Tetrahedron Letters, No.6, pp.5-8, 1959. Pergamon Press Ltd. Printed in Great Britain.

INTERCONVERSION OF SOME PENTYLBENZENES BY ALUMINUM CHLORIDE

Royston M. Roberts and Yuri W. Han

Department of Chemistry, University of Texas, Austin, Texas

(Received 5 May 1959)

AS a continuation of our study of alkylbenzenes we have examined the behavior of several pentylbenzenes in the presence of aluminum chloride.

Recently Nenitzescu and co-workers published an account of experiments quite similar to ours.[1] Their observation of the conversion of sec-butylbenzene into isobutylbenzene was in agreement with our own[2] but, owing to the qualitative nature of their analysis, they were unaware of the reversibility of this rearrangement. These workers also reported the conversion of t-pentylbenzene into 2-methyl-3-phenylbutane, and of the latter into neopentylbenzene by more extended treatment with aluminum chloride. We now wish to report the results of a quantitative study of the reaction of these three pentylbenzenes with aluminum chloride and to explain the relationship between them in terms of a mechanism which correlates this system with the rearrangements of propyl- and

---

[1] C. D. Nenitzescu, I. Necsoiu, A. Glatz and M. Zalman, Chem. Ber. **92**, 10 (1959).

[2] R. M. Roberts, Y. W. Han, C. H. Schmid and D. A. Davis, J. Amer. Chem. Soc. **81**, 640 (1959).

butylbenzenes.

Analysis of the pentylbenzenes after treatment with aluminum chloride was made by means of infrared spectrometry and vapor chromatography. The pentylbenzene fraction was previously separated from lower- and higher-boiling material by fractional distillation.

t-Pentylbenzene was first treated (100°, 1 hr) with water-activated aluminum chloride in the proportion used with sec- and isobutylbenzene.[2] The pentylbenzenes recovered were neopentylbenzene (65%), 2-methyl-3-phenylbutane (30%) and t-pentylbenzene (5%).[3] After milder treatment

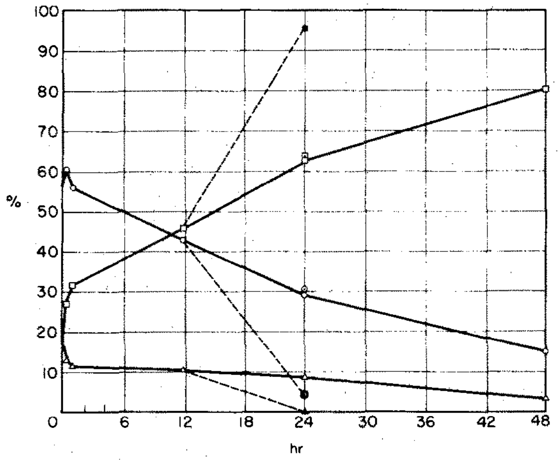


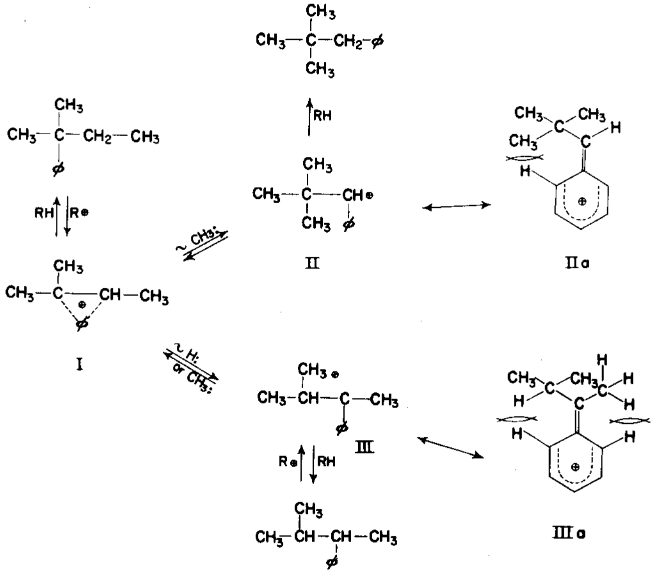
FIG. 1. Pentylbenzenes from Treatment with $AlCl_3 + H_2O$ in Benzene at 80° of
(a) t-Pentylbenzene: △ = t-pentylbenzene □ = neopentylbenzene
○ = 2-methyl-3-phenylbutane
▲■● = products from a second 12 hr treatment with fresh catalyst
(b) 2-Methyl-3-phenylbutane: △ = t-pentylbenzene □ = neopentylbenzene ○ = 2-methyl-3-phenylbutane

---

[3] These three pentylbenzenes made up 95% of the distillation fraction; the other 5% consisted of the cracking products sec- and/or isobutylbenzene (these two were not separated on the vapor chromatogram) and isopropylbenzene.

(in benzene solution at ca. 80°, 0.5 hr) however, the major component of the pentylbenzenes was 2-methyl-3-phenylbutane (60%) in accordance with Nenitzescu's finding, accompanied by neopentylbenzene (27%) and *t*-pentylbenzene (13%). Further experiments in which *t*-pentylbenzene was isomerized by heating with catalyst for various periods of time are summarized in Fig. 1. At first, 2-methyl-3-phenylbutane was produced rapidly, neopentylbenzene less rapidly, but the latter isomer was slowly converted into the former as *t*-pentylbenzene disappeared. When 2-methyl-3-phenylbutane was the starting material, essentially the same mixture of isomers was produced after 24 hr. When neopentylbenzene was treated similarly for 24 hr it was virtually unchanged; less than 2% of 2-methyl-3-phenylbutane and about 2% of cracking products were found. No evidence of the production of any other pentylbenzenes in any of the experiments was obtained by either infrared spectrometry or vapor chromatography.

A mechanism which is consistent with these data is outlined below:



This scheme is similar to those proposed by Nenitzescu,[1] but incorporates the suggestion of Schmerling and co-workers[4] of anchimeric assistance in the abstraction of $H{:}\ominus$ from _t_-pentylbenzene. It is directly analogous to those we have recently proposed for the rearrangements of propyl- and _sec_- and isobutylbenzenes.[5] In the present system, the intermediate ion III is favored over II energetically not only by the hyperconjugative effect, but also by the steric effect, since the _t_-butyl group causes severe steric inhibition of resonance in IIa.[6] Hence 2-methyl-3-phenylbutane is produced more rapidly than neopentylbenzene by the action of aluminum chloride on _t_-pentylbenzene. Although neopentylbenzene is produced more slowly, the reaction is irreversible. This must be due to the difficulty of abstracting $H{:}\ominus$ from the side-chain of neopentylbenzene. The nine primary hydrogens are γ to the ring, there are no β-hydrogens, and the two α-hydrogens are shielded by a _t_-butyl group. One is led to draw the interesting deduction that there is a significant steric requirement for hydride abstraction, by either aluminum chloride-water complex or by a carbonium ion. It is probable that this factor is involved in the lack of rearrangement of _n_-butylbenzene,[7] isoamylbenzene[1] and perhaps some other alkylbenzenes.[8]

---

[4] Who first described the rearrangement of _t_-pentylbenzene to 2-methyl-3-phenylbutane; L. Schmerling, R. W. Welch and J. P. Luvisi, _J. Amer. Chem. Soc._ **79**, 2636 (1957); L. Schmerling and J. P. West, _Ibid._ **76**, 1917 (1954).

[5] R. M. Roberts and J. E. Douglass, _Chem. & Ind._ In press (1959).

[6] G. Baddeley, J. Chadwick and H. T. Taylor, _J. Chem. Soc._ 2405 (1954); T. C. Van Hoek, P. E. Verkade and B. M. Wepster, _Rec. Trav. Chim._ **77**, 559 (1958).

[7] R. M. Roberts, S. G. Brandenberger and S. G. Panayides, _J. Amer. Chem. Soc._ **80**, 2507 (1958).

[8] We are grateful to the National Science Foundation for a grant which supported this research.