Tatsuo Takeshima,[1b] Masataka Yokoyama,[1b]
Tsuneo Imamoto,[1c] Makiko Akano,[1d] and Hiroe Asaba[1c]

Second Laboratory of Organic Chemistry,
Institute of Physical and Chemical Research,
Yamatomachi, Sartama-ken, Japan

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It was previously shown[2,3] that acetone and cyclohexanone, when allowed to react with carbon disulfide and ammonia, afforded thiazine derivatives. 2-Thio-1,3-thiazines were obtained from acetone, and 4-thiono-3,1-thiazine from cyclohexanone. Methyl ethyl ketone proved to give both types of compounds in this reaction.[3] Thus the structure of reactant ketone affected the course of reaction.

The present work was designed to test the behavior of cyclopentanone and cycloheptanone in the reaction concerned. Our finding is that cyclopentanone assumed the reaction pattern of cyclohexanone; however, the intermediate, 2-iminocyclopentanedithiocarboxylic acid (I), was isolated rather than the expected thiazine IIa. A number of thiazines were prepared by the coupling of I with ketone in the presence of morpholine: 4(1H)-thiono-5,6-dihydro-4H-3,1-cyclopentathiazine-2-spirocyclopentane (IIa), 2,2-dimethyl-4(1H)-thiono-5,6-dihydro-4H-3,1-cyclopentathiazine (IIb), 4(1H)-thiono-5,6-dihydro-4H-3,1-cyclopentathiazine-2-spirocyclohexane (IIc), 4(1H)-thiono-5,6-dihydro-4H-3,1-cyclopentathiazine-2-spirocycloheptane (IId), 2,2-diethyl-4(1H)-thiono-5,6-dihydro-4H-3,1-cyclopentathiazine (IIe), and 2-isopropyl-2-methyl-4(1H)-thiono-5,6-dihydro-4H-3,1-cyclopentathiazine (IIf). The reaction of I with methyl ethyl ketone was repeated several times, but it proved to be abortive. On the basis of infrared (ir), ultraviolet (uv), and nuclear magnetic resonance (nmr) spectra and the fact that it led to IIa, IIb, IIc, IId, IIe, and IIf, the structure I was assigned. In addition, when allowed to react with 2,4-dinitrophenylhydrazine, I gave cyclopentanone 2,4-dinitrophenylhydrazone accompanying dedithiocarboxylation. Comparison of ir and uv spectra of IIa, IIb, IIc, IId, IIe, and IIf with those of 4(1H)-thiono-5,6,7,8-tetrahydro-4H-3,1-benzothiazine-2-spirocyclohexane and 2-ethyl-2,5,6-trimethyl-4-(1H)-thiono-4H-3,1-thiazine in turn provided evidence for the assignments of the structures of IIa, IIb, IIc, IId, IIe, and IIf.

It may be noteworthy that I is much more sensitive to nickel ion than is dimethyl glyoxime and may be used for analytical purpose.[4]

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[1] (a) A part of this paper was read at the 21st Annual Meeting of the Chemical Society of Japan, Suita, April 1968. (b) Department of Chemistry, Faculty of Science, Chiba University. (c) Department of Chemistry, Faculty of Science, Shizuoka University. (d) The Institute of Physical and Chemical Research.

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