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SYNTHESIS OF CYCLOHEXANONE OXIME BY PHOTOREACTION OF NITROSYL CHLORIDE WITH CYCLOHEXANE

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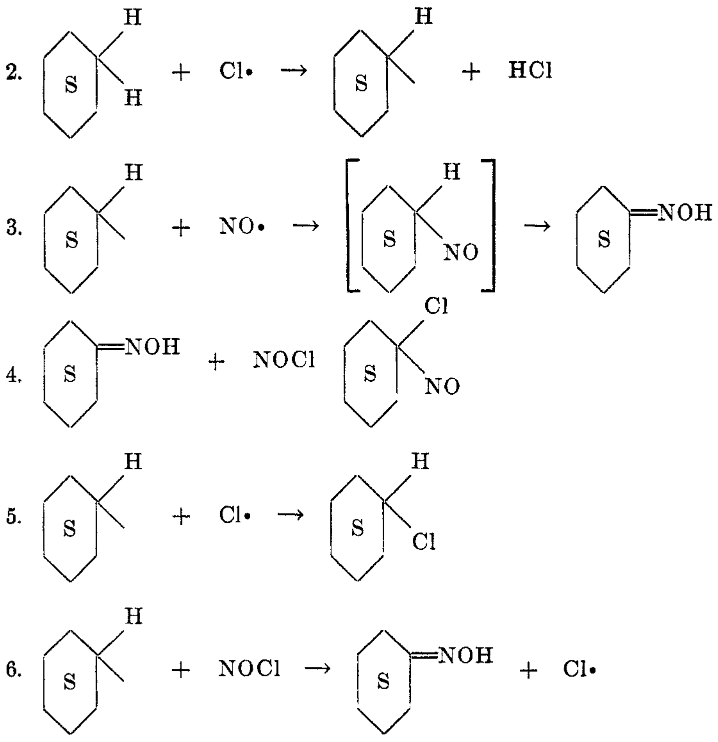
The reaction of aliphatic hydrocarbons with nitrosyl chloride under the influence of light was first described by Lynn in 1913 (1).

From this work it was shown that solutions of nitrosyl chloride in *n*-heptane on exposure to sunlight would form ketoximes and certain "blue oils." Ammonium chloride and hydroxylamine were also claimed to have been isolated. Later Mitchell and Carson suggested that the "blue oils" were actually chloronitroso derivatives of the hydrocarbons and not the nitroso tautomer of a ketoxime as Lynn originally suggested (2).

No efforts were made in this early work to determine the conditions for optimum yields of oxime or to prevent side reactions.

From results in the literature and work which we have carried out, it appears that the following reaction scheme may represent the routes by which cyclohexanone oxime and the principal by-products are formed.

1. $NOCl + h\nu \rightarrow NO\bullet + Cl\bullet$



Reactions 1, 2, and 3 seem to account for the formation of oxime (which forms a crystalline hydrochloride with the HCl produced). Reaction 4 may be responsible for the fact that high dilution of NOCl must be maintained if the formation of "blue oils" (chloronitroso derivatives) is to be avoided (3). Nitrosation of chlorocyclohexane formed in Reaction 5 might also lead to blue by-products. It will be noted that, if the reaction indicated in Equation 6 takes place, a chain reaction might result leading to quantum yields greater than 1. It was not possible to measure quantum yields however, because of side reactions which take place when measurable concentrations of NOCl are present in batch systems.

Our first orienting experiments were carried out at 20–30° by adding several grams of NOCl to 200–300 ml. of cyclohexane. Irradiation of this solution with a tungsten spot light gave a series of color changes red-brown → green → black. Analysis of these products indicated extensive by-product formation including dark blue chloronitroso compounds.

In view of these results and since NOCl is known to cause direct chlorination at elevated temperatures, it was felt that the formation of cyclohexanone oxime would be more favorable at low temperature. Consequently, experiments were carried out from -30 to 0°. In addition, the reaction of oximes with NOCl to give chlorinated derivatives (Reaction 4) suggested that the use of systems very dilute in NOCl would be advantageous (3). By maintaining low temperatures and by adding NOCl slowly and continuously so that only a slight trace of color was present at any instant, oxime hydrochloride crystallized as it was formed and could be filtered directly from the reaction mixture almost analytically pure. By-products formed in increasing quantities if conditions were such that a greenish-yellow color appeared during the course of a run. Localized high concentrations of NOCl were most undesirable.

Our yield figures based on NOCl varied considerably. This was due to mechanical losses of NOCl during work-up of the mixtures since only traces of substances other than unreacted starting materials could be found on complete fractionation of the filtrate after removal of solid oxime hydrochloride.

An attempt was made to determine the quantum yield of the reaction. The apparatus used is described in the experimental section. For this type of experiment it is desirable to add all of the NOCl in one portion at the beginning of the reaction. This procedure caused by-product formation as noted above and thus quantum yield determination did not give values representative of the oxime formation reaction. A decrease in acidity of hydrolyzed aliquots was nevertheless noted as the reaction progressed.

EXPERIMENTAL

Reagents. Cyclohexane was purified by passing it over freshly baked silica gel. This process removed aromatics and gave a very pure product, b.p. 80°, n_D^{20} 1.4260.

The *benzene* used to lower the freezing point of solutions in experiments carried out below the freezing point of cyclohexane was regular reagent grade, thiophene-free material.

The *NOCl* used was furnished by the Solvay Corporation. This product contained some N_2O_4 which was removed by fractionation through an all-glass, low temperature still at atmospheric pressure. The fraction boiling at −4° was collected and stored in sealed necked-down Carius tubes. Absorption curves at various concentrations are given in Figure 1.

Photoreactors. Several reactor designs were employed including systems with immersed lights and total reflection. The type most useful from an experimental and preparative standpoint is illustrated in Figure 2.

The reactor itself was essentially a vacuum jacketed, total reflux still head with the reaction taking place in the cold finger section. Temperature was maintained by circulating methanol at the desired temperature. The vacuum jacket prevented "sweating" and frosting on the outside, permitting efficient use of the four 150-w projector spot lights which were mounted around the reactor. Lights were turned on before NOCl was fed in and the inlet line was shielded from light. With this apparatus, certain photoreactions have been run at temperatures as low as −70°.

Another type of reactor which is adaptable for low temperature quantum yield determinations is shown in Figure 3. It was designed to operate at low temperature although it was operable at any temperature below the softening point of the "Lucite" acrylic resin enclosing the water-bath. The reactor was constructed from a 300-ml. culture flask. A rubber stopper was cut to fit the oblong neck of the flask and the stirrer, cooling coil, thermometer, and inlet and outlet tubes were run through it. The shape of the reactor, which is best described as a cylinder 5″ in diameter and 1¼″ thick, was provided with a dry air space on each side and with a circulating water-bath to remove infrared radiation from the light source. The 150-w tungsten projector spot light source was mounted 3½″ from the center of the reactor and was enclosed in a polished aluminum tube that led to the surface of the reactor. Circular gaskets separating the various faces of the reactor were made by heat-sealing "Tygon" tubing into circles of the appropriate size. Temperatures as low as −46° were maintained in this reactor by pumping methanol cooled in Dry Ice through the cooling coil. No frost appeared on the surfaces through which light passed.

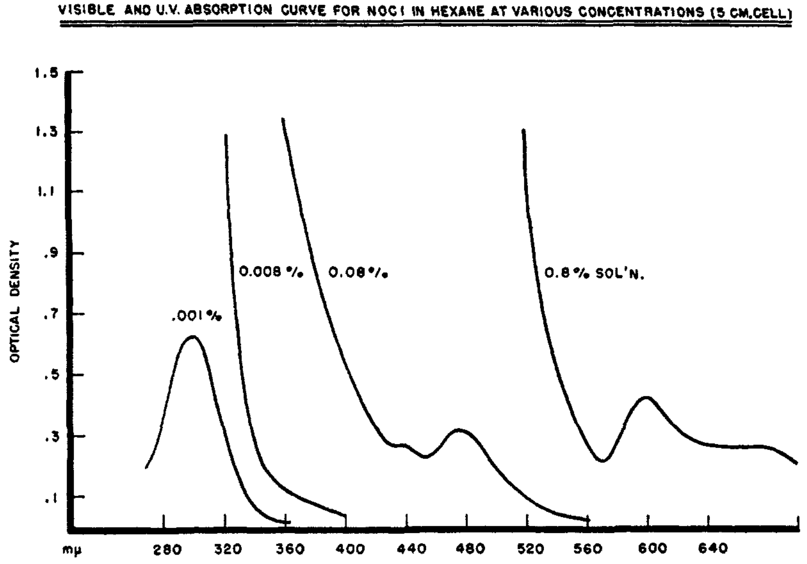


Figure 1

The vacuum-jacketed reactor was used in most of the experimental work. About 250 ml. of pure cyclohexane was used at temperatures above 10°. A 70:30 (by volume) solution of cyclohexane: benzene was employed at lower temperatures and did not begin to freeze until −30° was reached.

Continuous NOCl addition. In runs where NOCl was added slowly and continuously, the reagent was fed in from a Carius tube container immersed in an ice-salt bath. Dry nitrogen was used to sweep the NOCl into the reaction mixture and to prevent liquid from being sucked into the NOCl during the very slow addition. The rate of addition was controlled by regulating the depth of the Carius tube in the ice-bath. The more rapid flow rates of NOCl were measured with a glass rotameter equipped with a ceramic float and polytetrafluoroethylene stops. The inlet lines were protected from light with metal foil wrapping.

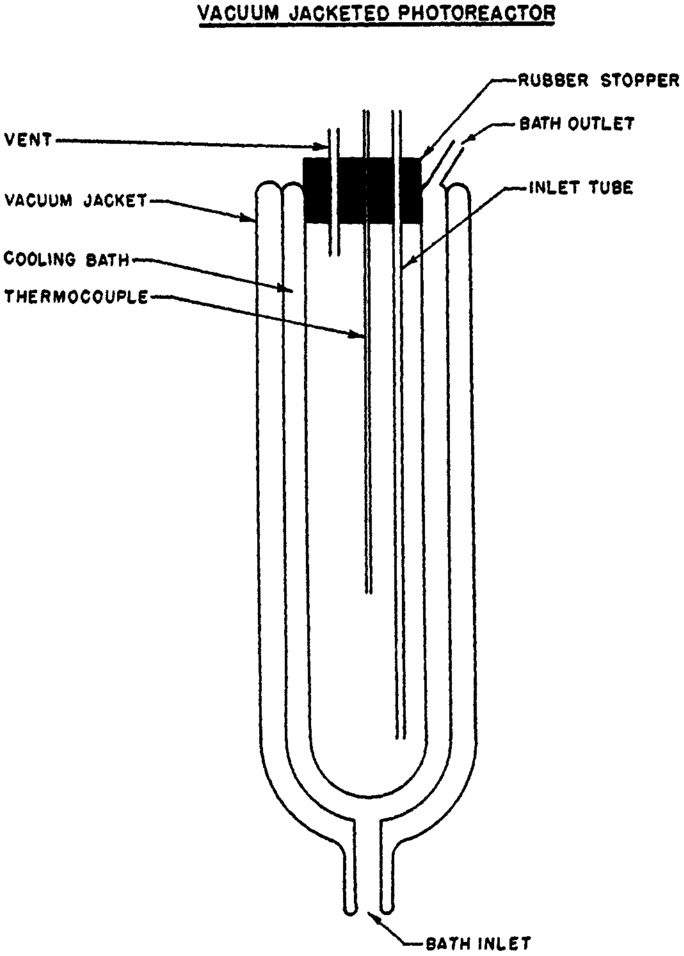

VACUUM JACKETED PHOTOREACTOR

FIGURE 2

Under favorable conditions, the solution got cloudy about 10 minutes after the reaction was started and oxime hydrochloride precipitated in 15–20 minutes with an operating temperature of −25°. When 7 g. of NOCl was passed in over a period of 5 hours, 9 g. of oxime hydrochloride was isolated after filtration, washing with ether, and drying in a vacuum desiccator. About 1.5 g. of NOCl was recovered unused from the filtrate indicating a yield of at least 71%. During complete fractionation of this filtrate, all the material came over below 81° except a black residue of less than 0.5 g. which had the odor of cyclohexanone.

The oxime hydrochloride is quite hygroscopic and melts over the range 70–88°. Titration with a *p*H meter gave an equivalent weight of 148.5, Calc'd: 149.6; N, Found: 9.38; Calc'd: 9.36.

As a further identification of the product, 8.0 g. of the oxime hydrochloride was suspended in 180 ml. of boiling dry ether, and dry ammonia was bubbled slowly through the mixture for several hours. After filtering off the NH_4Cl formed (theoretical yield), 6.0 g. of cyclohexanone oxime was isolated. After one recrystallization from 30°-petroleum ether, this material melted at 88° (lit. 88–90°); N, Found: 12.20; Calc'd: 12.38.

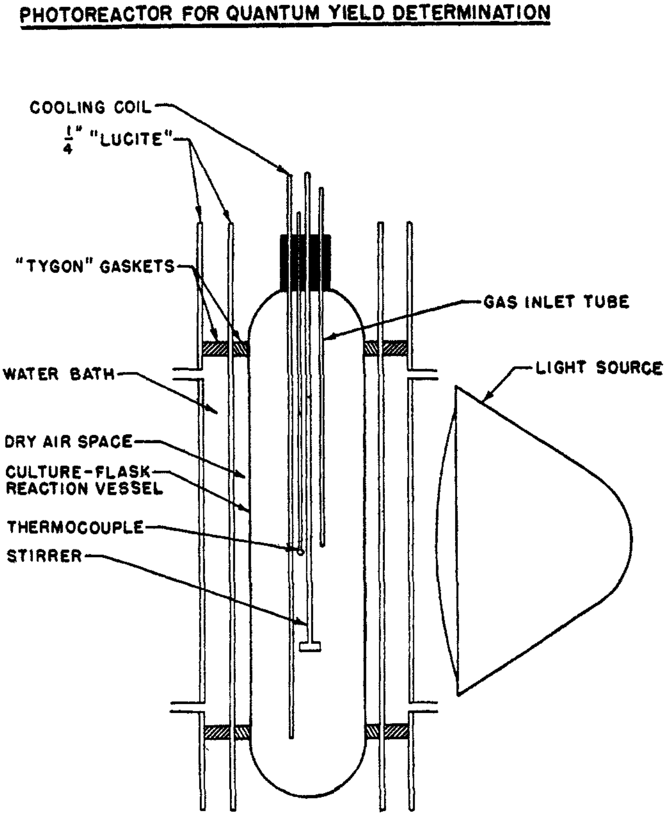


FIGURE 3

Batch reactions. Work-up of the preliminary runs carried out at 25° by irradiating a solution of 8 g. of NOCl in 200 ml. of cyclohexane gave the following results. The product was black and contained a separate semi-solid phase. The small heavy phase had the odor of cyclohexanone, and some crystals isolated melted at 148° suggesting the presence of hydroxylamine hydrochloride (lit. m.p. 151°). Fractionation of the bulk of the product gave unreacted NOCl, cyclohexane, and what appeared to be two fractions of "blue oils." As unreacted NOCl was removed from the product, the contents of the still pot gave the color changes black → green → turquoise blue. The highest boiling "blue oil" distilled at 43–44° at 5 mm.; n_D^{20} 1.4739; Cl, Found: 38.5; N, Found: 2.52. This material had a strong, distinctive odor and was undoubtedly a mixture. The nitrogen analysis, which was surprisingly low, was run by the Dumas method as were all other nitrogen values reported here. No further experiments were carried out on these by-products.

Acknowledgement. We wish to express our appreciation to Mr. W. P. Pickhardt for the nitrogen analyses reported.

SUMMARY

Conditions are described under which good yields (at least 71%) of cyclohexanone oxime may be obtained *via* the photoreaction of nitrosyl chloride with cyclohexane.

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REFERENCES

(1) LYNN, *J. Am. Chem. Soc.*, **41**, 368 (1919); LYNN AND HILTON, *J. Am. Chem. Soc.*, **44**, 645 (1922); LYNN AND ARKLEY, J. Am. Chem. Soc., **45**, 1045 (1923).

(2) MITCHELL AND CARSON, *J. Chem. Soc.*, 1005 (1936).

(3) RHEINBOLD AND DEWALD, *Ann.*, **451**, 273 (1927); *Ann.*, **455**, 300 (1927).