CHEMISTRY LETTERS, pp. 1185-1188, 1973. Published by the Chemical Society of Japan

A NEW TRICYCLOUNDECANE INTERMEDIATE IN AN ADAMANTANE REARRANGEMENT

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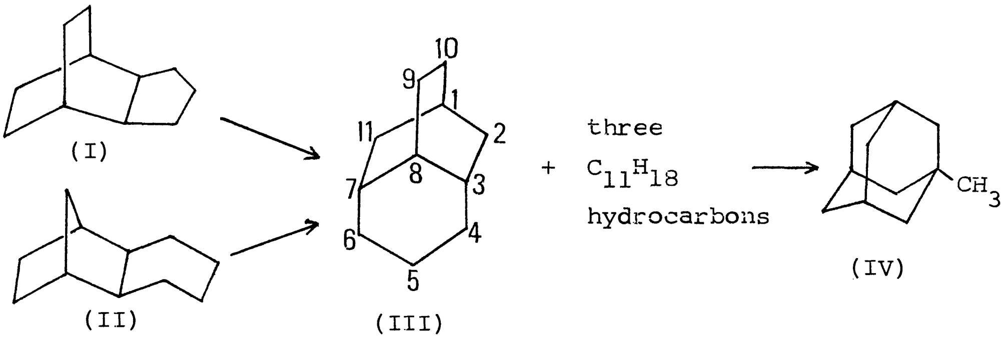
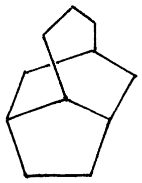
Isolation and characterization of a true intermediate in the adamantane rearrangement was made for the first time in the case of aluminum chloride-catalyzed isomerization of either tricyclo-[5.2.2.0^{2,6}]undecane (I) or tetramethylenenorbornane (II) to 1-methyladamantane, the intermediate in either case being tricyclo-[5.3.1.0^{3,8}]undecane (III) as determined by ^{13}C nmr spectroscopy.

Since the discovery by Schleyer$^{1)}$ of the Lewis acid-catalyzed rearrangement of a tricyclic saturated hydrocarbon to adamantane, a variety of the studies on this subject has been carried out.$^{2)}$ The research efforts, however, seem to be directed mainly to the finding of new precursors or to the improvements in the catalysts and solvents which lead to a better yield of adamantane, a few kinetic and mechanistic studies$^{3)}$ having been done mostly without isolation and characterization of the intermediates.

We wish to report our results of the isolation of an intermediate new $C_{11}H_{18}$ tricyclic hydrocarbon, for which we assigned the structure tricyclo[5.3.1.0^{3,8}]-undecane (III), during the acid-catalyzed isomerization of tricyclo[5.2.2.0^{2,6}]-undecane (I) or tetramethylenenorbornane (II) to 1-methyladamantane (IV).




(V)

Tricyclo[5.2.2.0^{2,6}]undecane (I), which is also a new $C_{11}H_{18}$ compound and easily prepared by hydrogenation of the Diels-Alder adduct$^{4)}$ of cyclohexa-1,3-diene with cyclopentadiene, was treated with 10 mole % of aluminum chloride ($AlCl_3$) in methylene chloride solvent at ambient temperature, while the reaction being monitored by vapor phase chromatography. After one hour, the starting I almost disappeared and changed into a mixture of four isomeric $C_{11}H_{18}$ hydrocarbon intermediates, whereas the final product 1-methyladamantane was just about to show up. After four hours of reaction, these intermediates in turn were vanished completely and 1-methyladamantane was obtained in an almost quantitative yield. A glpc analysis of the above intermediate mixture indicated the presence of 45% tricyclo[5.3.1.0^{3,8}]undecane (III) and three other unidentified tricycloundecanes in the amounts of 30, 20 and 5%, respectively. The same, four intermediates were formed, although the rates of formations were quite different from those in the case of I, also on the isomerization of tetramethylenenorbornane (II). The identity of intermediates in both cases were established by isolation of each of the intermediates on vapor phase chromatography followed by comparison of ir, nmr, and mass spectra of corresponding compounds.

The most abundant intermediate, tricyclo[5.3.1.0^{3,8}]undecane (III), was isolated from the intermediate reaction mixture by distillation collecting the fraction boiling at 111-112°C (36 mmHg) (yield 42%; mp (sealed capillary) 62-63°C). The ir spectrum (neat) is relatively simple with four sharp, strong peaks at 975, 940, 895 and 845 cm^{-1}. The 60 MHz ^{1}H nmr spectrum of III exhibited complex absorptions between δ 1.00 and 2.00. The ^{13}C nmr spectrum of III (in $CDCl_3$, TMS at 0 ppm) exhibited only eight distinct lines, with relative intensities and multiplicities as determined by the off-resonance proton deconpling technique shown in parentheses, absorbing at 15.2(1, t), 24.8(1, d), 26.3(1, t), 27.1(1, t), 30.9(2, d), 31.9(2, t), 32.2(2, t), and 33.1(1, d) ppm. The hydrocarbon gave a molecular ion peak at m/e 150 (relative intensity 100) with other major peaks at 122 (39), 121 (19), 80 (46), 79 (40), 67 (35), 41 (40), isotopic abundance being in accord with the empirical formula $C_{11}H_{18}$.

While conclusive proofs are still lacking, we believe this hydrocarbon to be best represented by structure III for the following reasons: The fact that the parent peak in the mass spectrum at m/e 150 is the most intensive of all suggests$^{5)}$ a reasonably symmetrical cage structure for this compound. Among the conceivable tricycloundecanes which possess eight different kinds of carbon atoms with respect to neighboring carbon and hydrogen atom arrangements, only two hydrocarbons, III and tricyclo[4.4.1.0^{2,8}]undecane (V), are devoid of containing any three- or four-membered rings. Of these two possibilities, V could be excluded because of two reasons. From a viewpoint of tortional energy, V contains a 7-membered and a puckered 5-membered rings which would necessarily render the hydrocarbon more tortional strain and eclipsed hydrogen nonbonding interactions than the alternative III has.

The ^{13}C nmr spectrum also seems to suggest the structure III for the intermediate. This is based on the presence of the methylene-C resonance at an abnormally high field (15.2 ppm), which would be assigned to the carbon at 5-position in III. The effect of 3-a̲-methyl and 4-e̲-methyl groups on the chemical shift change of 1-carbon in cyclohexane is known to be -5.4 and -0.3 ppm, respectively.6) These parameters for the additivity rule in cyclohexane system coupled with the fact of similar additivity in polycycloalkanes such as adamantane7) enables us to calculate the chemical shift value for 5-carbon in III, if the parameters for 2- and 11-methylene and for 9-methylene in III are approximated to those for 3-a̲-methyl and for 4-e̲-methyl in cyclohexane, respectively, the approximation of the value for methylene to that for methyl being highly rational in fused cyclohexane ring system.6) Thus the calculated value of the chemical shift of 5-carbon is 15.8 (26.9(the value for unsubstituted cyclohexane6)) -2 x 5.4 -0.3) ppm. A good agreement between the observed and the calculated values would support the existance of a triply substituted chair form cyclohexane partial structure and, hence, the structure III for the intermediate. Other ^{13}C nmr signals are tentatively assigned, with the aid of the chemical shift value of bicyclo[2.2.2]octane system,6) as follows: 24.8 ppm signal for 1-carbon, 26.3 or 27.1 for 9- or 10-, 30.9 for 3- and 7-, 31.9 or 32.3 either for 2- and 11- or for 4- and 6-, and 33.1 for 8-.

Kinetic studies of the reaction as well as an unequivocal synthesis of the intermediates are now in progress.

Acknowledgement. The authors thank Dr. S. Sato, Director of Applied Research Lab., Nippon Electric Varian Co., for the measurement of the ^{13}C nmr spectrum.

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Note added in proof. The compound III is considered, by the comparison of ms and pmr spectra, to be identical with the compound "C" with m.p.66.6-67.0°C, the structure of which has been left undetermined up until now, found in Prof. P.v.R. Schleyer's laboratory in Princeton University, during the rearrangement of tetramethylenenorbornane (K. R. Blanchard, Ph.D. Thesis, Princeton University (1966)). We came to know this when we received from Prof. Schleyer a copy of Blanchard's dissertation, which was sent to us via Dr. E. Osawa, Hokkaido University, whom we asked a collaboration on the further study of the subject by sending him a copy of the manuscript of this letter after it had been received for examination by the Chemical Society of Japan.

(Received July 26, 1973)