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THE PHOTOCHEMICAL ADDITION OF MONOCHLORAMINE TO CYCLOHEXENE[1]

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Abstract—The photochemical addition of monochloramine to cyclohexene in ether at 0° and −40° resulted in the 1:1 adduct, *trans*-2-chlorocyclohexylamine, together with *trans*-1,2-dichlorocyclohexane, *trans*-2-chlorocyclohexanol, 3-chlorocyclohexene, hexanenitrile, 3,3′-bicyclohexenyl and ammonium chloride. The effects of the reaction conditions on the best yield of *trans*-2-chlorocyclohexylamine (8·2%) was studied. The lower initial concentration of the reactants and the lower reaction temp are effective in raising the yield. A probable reaction scheme leading to the observed products is discussed.

THE photochemical additions of amines, e.g., butylamine and piperidine to olefins, e.g., 1-octene, has been reported.[2] As no information is available on the photochemical addition of monochloramine to olefins, this was undertaken as an extention of the photochemical amination of hydrocarbons.[3]

RESULTS AND DISCUSSION

The products and the effects of conditions. UV irradiation of an ethereal solution containing monochloramine and cyclohexene gave *d,l-trans*-2-chlorocyclohexylamine (I; 2·4–8·2%), *d,l-trans*-1,2-dichlorocyclohexane (II; 1·8-16%), *d,l-trans*-2-chlorocyclohexanol (III; 0·8–10%), 3-chlorocyclohexene (IV; 0·5–2·3%), hexanenitrile (V; <ca. 0·5%), 3,3′-bicyclohexenyl (VI; trace) and ammonium chloride. These products were identified by means of gas chromatography and/or IR spectrography. No *cis*-isomers were detected in the products by gas chromatography.

A series of experiments were carried out under various conditions to study the factors influencing the yields of the products. The results are shown in Table 1. The best yield (8·2%) of I was obtained by the irradiation of an ethereal solution of 0·034M monochloramine and 0·034M cyclohexene at −40° for 2 hr.

Figure 1 shows the relation between the yields of main products and the initial concentration of monochloramine with the molar ratio of monochloramine to cyclohexene 1:1 at −40°. The yields increase as the concentration of monochloramine is lowered. On the other hand, we found that a change in the molar ratio of the reagents showed no apparent effect on the yield.

Figure 2 shows typical conversion curves of monochloramine at 0° and −40°. The yields of the products increase with an increase of the irradiation time. The rate of the decomposition of monochloramine at −40° was slower than that at 0°. The yield of I increases as the reaction temperature is lowered, whereas those of other products decrease.

The above data indicates that the initial concentration of monochloramine and the reaction temperature are important factors for the formation of I.

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[1] Contribution No. 94.

[2] W. H. Urry and O. O. Juveland, *J. Amer. Chem. Soc.* **80**, 3322 (1958).

[3] Y. Ogata, Y. Izawa and H. Tomioka, *Tetrahedron* **22**, 483, 1557 (1966).

TABLE 1. THE YIELDS OF THE PRODUCTS AND THE REACTION CONDITIONS[a]

$[NH_2Cl]$ M	$[C_6H_{10}]$ M	Temp.	Yields, %[b] I	II	III	IV
0·067	0·067	0°	4·5	9·8	8·6	1·4
0·067[c]	0·067	0°	3·6	7·8	10	—
0·067	0·034	0°	4·8	9·4	7·6	0·5
0·067	0·270	0°	5·8	16	9·9	2·3
0·067	0·067	−40°	5·8	4·5	5·0	—
0·177	0·177	−40°	2·4	1·8	0·8	—
0·177	0·090	−40°	3·9	9·6	6·4	—
0·177	0·710	−40°	3·5	4·4	1·5	—
0·034	0·034	−40°	8·2	5·5	7·8	—

[a] Irradiation time is 2 hr.

[b] On the basis of monochloramine.

[c] The ethyl ether soln is not dehydrated before irradiation.

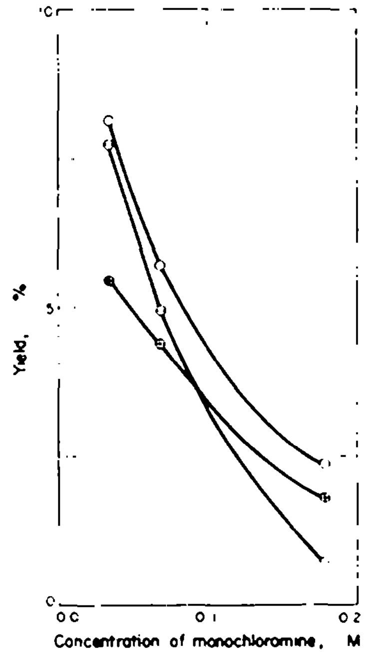
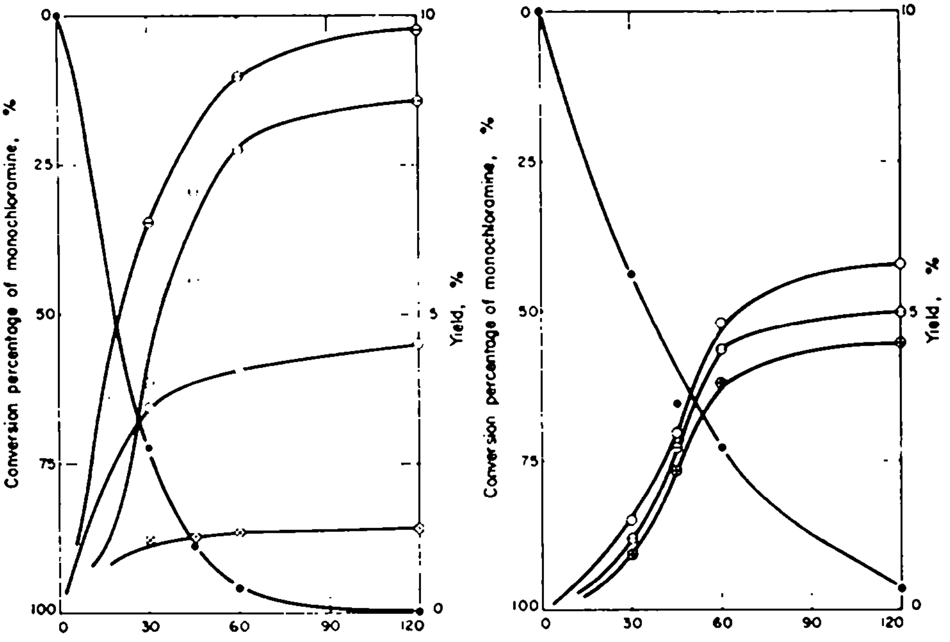


FIG. 1. The effect of the initial concentration of monochloramine on the yields of products: ○, 2-chlorocyclohexylamine; ⊖, 2-chlorocyclohexanol; ⊕, 1,2-dichlorocyclohexane.

Reaction scheme. It is well-known that monochloramine adds to some double bonds, e.g., diphenylchloroacetamide is formed from diphenylketene in an ionic scheme.[4] However, no detectable reaction occurred between monochloramine and cyclohexene in the dark for 3 hr at 0° i.e., the gas chromatographic analysis showed no peak corresponding to I. Furthermore, predominant formation of the *trans*-form in the present reaction is consistent with the well-known *trans*-addition of radicals to cyclohexene, especially at low temperature, on account of the relatively high energy

[4] G. H. Coleman, R. L. Peterson and G. H. Goheen, *J. Amer. Chem. Soc.* **58**, 1874 (1936).



(a) (b)

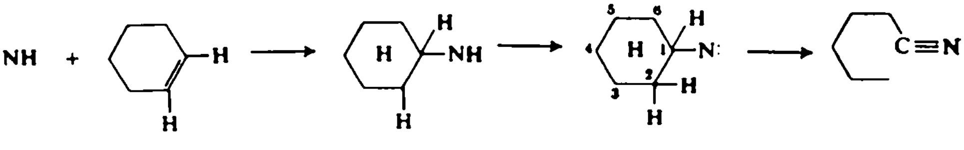
Fig. 2. Typical conversion curves of monochloramine for the reaction with cyclohexene at 0° (a) and −40° (b) with 0·067 M monochloramine and 0·067 M cyclohexene: ●, monochloramine; ○, 2-chlorocyclohexylamine; ⊖, 2-chlorocyclohexanol; ⊕, 1,2-dichlorocyclohexane; ⊗, 3-chlorocyclohexene.

barrier for the rotation about ·C—CX in the intermediate cyclohexyl radical in comparison with the other simple olefins.[5] These results together with the formation of 3-chlorocyclohexene (IV) and bicyclohexenyl (VI) strongly support the radical nature of the present reaction.

The photolysis of monochloramine has been studied in a solid state at −190°; the formation of imino radical as an intermediate has been suggested;[6]

$$NH_2Cl \overset{h\nu}{\rightleftarrows} :NH + HCl \qquad (1)$$

It has been reported that no trace of imine or amine is observed in the reaction of the imino radical with olefins.[7] Recently, it was reported that a triplet imino radical



VII (2)

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[5] E. L. Eliel, *Stereochemistry of Carbon Compounds* p. 363. McGraw-Hill, New York (1963).

[6] J. Jander and J. Fischer, *Z. anorg. allgem. Chem.* 313, 14 (1961).

[7] F. O. Rice and M. Freamo, *J. Amer. Chem. Soc.* 73, 5529 (1951); E. D. Miller, Ph.D. Dissertation, Catholic University of America, Catholic University of America Press, Washington, D.C. (1961).

can react with olefins (e.g., ethylene) to form nitriles (e.g., acetonitrile).[8] From the products of the present reaction, a small amount of hexanenitrile (V) was isolated; this product is expected according to the Cornell mechanism and implies the transient formation of imino radical. V may be formed by a direct addition of :NH to the double bond of cyclohexene followed by a transfer of a hydrogen atom and then the cleavage of bonds, C_1–C_2 and C_1–H, in the nitrene formed (VII). Although VII was also formed in the photolysis of cyclohexyl azide to give cyclohexylamine (45%) and cyclohexanone imine (21%) by the hydrogen abstraction,[9] we could not detect either compound and VII may contribute only to nitrile formation as above.

Cyclohexenimine, an expected intermediate of I, could not be detected in the present reaction. In addition, the formation of chlorides (II, III and IV) strongly indicates the presence of a chlorine atom or molecule in the reaction mixture; the energy (ca. 114 kcal/mole) given by the UV light is large enough to cleave the N–Cl bond (bond energy of N–Cl is ca. 40 kcal/mole[10]). Hence, the N–Cl bond fission of monochloramine forming $\cdot NH_2$ and $\cdot Cl$ in the photochemical primary process is plausible, which accounts for the formation of I; the similar fission was assumed in the photolysis of N-chloroalkylamine.[11]

Chlorohydrin (III) may be formed by the addition of hypochlorous acid to cyclohexene, since hypochlorous acid could be detected by UV spectrometry at the early stages of the reaction in the mixture, although its concentration decreases as the reaction proceeds. Hypochlorous acid may be formed by the following reaction of chlorine[12] and/or monochloramine[13] with water present in the ethereal solution;

$$Cl_2 + H_2O \rightarrow HOCl + HCl \tag{3}$$

$$NH_2Cl + H_2O \rightarrow HOCl + NH_3 \tag{4}$$

Compound III may also be formed by the reaction of the three-membered cyclic chloronium ion with water. In fact, the yield of III increases, when the ethereal solution of monochloramine is not dehydrated by anhydrous sodium sulphate before irradiation in spite of falling yields of other products (Table 1). It has been stated that a chlorine atom or molecule cannot be formed by the photolysis of hypochlorous acid.[14] Hence the chlorine atom or molecule detected in the reaction mixture may be produced directly from monochloramine alone.

The formation of ammonium chloride is rationalized by assuming the hydrogen abstraction of amino and/or imino radical from the hydrogen source such as cyclohexene.[7]

On the basis of these data, probable reaction pathways to account for the observed products are outlined in Scheme 1.

The scheme explains the results that the yield of I increases by lowering the temperature, while the yields of other products decrease; i.e., the lower temperature elongates the life of intermediary radicals, hence facilitates the coupling of radicals, but lowers the rates of radical chain and ionic reactions, e.g., the radical chain chlorination and the hydrolysis of chloronium ion.

[8] D. W. Cornell, R. S. Berry and W. Lwowski, *J. Amer. Chem. Soc.* **88**, 544 (1966).

[9] H. R. Barton and L. R. Morgan, Jr. *J. Chem. Soc.* 622 (1962).

[10] C. A. Walling, *Free Radicals in Solution* p. 48. Wiley, New York (1957).

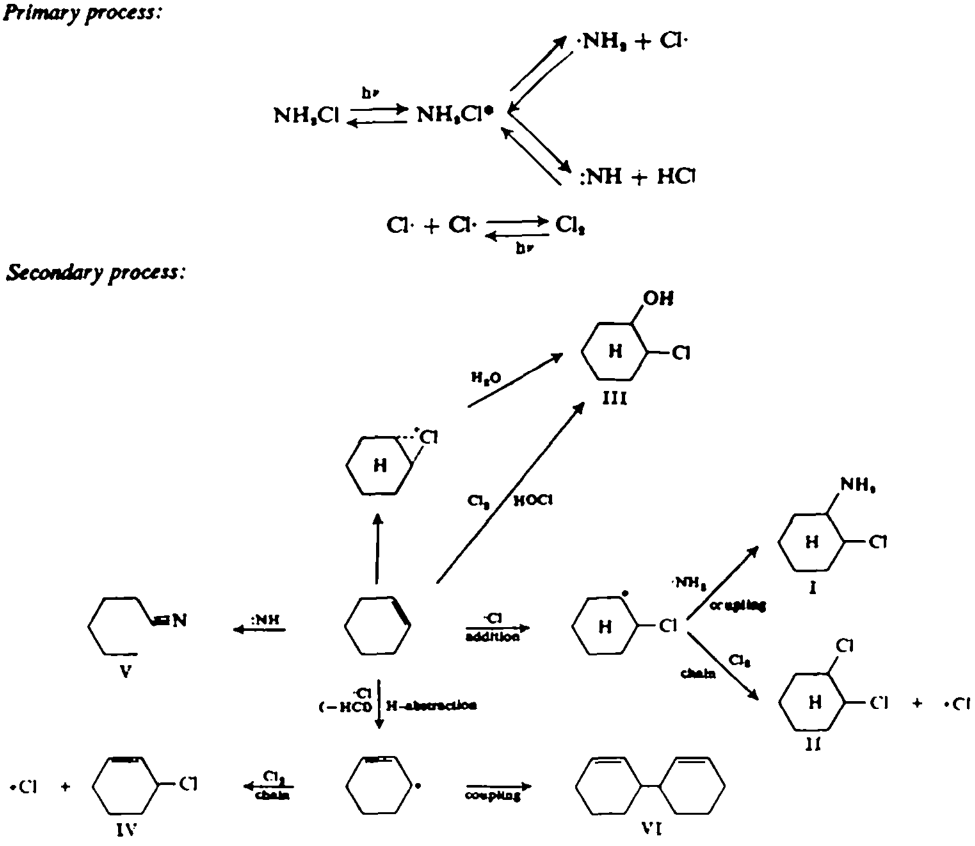
[11] W. S. Metcalf, *J. Chem. Soc.* 148 (1942).

[12] J. Sand, *Z. Physik. Chem.* **48**, 610 (1904).

[13] W. Marckwald and M. Wille, *Ber. Dtsch. Chem. Ges.* **56**, 1319 (1923).

[14] A. J. Allmand, P. W. Cunliffe and R. E. W. Maddison, *J. Chem. Soc.* 822 (1925); *Ibid.* 655 (1927).

Scheme 1



$$\cdot NH_2 \text{ (or :NH)} + \text{H source} \longrightarrow NH_3 \xrightarrow{HCl} NH_4Cl$$

EXPERIMENTAL

Materials. An ethereal solution of monochloramine was obtained by extracting[15] an aqueous soln of monochloramine prepared by the reaction of NaOCl aq with aqueous ammonia followed by drying overnight in a refrigerator with anhyd. Na_2SO_4. The concentration of monochloramine was determined by measuring its absorption at 254 mμ (ε 544). Cyclohexene was prepared by dehydration[16] of cyclohexanol by conc. H_2SO_4 and then purified by duplicate rectification, b.p. 81·5–82·0° (lit.[17] b.p. 83·6°), n_D^{20} 1·4473 (lit.[17] n_D^{20} 1·4465). Authentic III was prepared by the reaction[18] of HClO with cyclohexene at 0°, b.p. 79–81°/18 mm (lit.[19] b.p. 84–85°/16 mm), n_D^{20} 1·4830 (lit.[20] n_D^{20} 1·4910), characteristic IR spectrum (liquid film) 3550 and 3400 cm^{-1} (OH) and 739 cm^{-1} (C–Cl). Authentic I was

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[15] J. Kleinberg, M. Tecotzky and L. F. Audrieth, *Analyt. Chem.* **26**, 1388 (1954).

[16] G. H. Coleman and H. F. Johnstone, *Organic Syntheses* Coll. Vol. I, p. 183. Wiley. New York (1941).

[17] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *J. Amer. Chem. Soc.* **58**, 137 (1929).

[18] G. H. Coleman and H. F. Johnstone, *Organic Syntheses* Coll. Vol. I, p. 158. Wiley, New York (1941).

[19] M. Godchot and P. Bedos, *Bull. Soc. Chim. Fr.* **37**, 1454 (1911).

[20] M. Godchot, *C.R. Acad. Sci. Paris* **176**, 448 (1923).

prepared[21] as follows: *d,l-trans*-2-aminocyclohexanol, obtained by the reaction[22] of III with excess conc. NH_4OH, was converted by conc. H_2SO_4 to its sulphate, which was treated with NaOH aq to form imine and then with dry HCl to give I, m.p. of its hydrochloride, 204–206° (lit.[21] m.p. 205–207°), characteristic IR spectrum (liquid film) 3375, 3290 and 1590 cm^{-1} (NH_2), 1352 cm^{-1} (C—N) and 740 cm^{-1} (C–Cl). Authentic *d,l-cis*-2-chlorocyclohexylamine was prepared[23] by treating *d,l-trans*-2-aminocyclohexanol with PCl_5, m.p. of its hydrochloride, 182–183° (dec) (lit.[23] m.p. 185–186°, dec), characteristic IR spectrum of the hydrochloride (Nujol) 3480, 2720, 2609 and 1600 cm^{-1} (NH_3^+) and 741 and 698 cm^{-1} (C–Cl). Authentic *d,l-trans*-II was prepared[24] by passing Cl gas through cyclohexene at 30–40° in the dark, b.p. 75–77°/18 mm (lit.[24] b.p. 78·1°/20 mm), n_D^{20} 1·4883 (lit.[21] n_D^{20} 1·4902), characteristic IR spectrum (liquid film) 745, 738, 698 and 620 cm^{-1} (C–Cl). Authentic *d,l-cis*-1,2-dichlorocyclohexane was prepared by the reaction[24] of III with $SOCl_2$ in the presence of pyridine under reflux, b.p. 89–91°/21 mm (lit.[24] b.p. 91·0°/20 mm), n_D^{20} 1·4478 (lit.[24] n_D^{20} 1·4467), characteristic IR spectrum (liquid film) 745, 697 and 618 cm^{-1} (C–Cl). Authentic IV was prepared[25] by adding *t*-butyl hypochlorite, prepared[26] by the reaction of *t*-butanol with Cl gas, into boiling cyclohexene in the presence of benzoyl peroxide, b.p. 67·5–68·0°/52 mm (lit.[27] b.p. 65–66°/40 mm), characteristic IR spectrum (liquid film) 3050 cm^{-1} (=C—H), 1650, 1420 and 1400 cm^{-1} (C=C) and 745, 680 and 675 cm^{-1} (C–Cl). Authentic VI was prepared[28] by the Grignard reaction of IV with EtBr and Mg, b.p. 123–124°/28 mm (lit.[28] b.p. 127°/30 mm), characteristic IR spectrum (liquid film) 3060 and 3020 cm^{-1} (=C—H) and 1424 and 1405 cm^{-1} (C=C). Authentic V was prepared[29] by the reaction of acetonitrile with *n*-BuBr in the presence of $NaNH_2$, b.p. 162–164° (lit.[29] b.p. 163·9°), n_D^{20} 1·4095 (lit.[29] n_D^{20} 1·4069), characteristic IR spectrum 2250 cm^{-1} (CN).

General procedure. All experiments were carried out in a cylindrical quartz vessel (30 × 300 mm) equipped with a rubber stopper and a thermometer. A Halos high-press 400 W Hg lamp with a water-cooling quartz jacket was used as a light source. A soln of 0·03–0·2M monochloramine and 0·03–0·8M cyclohexene in ethyl ether (70 ml) were placed in the quartz vessel. The vessel together with the lamp immersed into a dry ice–MeOH bath and the vessel was irradiated without filter at a distance of 15 cm at 0 to −40° for 2 hr. For the examination of reaction proceeding, two aliquots of the reaction mixture were taken out simultaneously at appropriate intervals of time; one was diluted with ethyl ether to determine the decomposition percentage of monochloramine by UV spectrophotometry, and the other was evaporated under reduced press to determine the yield by means of gas chromatography.

Identification and the estimation of products. The analysis of the products was done by means of gas chromatography employing a Yanagimoto Model GCG-220 operated with a column (1·5 m × 4 mm) packed with PEG #2000 (20 wt %) on Celite 545 (5% KOH) of 80–100 mesh using He as a carrier gas (12 ml/min) at 151°. The similarity of the retention times of the peaks of authentic materials with those of the sample established their identity. The yields of the products were also estimated by means of gas chromatography under the same conditions using ethyl ether as an internal standard. All products were again confirmed by means of gas chromatography using a column (3·0 m × 4 mm) packed with Silicone DC 550 (30 wt %) on Celite 545 of 80–100 mesh with He as a carrier gas (35 ml/min) at 112°. *Cis*-isomers of I and II were not detected.

IR spectrum of the reaction mixture shows absorption at 3550 and 3400 cm^{-1} (OH), 3290 and 1325 cm^{-1} (NH_2), 2250 cm^{-1} (CN) and 745, 678 and 620 cm^{-1} (C–Cl). Hence, the formation of I, II, III and V was supported.

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