ether extract was decolorized with charcoal, filtered and dried over anhydrous sodium sulfate. After evaporation of the ether at reduced pressure, a yellow solid (5.3 g.) remained; recrystallization of the solid from ethyl ether-benzene gave a white crystalline solid (4.35 g.) and a red oil (0.86 g.). The white solid was identified as **2-hydroxy-3-nitropropionic acid** (72% yield); m.p. 75–76°, lit.[10,11] 76–77°; neut. equiv. (calcd.) 135, (found) 134.6. The red oil (filtrate) was characterized as glyoxylic acid by reaction with 2,4-dinitrophenylhydrazine.

COLUMBUS, OHIO

[CONTRIBUTION NO. 320 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Photodegradation of 1-Chlorocyclohexene[1]

BY R. V. LINDSEY, JR., AND J. N. INGRAHAM

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The products obtained by the photochemical decomposition of 1-chlorocyclohexene have been shown to include hydrogen chloride, cyclohexene, *cis*-1,2-dichlorocyclohexane and 3,3′-dichloro-1,1′-bi-2-cyclohexenyl. The formation of these products may be accounted for by a free radical chain reaction which involves homolytic cleavage of the carbon–chlorine bond as the initial step.

Although considerable work has been done on the photochemical decomposition of alkyl halides, no similar studies on vinyl halides have come to our attention except for the report of Bolland and Melville[2] that 2-chlorobutadiene is dissociated to hydrogen chloride and a residue, probably vinyl acetylene, by light of wave length less than 2000 Å. Accordingly, an investigation of the photolysis of the vinyl halide, 1-chlorocyclohexene, has been undertaken.

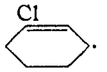
The products obtained by irradiation at 25–30° with light of wave length 2537 Å. were isolated and identified as follows. Those more volatile than 1-chlorocyclohexene comprised a liquid identified as cyclohexene by its physical constants and by oxidation to adipic acid, and a gas identified as hydrogen chloride by precipitation of silver chloride. The less volatile products gave on distillation four main fractions: (A) b.p. 41–42° (1–2 mm.), (B) b.p. 82–90° (1–2 mm.), (C) b.p. 110° (1–2 mm.), and a higher boiling residue. Fractions A and C were positively identified, and a tentative structure has been proposed for fraction B as discussed later.

Fraction A had an empirical formula approximating $C_6H_{10}Cl_2$ and its boiling point, refractive index and infrared spectrum were in excellent agreement with those reported for *cis*-1,2-dichlorocyclohexane.[3a,b]

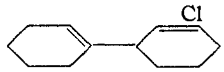
Fraction C (28.09% Cl) was shown to contain the bicyclohexenyl ring system by simultaneous dehydrogenation and dehydrohalogenation to biphenyl. Final identification was based on the congruence of the infrared spectrum of the unknown with those of samples of 3,3′-dichloro-1,1′-bi-2-cyclohexenyl prepared by two different routes. The absence of the corresponding 2,2′-dichloro isomer was demonstrated by the same method.

The observed products may be accounted for by assuming homolytic scission of the carbon–chlorine bond to give a cyclohexenyl free radical[4] and a chlorine atom. Strong support for this proposal is furnished by the formation of *cis*-1,2-dichlorocyclohexane which must be formed by attack by a chlorine atom at the double bond of 1-chlorocyclohexene. This process is entirely similar to the formation of *cis*-1,2-dibromocyclohexane during the peroxide or ultraviolet light catalyzed addition of hydrogen bromide to 1-bromocyclohexene.[5]

Stabilization of the primary radicals by the abstraction of hydrogen atoms accounts for the observed products, hydrogen chloride and cyclohexene. The isolation of 3,3′-dichloro-1,1′-bi-2-cyclohexenyl, and the absence of the isomeric 2,2′-dichloro derivative, indicate that a radical of type I is an intermediate species, and that free radical attack on 1-chlorocyclohexene occurs predominantly on the α-methylene group further removed from the chlorine atom.



I



II

Finally, it appears that fraction B (17.55% Cl), which was never obtained in pure form, may contain the monochlorobicyclohexenyl II (18.05% Cl) formed by combination of a cyclohexenyl radical with I.

Experimental

Preparation of 1-Chlorocyclohexene.—1-Chlorocyclohexene was prepared from cyclohexanone and phosphorus pentachloride, b.p. 143°, n^{25}_D 1.4788 (lit. values[6] b.p. 143°, n^{20}_D 1.4797).

Photolysis.—1-Chlorocyclohexene was distilled in a nitrogen atmosphere at a pressure of about 20 mm. into a vertical condenser from which the condensate dripped into a quartz tube surrounded by the spiral of a mercury resonance lamp (principal output at 2537 Å.). Displaced liquid was returned to the distilling flask through an overflow tube leading from the bottom of the quartz vessel. Thus, the high boiling photolysis products were concentrated in the

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[1] Presented before the Division of Organic Chemistry at the 123rd Meeting of the American Chemical Society, Los Angeles, California, March 18, 1953.

[2] J. L. Bolland and H. W. Melville, Proc. Rubber Tech. Conf. London, Paper No. 90, page 239 (1938).

[3] (a) Ben Carroll, D. G. Kubler, H. W. Davis and A. M. Whaley, THIS JOURNAL, **73**, 5382 (1951); (b) H. C. Stevens and O. Grummitt, *ibid.*, **74**, 4876 (1952).

[4] A. W. Tickner and D. J. LeRoy, *J. Chem. Phys.*, **19**, 1247 (1951), have postulated vinyl radical intermediates in the reaction of sodium vapor with vinyl iodide to account for the formation of ethylene, acetylene and butadiene.

[5] H. L. Goering, P. I. Abell and B. F. Aycock, THIS JOURNAL, **74**, 3588 (1952).

[6] M. Mousseron, F. Winternitz and R. Jacquier, *Bull. soc. chim.*, [5] **15**, 260 (1948).

distilling flask while unchanged 1-chlorocyclohexene was recycled. More volatile products which escaped through the condenser were collected in a cold trap. Runs were conducted for about five days, after which the decomposition product (average 15 g. from about 100 g. of starting material) was isolated by stripping off unchanged 1-chlorocyclohexene. The quartz tube was carefully cleaned between runs to remove traces of opaque film which reduced the light intensity appreciably. The products of several such runs were combined for characterization studies.

Isolation and Characterization of Photolysis Products.—**Hydrogen chloride** was established as a degradation product in preliminary experiments by passing a stream of dry nitrogen through an irradiated sample of 1-chlorocyclohexene, then through a cold trap and finally through a bubbler containing aqueous potassium hydroxide. The presence of chloride ion in the potassium hydroxide solution was demonstrated by precipitation of silver chloride.

Cyclohexene.—Careful distillation of the volatile products collected in the cold trap (4 g.) gave a liquid, b.p. 81–82°, n^{25}_{D} 1.4435, identified as cyclohexene by its physical constants (lit. values b.p. 83°, n^{20}_{D} 1.4464[7]), and by oxidation with potassium permanganate to an acid, m.p. 146–149°, which did not depress the melting point of an authentic sample of adipic acid.

Higher Boiling Products.—By distillation of 24 g. of accumulated decomposition products, fractions were obtained boiling at (A) 38–40° (1–2 mm.), n^{25}_{D} 1.4974, 2.5 g.; (B) 82–90° (1–2 mm.), n^{25}_{D} 1.5265, 4.5 g.; (C) 108–111° (1–2 mm.), n^{25}_{D} 1.5358, 7 g.; and (D) higher boiling residue, 5 g. Fractions A, B and C were characterized as described below.

***cis*-1,2-Dichlorocyclohexane. Fraction A.**—After ozonization in carbon tetrachloride solution to remove a small amount of unsaturated impurity, the major portion of the sample was recovered as a clear liquid, b.p. 41–42° (1–2 mm.), n^{25}_{D} 1.4938. These constants are in excellent agreement with the reported[3a,b] values, b.p. 101° (30 mm.), n^{25}_{D} 1.4945, for *cis*-1,2-dichlorocyclohexane and clearly eliminate the *trans* derivative, b.p. 85° (30 mm.), n^{25}_{D} 1.4879. The *cis* configuration and 1,2-structure were confirmed by refluxing a sample of the purified product with alcoholic potassium hydroxide to obtain 1-chlorocyclohexene, b.p. 140–142°, n^{25}_{D} 1.4770. The latter was characterized by oxidation with potassium permanganate to give an acid, m.p. 147–148°, which did not depress the melting point of an authentic sample of adipic acid.

3,3'-Dichloro-1,1'-bi-2-cyclohexenyl. Fraction C.—Redistillation gave a viscous liquid, b.p. 110° (1–2 mm.), which contained 28.09% chlorine and had a molecular weight of 235. It darkened slowly on exposure to air, decolorized bromine in carbon tetrachloride, and was readily oxidized by neutral potassium permanganate. The carbon skeleton of the product was established as follows. A sample of the unknown was heated to 180–200° for 1 hr. in the presence of palladium-on-charcoal (10% Pd). The reaction mixture was treated with ether, filtered and distilled to obtain a product, b.p. 71–72° (1 mm.), which crystallized on cooling. The solid, after recrystallization from ether, melted at 67–69° and showed no depression in a mixed melting point determination with an authentic sample of biphenyl. These results clearly showed the product to be a dichlorobicyclohexenyl. The exact structure was established by comparison of the infrared spectrum with those of samples of 3,3'-dichloro-1,1'-bi-2-cyclohexenyl (Cl, 30.7%; mol. wt., 231), prepared by two independent methods as described below.

Synthesis of 2,2'-Dichloro-1,1'-bi-2-cyclohexenyl.—This compound was prepared as described by Domnin[8] by heating 1,6-dichlorocyclohexene with zinc dust in moist dioxane. A product, b.p. 95–110° (1 mm.), which partially crystallized on cooling, was obtained. Recrystallization from alcohol gave a white crystalline solid melting at 78–79°. Domnin reported a melting point of 91–92°.

Anal. Calcd. for $C_{12}H_{16}Cl_2$: Cl, 30.65. Found: Cl, 30.47.

Synthesis of 3,3'-Dichloro-1,1'-bi-2-cyclohexenyl (Method A).—The method is essentially that employed by Farmer and Moore[9] for the preparation of 1,1'-bi-2-cyclohexenyl. 1-Chlorocyclohexene (96 g.) was heated with di-(*t*-butyl) peroxide (20 g.) at 140° for 48 hr. in a Parr bomb equipped with a glass liner. A product, b.p. 106° (0.9 mm.), n^{25}_{D} 1.5427, was isolated by distillation.

Anal. Calcd. for $C_{12}H_{16}Cl_2$: C, 62.35; H, 6.98; Cl, 30.68. Found: C, 62.92; H, 7.12; Cl, 28.50.[10]

(Method B).—A solution of 15 g. of 3-bromo-1-chlorocyclohexene, prepared by the reaction of 1-chlorocyclohexene with N-bromosuccinimide,[11] in 15 ml. of dry ether was dropped slowly into a stirred suspension of 10 g. of zinc dust in 50 ml. of ether. The mixture was heated to reflux during the addition and for two hours thereafter, filtered, washed with water, dried and distilled to obtain a product boiling at 112–114° (1–2 mm.), n^{25}_{D} 1.5410. The infrared spectrum of the product showed an exact correspondence with that of the product prepared as described above.

3-(1'-Cyclohexenyl)-1-chlorocyclohexene (?).—Fraction B, a faintly yellow liquid which contained 17.55% chlorine compared to a calculated value of 18.05% for a monochlorobicyclohexenyl, was unsaturated, and did not react with alcoholic potassium hydroxide.

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(7) E. H. Huntress and R. S. Mulliken, "Identification of Pure Organic Compounds," Order I, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 570.

(8) N. A. Domnin, *J. Gen. Chem.* (*USSR*), **15**, 461 (1945), *C. A.*, **40**, 4682 (1946).

(9) E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, 131 (1951).

(10) The samples of this compound prepared by two different synthetic routes as well as the degradation product gave consistently low chlorine analyses.

(11) M. Mousseron, F. Winternitz and J. Jacquier, *Compt. rend.*, **224**, 1062 (1947).