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MIGRATION OF METHYL GROUP IN HEPTAMETHYLBENZENONIUM ION
A NEW ROUTE TO PERDEUTEROHEXAMETHYLBENZENE

V.A.Koptyug, V.G.Shubin, D.V.Korchagina
Institute of Organic Chemistry, USSR Academy of Sciences,
Siberian Division, Novosibirsk, U.S.S.R.

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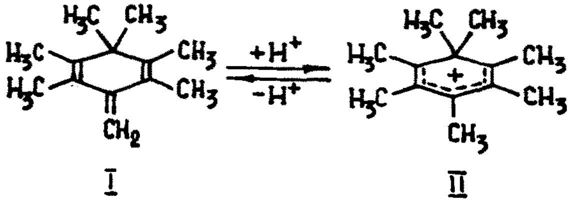
Completely deuterated hexamethylbenzene was obtained earlier by isotopic exchange reaction with liquid deuterated ammonia in presence of potassium amide (1).

We offer a new route to perdeuterohexamethylbenzene via heptamethylbenzenonium ion (II) shown by Doering et al.(2) to be formed as a result of protonation of 4-methylene-1,1,2,3,5,6-hexamethylcyclohexadiene-2,5(I).



Since this reaction is reversible the incorporation of deuterium into 4-CH_3 group must occur in deuteroacids.

We have recently found all the methyl n.m.r. peaks of II in trifluoroacetic acid to collapse to a single line at elevated temperatures. This has been explained by the rapid intramolecular migration of methyl group in II (3). The combination of migration with isotopic exchange reaction of hydrogen in 4-CH_3 group affords the possibility of replacing all hydrogen atoms of II by deuterium. The elimination of one of geminal CD_3 groups leads to perdeuterohexamethylbenzene.

A solution of I(605 mg.) in 9 ml. of deuterotrifluoroacetic acid was held at 70° for 15 min. under a dry nitrogen atmosphere and the most part of acid (ca.90%) was removed in vacuo at room temperature. After 6-fold repetition of this procedure 2 ml. of deuterotrifluoroacetic acid and 2 ml. of deuterium oxide were added to the residue (1.8 g.) and the solution was held at 70° for 48 hrs. The solid was separated and dissolved in benzene, and the solution was washed with concentrated hydrochloric acid and water. The evaporation of benzene yielded 425 mg. of solid, m.p.165°(EtOH), lit.(1) m.p. 165,5°. Mass spectral analysis showed the total content of deuterium in hexamethylbenzene obtained to be 98 atom %. Infrared spectrum: $\nu_{max.}^{KBr}$ 2250 (s), 2200 (s), 2187 (sh), 2173 (sh), 2117 (s), 2075 (vs), 1630 (m), 1412 (vs), 1093 (sh), 1047 (s), 900 (m), 675 (w) cm^{-1}.

When carrying out the isotopic exchange reaction of hydrogen in II in the presence of hexamethylbenzene the latter incorporated no deuterium. This confirms the intramolecular mechanism of migration of the methyl group in II.

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