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Recently, Franzus and Hudson (3), and Russell and co-workers (4) reported an extensive study of 1,3-dibromocyclohexanes and 1,3- and 1,4-dichlorocyclohexanes. Acidic treatment, with either hydrobromic acid or hydrochloric acid of 1.4- (or 1.3-) cyclohexanediols yielded cis-trans mixtures of dihalogen-substituted cyclohexanes.

The bulk of our product  $(F_1)$ , when isolated and recrystallized from ethanol, melts at 102-103°, in agreement with trans-1,4-dichlorocyclohexane prepared by Russell and co-workers by a similar procedure. Proton magnetic resonance spectra show a peak at  $\tau = 5.9$  (Russell *et al.*  $\tau = 5.82$ ), due to the methine protons in 1,4-dichlorocyclohexane, the C-1 and C-4 protons being predominantly diaxial. Proton magnetic resonance spectra of F<sub>4</sub> showed presence of *trans*-1,4-dichlorocyclohexane ( $\tau = 5.9$ ) and a peak at  $\tau = 5.67$ , consistent with the signal due to methine protons of trans-1.3-dichlorocyclohexane (4). The reaction between 1,4-cyclohexanediol and hydrochloric acid was then followed up in the manner described below.

A series of Carius tubes each containing 0.98 moles of the diol and 4.1 moles of hydrochloric acid were sealed and heated at 80–90°. At regular intervals one tube was cooled, and the reaction mixture worked up as described at the beginning of the note. The isolated products were then analyzed by n.m.r. (30% carbon tetrachloride solution, int. TMS). In addition to unreacted material, 4-chlorocyclohexanol, 1,4-dichlorocyclohexane, peaks at  $\tau = 4.45$  and  $\tau = 2.9$  appeared. The  $\tau = 4.45$  peak is consistent with formation of 1,4-cyclohexadiene and the  $\tau = 2.9$  peak is consistent with formation of aromatic byproducts. Presence of 1,3-dichlorocyclohexane in our  $F_4$  fraction can thus be explained as due to the random addition of hydrochloric acid across the double bonds in 1,4-cyclohexadiene.

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## CONDENSATION OF HEXACHLOROCYCLOPENTADIENE WITH DIETHANOLAMINE\*

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The reactivity of the allylic chlorine atoms in hexachlorocyclopentadiene and the ease of their displacement by nucleophiles had been previously demonstrated by other workers (1, 2). Recently, McBee and co-workers (3) demonstrated this type of reaction with secondary amines.

We wish to report the reaction between the amino alcohol diethanolamine and hexachlorocyclopentadiene. In this reaction the expected product (I) was not isolated. Instead, the spiro compound (II) resulting from the condensation of 1 mole of diethanolamine with hexachlorocyclopentadiene followed by a cyclization step with the elimination of a mole of hydrogen chloride was obtained.

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1500

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The structure of II was elucidated by mass spectrometry, nuclear magnetic resonance, and infrared spectra. The mass spectrum showed a parent peak at 303 (based on Cl<sup>35</sup> isomer) with characteristic isotope peaks for an ion containing 4 Cl atoms. The n.m.r. spectrum showed a pair of triplets for the ring  $-CH_2-N$  and  $-CH_2-O$  protons at 3.39 and 4.28 p.p.m. respectively. Another pair of triplets for the open chain  $-CH_2-N$  and  $-CH_2-N$  and -

This cyclization is presumably favored over the further condensation of another diethanolamine molecule which would give the 5,5-bis-(dihydroxyethylamino)-1,2,3,4tetrachlorocyclopentadiene (I). Steric factors probably contribute to the tendency toward cyclization.

The aminoketal product (II) is easily hydrolyzed in an acid medium to give octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione (III). The diketone is undoubtedly the product obtained by the dimerization of the unstable intermediate tetrachlorocyclopentadienone (4).



The diketone III was readily converted to hexachloroindone IV by treatment with aqueous acetone (5).

### EXPERIMENTAL\*

#### 1-Oxa-4-hydroxyethylazaspiro[4.4]6,7,8,9-tetrachloronona-6,9-diene [II]

Potassium hydroxide (22.4 g) was dissolved in 200 ml of isopropanol in a 500-ml, three-necked flask fitted with a stirrer, a thermometer, and a water-cooled condenser. Forty-two grams of diethanolamine and 54.6 g of hexachlorocyclopentadiene were added to the above solution. An immediate exothermic reaction occurred raising the temperature to about 75° C and a solid began to form. The flask was cooled with an ice-water bath to 30° C. The mixture was stirred for 48 hours while the temperature was maintained at 30° C  $\pm$ 5°. The solid which was formed was filtered and identified as potassium chloride. After removing the solvent under reduced pressure, the dark viscous residue was dissolved in benzene and extracted several times with a slightly acidic 20% sodium chloride solution until the aqueous phase was acidic. The organic phase was washed with water and then dried over anhydrous sodium sulphate. The solvent was then removed and pentane added to the residue.<sup>†</sup> After cooling in an ice bath 48.7 g of solid material was formed. The solid was dissolved in Skelly-B, the solution treated with charcoal, filtered, and the filtrate cooled to give 35.0 g (57%) of white needles II, m.p. 61-63° C. Anal. Calc. for C<sub>9</sub>H<sub>9</sub>NO<sub>2</sub>Cl<sub>4</sub>: C, 35.45; H, 2.97; N, 4.59; Cl, 46.51. Found: C. 35.76; H. 3.07; N. 4.91; Cl. 46.23.

The infrared spectrum of the product in carbon tetrachloride showed the following peaks between 6.17 and 10.47  $\mu$ : 6.17 (s), 6.29 (w-m), 8.28 (s), 8.54 (m), 8.86 (m), 9.32 (s), 9.97 (s), and 10.47 (s)  $\mu$ .

#### Acid Hydrolysis of II

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A solution of II (18 g) in 240 ml of acetone and 600 ml of concentrated hydrochloric acid was refluxed for 90 minutes. After the solution was cooled to room temperature, the precipitate was filtered. The solid was dried in a vacuum oven to give 11.9 g of III, m.p. 159–161° C dec. Recrystallization from hexane gave 11.7 g (92%) of pure product, m.p. 160–161° C dec.;  $\lambda_{max}^{KBr}$  5.40 (s), 5.68 (s), 6.27 (s)  $\mu$ ;  $\epsilon$  mol. = 9100 at 255 mµ in cyclohexane. Anal. Calc. for C10O2Cl3: Cl, 65.09. Found: Cl, 64.90.

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\*All melting points are uncorrected. The mass and n.m.r. spectra were furnished by Dr. L. E. Peterson, General Mills. A 10% concentration of the compound in CCl<sub>4</sub> was used for the n.m.r. and chemical shifts are reported in p.p.m. relative to internal tetramethylsilane. Infrared and ultraviolet spectra were furnished by Mr. Robert Fisher and Miss Delores Bell, General Mills.

 $\dagger An$  attempt to distill the residue prior to the addition of pentane resulted in heavy gas evolution with a great deal of exotherm. Thus, distillation would not be recommended as a purification method.

## REARRANGEMENT STUDIES WITH <sup>14</sup>C. XX. SOME OBSERVATIONS ON REACTIONS BETWEEN GRIGNARD REAGENT, COBALTOUS BROMIDE, AND 2-PHENYLETHYL BROMIDE

### C. C. LEE AND D. P. THORNHILL\*

In a previous paper (1), it was demonstrated that contrary to an earlier report of Smith and Anderson (2), the reaction of 2-phenyl-1-4C-ethyl bromide with magnesium and cobaltous bromide in refluxing ether gave ethylbenzene and styrene with no isotope position rearrangement. Since this reaction has some resemblance to the cobaltous halide catalyzed reaction between a Grignard reagent and an organic halide (designated by Slaugh (3) as the Kharasch reaction), which is believed to involve intermediate free radicals

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Canadian Journal of Chemistry. Volume 42 (1964)

1502