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# THE REARRANGEMENT OF CYCLOBUTYL CATION AND THE USE OF MICROWAVE SPECTRA FOR THE ANALYSIS OF ISOTOPICALLY SUBSTITUTED REARRANGEMENT PRODUCTS*

Hyunyong Kim and William D. Gwinn

Department of Chemistry, University of California
Berkeley, California, U.S.A.

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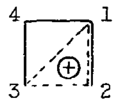
In 1959, Roberts and coworkers (1) proposed a reaction intermediate, which was used to explain large solvolytic reactivity of cyclopropylcarbinyl and cyclobutyl chloride in aqueous ethanol (2) and the methylene group rearrangement in cyclopropylcarbinyl derivatives (1). The intermediate embodies the structural feature of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl cations and is represented by I.



I

This reaction was also cited as an example of "internal return" from an "intimate" ion pair as proposed by Winstein, et al. (3). In these and subsequent works (4,5), it has been well

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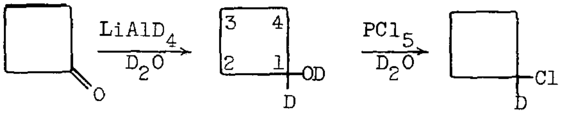
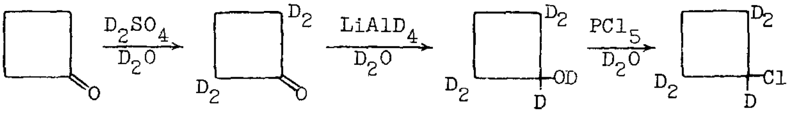
established that the methylene groups undergo extensive rearrangement among the 2, 3, and 4 positions.

In the course of the microwave spectroscopic study of the structure of cyclobutyl chloride (6), we have prepared the normal cyclobutyl chloride, $\overline{\mathrm{CH_2CH_2CH_2CH}}{}^{35}\mathrm{Cl}$ (I) and $\overline{\mathrm{CH_2CH_2CH_2CH}}{}^{37}\mathrm{Cl}$ (II), by the vapor-phase photochlorination of cyclobutane (2) and the deuterated species from the reaction of cyclobutanol with phosphorous pentachloride, following the method of Perkins (7). When the microwave spectrum of these products was observed, several complete rotational spectra were found. The assignment of these rotational spectra gave the moments of inertia of each species. These observed moments of inertia gave a definitive identification of the isotopic species under observation and the microwave intensity measurements enabled us to determine the relative abundance of the products. It was found that there is extensive rearrangement of methylene groups during the reaction between cyclobutanol and $PCl_5$ and the rearranged methylene groups are statistically distributed among the 2, 3, and 4 positions. This is consistent with the intermediate and mechanism proposed by Roberts and coworkers (1). Furthermore, microwave spectroscopy provided positive evidence that there is no rearrangement involving the transfer of hydrogens alone. The use of microwave spectroscopy has an advantage over the previous methods used, in that the observation is made upon an individual isotopic species in distinct quantum state and therefore the presence of other species in the sample is not a concern. Very minor change in isotopic arrangement gives rise to large change in the microwave spectrum. For example, for one of the lines studied for this compound, exchange of an α-hydrogen with a β-deuterium would shift the frequency of line a couple hundred megacycles and the line is measured to within an uncertainty of 0.02 megacycle.

The synthetic steps for the deuterated species were as follows:



(1)



(2)

Roberts and Mazur (2) noted that the purity of Perkin's preparation was questionable in view of the possibilities for the rearrangement during the reaction. To find the extent of this rearrangement, we have made a test run without deuteration. Cyclobutanone was treated with lithium aluminum hydride to yield cyclobutanol (2), and then the dried cyclobutanol was allowed to react with phosphorous pentachloride. Gas chromatographic analysis of the product gave two fractions of 20% and 80% in relative integrated intensity. The retention time and the infrared spectrum of the 80% fraction agreed with that expected for cyclobutyl chloride, and the 20% fraction which has a shorter retention time gave the infrared spectrum comparable to that of allylcarbinyl chloride (4-chloro-1-butene).

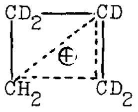
α-D-Cyclobutyl chloride was prepared according to (1). $D_2O$ was used in place of $H_2O$ as solvent. Gas chromatographic analysis gave similar results. From the microwave spectra of this product, $\overline{CH_2CH_2CH_2C}D^{35}Cl$ (III) and $\overline{CH_2CH_2CH_2C}D^{37}Cl$ (IV) were identified by their rotational constants, and no other species were found to be present.

In (2), deuterium exchange at the β-carbon was carried out with $D_2SO_4$ as catalyst, and the progress of exchange was followed by the NMR spectra. Better than 95% $D_4$ was obtained after five exchanges, each exchange requiring about 24 hours of refluxing at 80°C. From this product, the rotational spectra of $\overline{CD_2CH_2CD_2C}D^{35}Cl$ (V) and $\overline{CD_2CH_2CD_2C}D^{37}Cl$ (VI) were assigned. Besides these two species, two more rotational spectra, VII and VIII, were assigned. Based on the rotational constants, intensity ratio, and the chlorine nuclear quadrupole hyperfine structure, spectra VII and VIII were assigned to two species which differ only in the chlorine isotope. The ratio of the intensities of these species to the intensities of species V and VI was found to be 2.0 : 1 with an uncertainty of 5%.

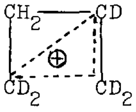
Species VII and VIII were identified as $\overline{CD_2CD_2CH_2C}D^{35}Cl$ and $\overline{CD_2CD_2CH_2C}D^{37}Cl$ at first by comparison between the experimental value of $\sum_i m_i y_i^2 = I_x + I_z - I_y$ and the values calculated from the structure based on species I through VI. This value is primarily dependent upon the masses of the β-carbons and the β-hydrogens and their distances from the plane containing the α- and the γ-methylene groups. The experimental value was 90.93 ± 0.05 amu $\text{Å}^2$ for species VII and VIII. This value is to be compared with 79.74 amu $\text{Å}^2$ for species I through

IV and 102.85 amu Å$^2$ for species V and VI. The calculated rotational constants of $\overline{CD_2CD_2CH_2C}D^{35}Cl$ and $\overline{CD_2CD_2CH_2C}D^{37}Cl$ were found to agree with the experimental rotational constants of VII and VIII within 0.04%. Thus we have identified the molecular species which were produced along with species V and VI. The extensive rearrangement among 2, 3, and 4 methylene groups has taken place during the reaction without any proton migration. Judging from the signal-to-noise ratio of the observed lines, any isotopic species, such as $\overline{CD_2CDHCHDC}DCl$ and $\overline{CD_2CD_2CHDC}HCl$, that may have been produced through proton migration were found to be less than 1% of the product.

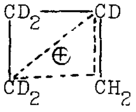
When the intermediate I is assumed to occur in our reactions, we would expect the following structures from (2).



A



B



C

The structure A corresponds to species V and VI, and B and C correspond to species VII and VIII. The expected product ratio of species VII and VIII to V and VI would then be 2 : 1. The observed product ratio of 2.0 : 1 ± 5% lends support to the assumption of rapid interconversion among these three species. In (1), the interconversion among 2, 3, and 4 methylene groups would give no other species but III and IV.

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