Photonitrosation of Cycloalkanes with Nitrosyl Chloride. I. Synthesis of Cyclohexanone Oxime*

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Introduction

It has been reported[1] that nitrosyl chloride reacts with most of the organic compounds and may cause various types of reactions such as nitrosation, chlorination, chloronitrosation, oxydation and diazotization. Of these reactions, nitrosation of hydrocarbons under the influence of light is particularly interesting. This reaction was first investigated by Lynn[2] and Hilton[3] and later by Mitchell and Carson[4]. From their work it was found that aliphatic hydrocarbons, for example, *n*-heptane or *n*-hexane, may be nitrosated by nitrosyl chloride under the influence of light and subsequently isomerized to the corresponding ketoximes. If ketoximes are obtainable from cycloalkanes in this way, this procedure will probably present a new route to prepare cycloalkanone oximes which are important intermediates of polyamide from lactam.

From this point of view, the author has investigated the nitrosation of cycloalkanes with nitrosyl chloride, and, first of all, cyclohexane was used as cycloalkane. From the results of preliminary experiments it was found that cyclohexane is unable to react with nitrosyl chloride at room temperature in the dark, but reacts immediately in the presence of sunlight, forming cyclohexanone oxime. However, this photonitrosation is generally accompanied by various side reactions corresponding to the reaction conditions. Therefore, for the purpose of obtaining cyclohexanone oxime in a good yield, it is necessary to find the optimum conditions under which the side reactions are reduced as far as possible and the rate of photonitrosation is favorably rapid.

Naylor and Anderson[5] reported a similar photonitrosation of cyclohexane, and according to their work, cyclohexanone oxime was obtained in a good yield (at least 71%) by adding nitrosyl chloride slowly and continuously into cyclohexane so that only a slight trace of color was present at any instant, maintaining the reaction liquid at low temperature (−30~0°C). According to the author's results, it seems that such low temperature (−30~0°C) and such low concentrations of nitrosyl chloride in cyclohexane, which Naylor proposed for the optimum conditions, may not always be necessary.

The present paper deals with the photonitrosation of cyclohexane with nitrosyl chloride and shows the effects of reaction conditions on the yield of cyclohexanone oxime.

Experimental

Reagents.—Crude cyclohexane obtained by the hydrogenation of pure benzene was purified by treating it with mixed acid (a ratio of sulphuric acid to nitric acid is 1.5 : 1) and washing it thoroughly with water followed by distillation. Physical constants of such purified cyclohexane are:

b. p. 80.2°C, n_D^{15} 1.4290, d_4^{15} 0.7991.

Nitrosyl chloride was prepared by adding a solution of nitrosyl sulfuric acid in conc. sulfuric acid to dried sodium chloride at 80°C. Pure

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* This work was presented in the 6th annual meeting of the Chemical Society of Japan in April, 1953, in Kyoto.

[1] L. J. Beckham, W. A. Fessler and M. Kise, *Chem. Rev.*, **48**, 320-96 (1951).

[2] E. V. Lynn, *J. Am. Chem. Soc.*, **41**, 368 (1919).

[3] E. V. Lynn and Hilton, ibid., **44**, 645 (1922).

[4] S. Mitchell and S. C. Carson, *J. Chem. Soc.*, **1936**, 1005.

[5] M. A Naylor and A. W. Anderson, *J. Org. Chem.*, **18**, 115-20 (1953).

nitrosyl sulfuric acid was prepared following the method described in a piece of literature[6]. Pure nitrosyl chloride (b. p. −5.5°C) was obtained by condensing crude nitrosyl chloride gas and then rectifing it repeatedly.

Apparatus.—A photoreactor employed for continuous reaction is shown in Fig. 1. One of the most effective and convenient light sources for this reaction was the high vapor pressure mercury lamp of [ca. 2 atm. of which the spectrum is shown in Fig. 3. Another type of photoreactor which is shown in Fig. 2 was also employed for the investigations of reaction conditions.

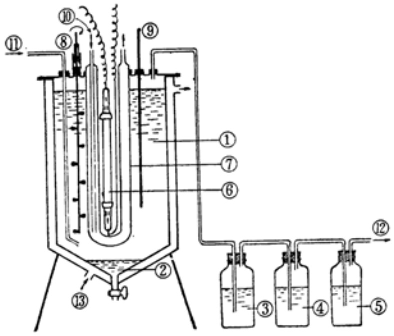

Fig. 1. Photoreactor for continuous reaction.

1. Cyclohexane	9. Thermometer
2. Oily products	10. Cooling water
3. Sulphuric acid	11. Gas inlet
4. Aqueous caustic soda	
5. Liquid paraffin	12. Gas outlet
6. Mercury lamp	13. Brine inlet
7. Cooling glass tube	
8. Stirrer	

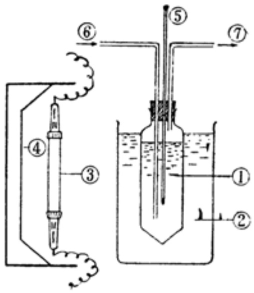

Fig. 2. Photoreactor for batch reaction.

1. Glass reactor	5. Thermometer
2. Cooling bath	6. Gas inlet
3. Mercury lamp	7. Gas out let
4. Reflector	

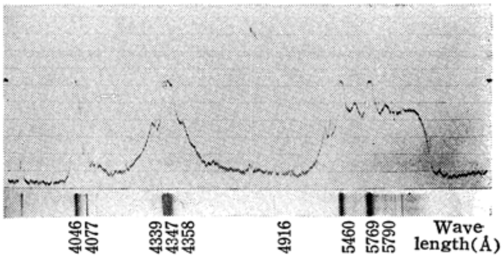

Fig. 3. Spectrum of high vapor pressure mercury lamp.

Procedure.—(1) **Batch Reaction.**—100 ml. of cyclohexane were charged into a reactor (Fig. 2) and nitrosyl chloride was blown into cyclohexane under irradiation. The color of the reaction liquid changed from colorless to cloudy yellow and oily substances began to separate from the reaction liquid. After completion of the addition of nitrosyl chloride, the reaction product was separated from unreacted cyclohexane, dissolved in cold water and then neutralized with 20% aqueous caustic soda until it had pH 6.5. Crystals of precipitated oxime were separated from the mother liquor and dried. Additional amounts of crude oximes were obtained by extracting the latter with cyclohexane. Crude oximes were purified by recrystallization with methanol.

(2) **Continuous Reaction.**—4.7 l. of cyclohexane were charged into a reaction vessel (Fig. 1) and irradiation was applied with sufficient stirring. A gaseous mixture of nitrosyl chloride

TABLE I
EFFECT OF TEMPERATURE

Temperature*	Reaction time	Nitrosyl sulfuric*** acid used	Color of reaction liquid	Pure oxime	Yield****
°C	hr.	g.		g.	%
0**	5	14.1	Yellow	5.36	63.3
5**	5	15.3	Yellow	5.38	63.5
10	5	14.6	Yellow	5.89	65.4
15	5	13.2	Yellow	5.41	63.9
20	5	14.6	Yellow	4.48	52.8
25	5	15.6	Greenish yellow	2.93	37.6
30	5	14.3	Greenish yellow	3.57	44.5

* Temperature was controlled within a range of ±1°C.
** A mixture of cyclohexane and benzene (80:20, by volume) was used.
*** Nitrosyl sulfuric acid was used as a solution in conc. sulfuric acid (1:1, by weight).
**** The yield is that based on the consumed cyclohexane.

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[6] Coleman, Lillis and Gohen, "Inorganic Syntheses", (1939), I, p. 55.

and hydrogen chloride was continuously bubbled into cyclohexane at a definite rate. After about thirty minutes, the oily products were withdrawn from the bottom of the vessel and, at the same time, cyclohexane was added through the top inlet. The gases drawn off from the reactor were led in sequence–conc. sulfuric acid, aqueous caustic soda and liquid paraffin. Nitrosyl chloride was caught by sulfuric acid to form nitrosyl sulfuric acid, hydrogen chloride by caustic soda, and cyclohexane by liquid paraffin.

(3) The Identification of Reaction Product.— 100 ml. of cyclohexane was placed in a photoreactor (Fig. 2) and irradiated with a mercury lamp. Five grams of nitrosyl chloride together with 2.8 g. of hydrogen chloride were blown into cyclohexane over a period of three hours at 10°C. After about twenty minutes, oily substances began to deposit at the bottom of the reactor, which increased gradually as reaction proceeded. 6.2 g. of this oily produdt was obtained. After treating the product following the method described above, 3.4 g. of purified crystals were obtained, m. p. 88–89°C, which did not depress the melting point of pure cyclohexanone oxime (m. p. 89°C).

TABLE II

EFFECT OF HYDROGEN CHLORIDE

Mol. ratio NOCl : HCl	Oily product obtained	Color of reaction liquid	Pure oxime obtained	Yield of oxime based on added NOCl
	g.		g.	%
1 : 0	4.0	Greenish yellow	2.17	20.9
1 : 0.9	7.1	Yellow	4.16	39.6
1 : 2.7	6.2	Yellow	3.69	35.2
1 : 4.5	8.2	Yellow	3.86	36.8
1 : 6.3	6.9	Yellow	3.79	36.1

(4) Effect of Temperature.— : Consult Table I.

(5) Effect of Hydrogen Chloride.— : Consult Table II.

Note: A 270 W. mercury lamp was used for light source. 6.2 g. of nitrosyl chloride and various amounts of hydrogen chloride were continuously blown into 150 ml. of cyclohexane at 10°C during a period of five hours.

From these results it may be said that hydrogen chloride added to nitrosyl chloride may act not only as a diluent for nitrosyl chloride but also as an accelerator for the formation of oxime hydrochloride.

(6) Flow Rate of Nitrosyl Chloride.— : Consult Table III.

It seemed that side reactions are mainly affected by the concentrations of nitrosyl chloride in the system. The addition rate of nitrosyl chloride should thus be controlled according to the concentration of nitrosyl chloride at every instance. However, it is practically difficult to measure the concentration of nitrosyl chloride quantitatively by analysing the reaction liquid, because of the very low concentration of nitrosyl chloride which favours the yields of the oxime. Since the solution of nitrosyl chloride in cyclohexane has a characteristic color–reddish brown at high concentrations, and yellow or pale yellow at low concentrations–and since the by-products formed in the system are characterized by blue or green color, the concentration of nitrosyl chloride can be inferred conveniently by this change of color.

The addition rate of nitrosyl chloride must be controlled so as to maintain the yellow or pale yellow color for the purpose of the good yield.

(7) The Influence of Water present in Reaction Mixtures.—Here, crude cyclohexane containing small amounts of water was used in order

TABLE III

EFFECT OF FLOW RATE OF NYTROSYL CHLORIDE

Flow rate of NOCl*	Oily product obtained after 5 hr.	Color of reaction liquid	Pure oxime obtained	Yield of oxime based on added NOCl	Yield of oxime based on consumed cyclohexane
g./hr.	g.		g.	%	%
0.63	4.50	Pale yellow	2.22	40.8	53.0
0.97	5.30	Yellow	2.86	34.2	54.0
1.21	7.55	Yellow	4.33	41.2	69.0
1.90	8.40	Deep yellow	4.46	30.9	70.9
3.64	13.60	Brown	6.16	19.8	49.1

* Hydrogen chloride was added to nitrosyl chloride in a mol. ratio of 1 : 1.

TABLE IV

THE INFLUENCE OF WATER PRESENT IN REACTION MIXTURES

Addition of water	NOCl added for 5 hr.	Temperature	Oily product obtained	Color of reaction liquid	Pure oxime	Yield based on added NOCl
	g.	°C	g.		g.	%
None	6.2	10	9.3	Yellow	5.04	48.5
1%	6.2	10	10.0	Yellow	5.70	53.2
None	8.0	25	6.6	Greenish yellow	2.93	21.3
1%	6.7	25	4.0	Greenish yellow	1.10	10.5

to examine the influence of water on the photonitrosation. The results obtained are listed in Table IV. These results show that the photonitrosation is scarcely influenced by the presence of water at 10°C, but much more influenced at 25°C. It may be reasonable to consider that, on account of its very hygroscopic nature, the oxime hydrochloride formed in reaction mixture absorbs even a trace of water present and forms an oily substance which is insoluble in cyclohexane and is fairly stable below 10°C. At 25°C, oxime hydrochloride present in an oily substance, seems to be gradually hydrolized to cyclohexanone oxime and hydroxylamine.

(8) Continuous Reaction.—A continuous reaction was carried out under the favorable conditions which were established for batch reaction (consult Table V).

TABLE V

CONTINUOUS REACTION

Conditions :—	
Temperature	10±1°C
Mol. ratio of NOCl : HCl	1 : 2
Flow rate of NOCl	51.6 g./hr.
Reaction time	10 hr.
Light source	1 kW. high vapor pressure mercury lamp.
Results :—	
Oily product	914 g.
Pure oxime obtained	463 g.
Consumed cyclohexane	520 g.
Unreacted NOCl	124 g.
Yield based on consumed cyclohexane	72.4%
Yield based on reacted NOCl	74.0%

The yields of oxime based on consumed cyclohexane and reacted nitrosyl chloride were 72.4% and 74.0% respectively. Moreover, these yields may be raised considerably by minimizing the loss of cyclohexane and nitrosyl chloride during operation.

Summary

The photonitrosation of cyclohexane with nitrosyl chloride was investigated. It was established that cyclohexanone oxime may be easily produced in good yield (72%) under suitable conditions. The dilution of nitrosyl chloride with hydrogen chloride was most effective for preventing the side reactions, and the photonitrosation of cyclohexane was carried out successsfully at a temperature of 10°C.

The color of the reaction liquid played the role of indicator for a successful photonitrosation; the side reactions seemed not to occur practically so long as the color of the reaction liquid is yellow, and hence, the addition rate of nitrosyl chloride into cyclohexane should be controlled following the color change of reaction liquid.

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