to R. Evans (Berkeley, Cal.) for the radium determinations and to A. H. Compton and J. Dempster for the privilege of using the facilities of the Dept. of Physics.

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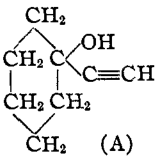
RECEIVED JULY 5, 1934

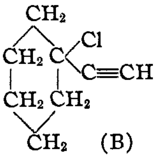
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

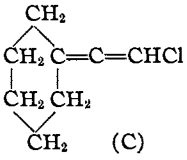
Experiments with Ethynylcyclohexanol and Related Compounds

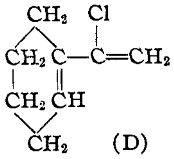
BY CHARLES D. HURD AND RALPH N. JONES[1]

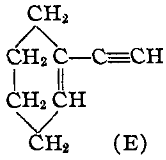
It was of interest to decide whether the product formed by the interaction of chlorinating agents on 1-ethynyl-1-cyclohexanol (A) was 1-ethynyl-1-chlorocyclohexane (B), or cyclohexylidenevinyl chloride (C), or 1-α-chlorovinyl-1-cyclohexene (D). Structure (B) was eliminated since it should have displayed acetylene reactions and possessed a reactive chlorine atom, neither of which it did. To decide between structures (C) and (D) the product was ozonized. Acids would result from either structure but (C) alone should give rise to cyclohexanone. Since cyclohexanone was not found, structure (C) was eliminated and (D) alone remained for consideration. It is true that cyclohexanone does change in part into adipic acid by ozonization[2] but in our work an excess of ozone was purposely avoided. Therefore, the non-detection of cyclohexanone must bear witness to its non-production.


(A)


(B)


(C)


(D)


(E)

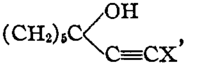
Carothers and Coffman[3] prepared compound (D) by the addition of hydrochloric acid to 1-ethynyl-1-cyclohexene (E) in the presence of cuprous and ammonium chlorides. That their "chloro-2-tetramethylene-3,4-butadiene-1,3" was identical to our compound (D) was confirmed by the following data.

	C. and C.	H. and J.
B. p., °C............	55–57 (1 mm.)	89–92 (21 mm.)
n^{20}_D..................	1.5240	1.5230
M. p. of derivative with naphthoquinone....	191–192° (copper block)	185–187° (capillary tube)

Presumably (E) was an intermediate in the transformation of (A) to (D). Some of this enyne (E) was present in the reaction products. Whether the change from (A) into (E) is direct or via (B) cannot be answered.

There were two reasons for considering the allene (C) as a possible reaction product. First, Willemart[4] has postulated, but never isolated, chloroallenes as intermediates in the synthesis of rubrene hydrocarbons from ethynylcarbinols. Secondly, Rupe[5] has reported the transformation of (A) by formic acid into cyclohexylideneacetaldehyde, $(CH_2)_5C{=}CH{-}CHO$. The enol form of this aldehyde, postulated by Rupe as an intermediate, is strictly analogous to (C).

1-Ethyl-1-chlorocyclohexane was prepared normally from 1-ethyl-1-cyclohexanol. This chloride, with a structure analogous to (B), reacted readily with alcoholic potash. 1-Phenyl-1-cyclohexanol was sluggish toward phosphorus pentachloride but the chloride produced was hydrolyzable. In the chlorination (by PCl_5 or $SOCl_2$) of substituted ethynylcyclohexanols,


$(CH_2)_5C{<}^{OH}_{C\equiv CX}$

, wherein X represents Cl, Br, C_6H_5, there was extensive dehydration to an enyne as well as chlorination.

Experimental Part

Preparation of the Cyclohexanols.—1-Ethyl-1-cyclohexanol,[6] 1-phenyl-1-cyclohexanol,[6] 1-chloroethynyl-1-cyclohexanol[7] and 1-bromoethynyl-1-cyclohexanol[7] were prepared by literature methods. 1-Phenylethynyl-1-cyclohexanol was synthesized by the method of Hurd and Cohen,[8] and since it was not previously characterized, its analysis is given here.

Anal. Calcd. for $C_{14}H_{16}O$: C, 84.0; H, 8.0. Found: C, 84.0; H, 8.26.

Slight modifications of Rupe's directions[5] were introduced in the synthesis of 1-ethynyl-1-cyclohexanol. In-

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(1) Du Pont Fellow in Chemistry, 1930–1931.

(2) Rupe, Messner and Kambli, *Helv. Chim. Acta*, **11**, 459 (1928).

(3) Carothers and Coffman, THIS JOURNAL, **54**, 4075 (1932).

(4) Willemart, *Compt. rend.*, **187**, 385 (1928).

(5) Rupe, Messner and Kambli, *Helv. Chim. Acta*, **11**, 449 (1928).

(6) Sabatier and Mailhe, *Ann. chim.*, [8] **10**, 544 (1907).

(7) Straus, Kollek and Heyn, *Ber.*, **63**, 1868 (1930).

(8) Hurd and Cohen, THIS JOURNAL, **53**, 1074 (1931).

stead of adding the acetylene under pressure, it was found simpler to bubble the acetylene through a cooled, stirred ether solution of the sodium enolate of cyclohexanone until stirring became difficult (about eight hours) and then let stand in the ice chest overnight.

1-α-Chlorovinyl-1-cyclohexene.—Thirty-three grams (0.27 mole) of 1-ethynyl-1-cyclohexanol and 23 g. (0.30 mole) of dry pyridine were placed in a 500-cc. three-necked flask equipped with a stirrer, dropping funnel and thermometer. Drop by drop into the above mixture was added 36 g. (0.30 mole) of thionyl chloride. The solution was stirred rapidly. The temperature was maintained at 50–60° during addition and for three hours thereafter. When cool, the pyridine hydrochloride was filtered off and rinsed with ether. Then the filtrate was washed with water, dried and distilled at 21 mm.: fraction (1) 64–68°, 4 g.; (2) 68–85°, 8 g.; (3) 89–92°, 15 g. This preparation was confirmed by Mr. Robert Christ.

Fractions (1) and (2), which contained, respectively, 18.2 and 22.0% of chlorine, were thought to be a mixture of 1-ethynyl-1-cyclohexene and the desired chloride. In confirmation of this, it was found that the chlorine content of another similar specimen, b. p. 60–65° at 40 mm., was 14.6% and the molecular weight 117 (calcd. mol. wt. for C_8H_{10} and $C_8H_{11}Cl$: 106 and 142.5). Fraction (3) gave analytical data which were satisfactory for 1-α-chlorovinyl-1-cyclohexene.

Anal. (Chlorine). Calcd. for $C_8H_{11}Cl$: Cl, 24.9. Found: Cl, 25.4. (Unsaturation.) Subs. 0.331 g. Volume of 0.392 molar bromine solution (in CCl_4), 11.0 cc. Calcd. cc. for a diene: 11.9. For standardization of the bromine soln., 0.517 g. of 2-pentene decolorized 18.9 cc. of it.

Inertness of the Chloride.—On refluxing for several hours with aqueous or with alcoholic potassium hydroxide, the chlorine content was still high (18–22%), revealing a negligible action.

Stirring the chloride for two days with alkaline potassium hypochlorite in the manner of Straus, Kollek and Heyn[7] was non-productive. Ten grams of an original 18 g. was recovered and there was 5 g. of sticky intractable residue.

Absolutely no reaction between the chlorovinylcyclohexene (in absolute ether) and magnesium occurred in three days. Ethyl bromide was ineffective in promoting the reaction. There appeared also to be no reaction between the chloride and ethylmagnesium bromide. No test for the —C≡CH group was obtained when the chloride was treated with ammoniacal silver nitrate.

Ozonization.—Three grams of 1-α-chlorovinyl-1-cyclohexene (in 75 cc. of carbon tetrachloride) was converted into about 5 cc. of liquid ozonide by the use of slightly less than the calculated quantity of ozone. The ozonide was hydrolyzed and the resulting strongly acidic solution was treated with an excess of sodium bicarbonate. This was extracted with pure ether. Evaporation of the ether left 0.7 cc. of liquid residue which seemed to be chiefly unchanged (D). That no cyclohexanone was present was established by its non-reaction with hydroxylamine, phenylhydrazine or sodium bisulfite. This ozonization was performed by M. L. Moore and J. W. Williams.

Ethynylcyclohexanol and Hydrobromic Acid.—A mixture of 20 g. of (A), 21 g. of 48% hydrobromic acid and 12 g. of sulfuric acid was warmed and stirred. Then 12 g. of sulfuric acid was added dropwise. Distillation was permitted, two layers resulting. The non-aqueous layer was separated, washed, dried and distilled. A 10-g. fraction boiled at 49–50° (30 mm.); d_4^{20} 0.980. Its mol. wt. value of 126.5 and its analysis suggested it to be a mixture of (E) and 1-α-bromovinyl-1-cyclohexene. As with the chloride, no Grignard reagent could be prepared.

Anal. Calcd. for C_8H_{10} and $C_8H_{11}Br$: C, 90.5, 51.4; H, 9.45, 5.90; Br, 0.0, 42.7. Found: C, 73.1 (av.); H, 8.4 (av.); Br, 16.6.

1-Ethyl-1-chlorocyclohexane.—Twenty-three grams of thionyl chloride was added dropwise into a mixture of 21 g. of 1-ethyl-1-cyclohexanol and 15 g. of pyridine. The mixture was stirred and refluxed for an hour on a steam-bath. Then it was treated with dilute alkali, water, dried and distilled at 50 mm. Five grams distilled below 90°, then 8 g. of ethylchlorocyclohexane was collected at 90–93°.

Anal. Calcd. for $C_8H_{15}Cl$: Cl, 24.2. Found: Cl, 24.03.

When 5 g. of this chloride was heated for six hours at 100° with 25 cc. of alcoholic potassium hydroxide (10 g. of potassium hydroxide) there was obtained 3 g. of an unsaturated hydrocarbon, presumably ethylcyclohexene, which boiled at 135–139°. There was no higher boiling residue.

1-Phenyl-1-cyclohexanol and Phosphorus Pentachloride.—When 5 g. of phosphorus pentachloride, 30 cc. of dry ether and 6 g. of 1-phenyl-1-cyclohexanol were heated for ten hours, much of the hexanol was unchanged. The product, washed and dried, contained only 6.3% Cl. It was a solid which distilled at 162–163° (50 mm.). It was converted completely into phenylcyclohexanol, m. p. 57–60°, by refluxing for four hours with alcoholic potassium hydroxide. Thus, whatever chloride was present was hydrolyzable.

1-Phenylethynyl-1-cyclohexene.—Forty grams of 1-phenylethynyl-1-cyclohexanol, in 200 cc. of cold, absolute ether, was dehydrated by standing with 47 g. of phosphorus pentachloride for twelve hours. After customary washing and drying, 24 g. of distillate was collected from 167–170° (16 mm.). Its chlorine content was 2.8%. Hence it was refluxed for five hours with alcoholic potash, then distilled and analyzed. Chlorine was negative but a slight oxygen-containing impurity was indicated.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.3; H, 7.69. Found: C, 91.0, 90.8, 90.7; H, 7.77, 7.78, 8.01.

When phenylethynylcyclohexanol, pyridine and thionyl chloride were stirred at 50–60°, similar results were obtained. It is of interest to note that this hydrocarbon was capable of adding only 1.3 moles of bromine (in carbon tetrachloride) instead of the calculated 3 moles.

1-Chloroethynyl-1-cyclohexanol and Thionyl Chloride.—Eighteen grams of this hexanol (b. p. 120–124° at 40 mm.; m. p. 51°), 9.7 g. of pyridine and 14.3 g. of thionyl chloride reacted for an hour at 70–80°. After filtering off the pyridine hydrochloride, the liquid reaction product was washed, dried and distilled. Ten grams was collected at 105–110° and 40 mm. As in the preceding cases, the analytical results pointed to a mixture of 1-chloroethynylcyclohexene and 1-(dichlorovinyl)-1-cyclohexene.

Anal. Calcd. for $C_6H_9(C{\equiv}CCl)$, $C_8H_{10}Cl_2$: Cl, 25.3, 40.1; mol. wt., 140.5, 177. Found: Cl, 32.0; mol. wt., 157, 159.

When 1-bromoethynyl-1-cyclohexanol was treated similarly with pyridine and thionyl chloride a mixture of 1-bromoethynyl-1-cyclohexene and 1-(chlorobromovinyl)-1-cyclohexene was formed. From 23 g. of the hexanol, there was produced 4 g. of product distilling at 120–130° (34 mm.) and 4.5 g. at 130–140°.

Summary

1-α-Chlorovinyl-1-cyclohexene was prepared by the action of thionyl chloride on ethynylcyclohexanol in pyridine and some ethynylcyclohexene was obtained also. 1-Ethynyl-1-chlorocyclohexane and cyclohexylidenevinyl chloride were proved absent.

1-Phenylethynyl-1-cyclohexanol, 1-chloroethynyl-1-cyclohexanol and 1-bromoethynyl-1-cyclohexanol underwent more dehydration than chlorination by thionyl chloride or phosphorus pentachloride.

1-Ethyl-1-chlorocyclohexane was prepared readily from 1-ethyl-1-cyclohexanol but 1-phenyl-1-cyclohexanol resisted chlorination.

EVANSTON, ILL. RECEIVED DECEMBER 11, 1933

[UNIVERSAL OIL PRODUCTS COMPANY RESEARCH LABORATORIES, RIVERSIDE, ILLINOIS]

The Action of Aluminum Chloride on Benzene and Cyclohexane

BY V. N. IPATIEFF AND V. I. KOMAREWSKY

In this study our observations are reported on the action of aluminum chloride on benzene and cyclohexane.

The numerous published references[1] on the action of aluminum chloride on benzene show quite different results on account of the use of different conditions in the experiments. Therefore, we decided to study this reaction under a definite set of conditions.

In a closed autoclave, in the absence of air and in the presence of dry hydrogen chloride, the action of aluminum chloride on benzene at 125° gave 1.7% of ethylbenzene and 0.84% of diphenyl calculated on the benzene charged.

To compare these results properly with the results of other investigators, it is necessary to note the following: (1) The absence of oxygen in our experiments accounts for the absence in our products of phenols and other oxygen-containing compounds (obtained by Wertyporoch and Sagel[1e] and Senff[1d]). It is evident that in the experiments of these investigators the oxygen of air and water has taken part in the reaction.

(2) The reaction of benzene with aluminum chloride under our conditions proceeds much more rapidly.

(3) The main products of reaction are ethylbenzene and diphenyl. The formation of these two compounds makes probable the following scheme of the reaction: (a) two parts of benzene combine to form diphenyl, liberating hydrogen; (b) a destructive hydrogenation of benzene occurs during which benzene decomposes, and the *decomposed fragments are hydrogenated* to form ethylene; (c) ethylene *alkylates* the unchanged benzene to form ethylbenzene.

The reaction of the first type (a) was observed by Friedel and Crafts,[1b] Scholl[2] and Scholl and Seer.[3] In the other two reactions, (b) and (c), we observed first a decomposition (destruction) and then an alkylation.

The proof that benzene decomposes in this manner follows: (1) from the formation of ethylbenzene, and (2) from the discovery, in the lower layer, containing aluminum chloride, of unsaturated ethylene polymers. Therefore, it is suggested that reactions (b) and (c) be called *destructive alkylation.*

From previous works by Aschan and others[4] it is known that cyclohexane isomerizes to methylcyclopentane in the presence of aluminum chloride.

In studying the action of aluminum chloride on cyclohexane under our experimental conditions, we have observed more fundamental changes.

By the action of aluminum chloride on cyclohexane in closed autoclaves in the presence of hydrogen chloride and in the absence of air at a

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[1] (a) Fr. Fischer and Niggemann, *Ber.*, **49**, 1475 (1916); (b) Friedel and Crafts, *Bull. de soc. chem. de Fr.*, **39**, 195, 306 (1883); (c) Gustavson, *Compt. rend.*, **146**, 640 (1908); (d) Senff, *Ann.*, **220**, 232 (1883); (e) Wertyporoch and Sagel, *Ber.*, **66**, 1306 (1933).

[2] Scholl, *Ber.*, **43**, 1737, 2202 (1910).

[3] Scholl and Seer, *Ann.*, **394**, 111 (1912).

[4] (a) Aschan, *ibid.*, **324**, 1 (1902); (b) Ipatieff and v. Grosse, in publication; (c) Nenitzescu and Cantuniari, *Ber.*, **66**, 1097 (1933); (d) Zelinsky, Turowa and Pollak, *ibid.*, **65**, 1171 (1932).