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EVIDENCE FOR A LADENBURG BENZENE INTERMEDIATE IN THE PHOTO-ISOMERIZATION OF 1,2,4,5-TETRA-t-BUTYLBENZENE TO 1,2,3,5-TETRA-t-BUTYLBENZENE(1,2)

by

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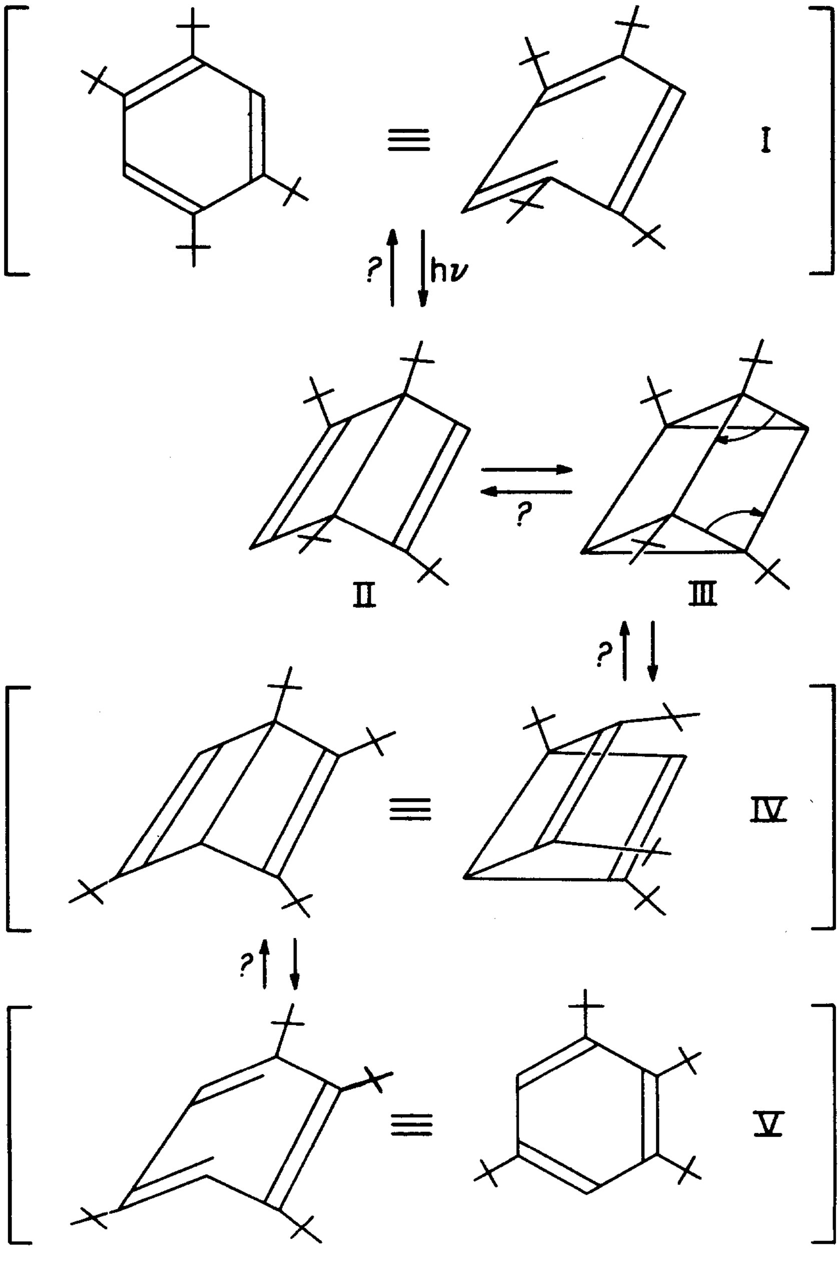
1,2,4,5-Tetra-t-butylbenzene(3,4) (TTBB) is believed to be a highly strained boat-shaped molecule(4) (I) and so might be expected to undergo photoisomerization to a Dewar benzene (II) more readily than does 1,2,4-tri-t-butylbenzene(5,6), which was the first compound reported to undergo such a conversion. We find, in fact, that upon mild irradiation it is converted to a number of products, including 1,2,3,5-TTBB (V) and its related Dewar benzene (IV). To our knowledge, V is the first reported example of an aromatic system bearing three very bulky groups on adjacent carbon atoms. As might be expected, it gives evidence of being more highly strained than the starting compound (I); and its formation here, along with IV, will be shown as evidence in support of Burgstahler's recent suggestion(7) that intermediates with the Ladenburg(8) "prismane" nucleus may be involved in photo-rearrangements of some benzene systems.

Upon examining the irradiation products of I, we were surprised to find an isomeric tetra-t-butylbenzene. Although previously reported poly-t-butylbenzenes with adjacent t-butyl groups have shown rather normal benzene spectra in the ultraviolet region (the main point of interest being a decrease in the intensity and fine structure of the band in the 270 mμ region(3)), the new compound (V) has a spectrum more like that for a highly distorted benzene(9), absorbing at λ_{max} = 307 mμ (ϵ = 434) in contrast to λ_{max} = 273 mμ and ϵ = 371 for the starting compound; 1,2,4,5-TTBB (I). The relatively high molar absorbtivity index for V in this region occurs because of overlap with a very intense band (λ_{max} = 254 mμ and $\epsilon = 10^4$), which may be a strongly bathochromically shifted benzene K band. This evidence that 1,2,3,5-TTBB is considerably more strained than even its badly distorted 1,2,4,5-isomer is supported by the relative stabilities of the two compounds to heat and is easily arrived at from examination of Dreiding models, which show that much more strain should be introduced into a benzene ring by placing a third t-butyl group next to a pair of adjacent t-butyl groups than results from making the original ortho-di-t-butyl arrangement. Fisher-Hirshfelder models do not even permit the juxtaposition of two t-butyl groups and so cannot be used to compare strain effects in this series. The 1,2,3,5-tetra-t-butylbenzene structure (V) was assigned to the new compound on the basis of the following evidence: Anal. (Schwarzkopf and Galbraith) calcd. for $C_{22}H_{38}$: C, 87.34; H, 12.66. Found: C, 87.24, 87.19; H, 12.60, 12.80. Molecular weight. Calcd., 302. Found (mass spectrometer at an inlet temperature of 150°), 302; (vapor pressure osmometer) 319; a sample of I run at the same time giving 288. The infrared spectrum was very similar to that of I(3) but showed several small bands (e.g. at 1587 cm^{-1}) and intensity ratios that were different from those in pure I. The NMR spectrum showed a normal aromatic singlet at τ = 3.07 ppm. in CCl_4 and absorption in the methyl region which could be resolved into three peaks at τ = 8.72, 8.61 and 8.59 ppm. when benzene (but not carbon tetrachloride) was used as solvent. The close overlap of these bands prevented good integration on our small sample, but they appeared to be in the proper ratio of 2:1:1 expected for the three kinds of t-butyl peaks in V. The total area for the methyl hydrogens was nearly 18 times that for the aromatic peak. Neither the infrared nor NMR spectrum suggested the presence of olefinic hydrogen.

When the new compound was heated in a sealed tube at 300 ± 10° for 30 minutes, it was almost quantitatively converted into 1,3,5-tri-t-butylbenzene and a gas (presumably isobutene), but a control tube containing 1,2,4,5-TTBB showed no change when subjected (side by side) to the same treatment. Analysis of the products from both tetra-t-butylbenzenes was done using two different g.l.c. columns and bona fide samples of the tri-t-butylbenzenes as controls. A small sample of the g.l.c. effluent attributed to 1,3,5-tri-t-butylbenzene was collected and had the correct melting point for that compound.

Wilzbach and Kaplan(10) presented evidence that the photoisomerization of xylenes is intramolecular and does not occur through radical migration. More immediately, Burgstahler(7) showed that the photorearrangement of ortho-di-t-butylbenzene(11,12) to its meta and para isomers is intramolecular and has made the interesting suggestion that the rearrangement might proceed through a prismane intermediate. However, his rearrangement goes from a less stable to a more stable structure in the same direction as might be expected if it occurred through an intramolecular shift of a t-butyl ion or radical from one carbon to another in the excited state. The spontaneous formation of an ortho-di-t-butylbenzene system by substitution or rearrangement of t-butyl ions or radicals is unknown. However, the photolysis which we have observed appears to go from a more stable to a less stable structure, as shown by the model, the ultra-violet spectrum, and pyrolysis. Actual thermodynamic comparison of stabilities must await heat of combustion measurements.

From what is known at present about crowded benzene systems, it seems highly unlikely to us that I will suffer either an intermolecular or intramolecular transfer of a t-butyl moiety from one carbon to another to produce a system with three t-butyl groups in a row; therefore, the rearrangement seems better explained by Burgstahler's prismane mechanism, which proceeds through reasonable bond reorganizations, rather than by t-butyl migration.



I
?
hν
?
II
III
?
IV
?
V

Other bridged intermediates are easily envisioned, but this seems to be the most easily reconciled with all of the facts reported here.

The starting material I is probably warped into a boat configuration ideally arranged for conversion to the Dewar benzene II, a structure for which there is now good precedent.(5,13) This should be closed easily by bond reorganization under photolysis to the prismane III. Direct reversion of the prismane nucleus to Dewar structures may occur in three ways, two of which lead to IV and the other to II. Although the energetic details of the change are at present obscure (we do not know yet about reversibility of the steps), it is difficult to see a less costly pathway here.

Supporting this mechanism is the fact that most of the rest of the photolysis residue has properties consistent with structure IV for the Dewar benzene of 1,2,3,5-TTBB. Although this might have been formed from photolysis of V, which in turn was produced by an unknown path, the most economical mechanism at present seems to be that shown here.

Irradiation of 689.7 mg. of I in 200 ml. of freshly distilled Skellysolve B was conducted for 22 hours in a Vycor flask in a Rayonet Srinivasan-Griffin chamber reactor with 16 mercury lamps whose main output is at 2537 A°.

Removal of the solvent left a small residue of oil, which was spotted on four plates (8" x 8") covered with a 250 micron layer of Silica Gel G. Development with hexane produced two yellow bands, the faster moving of which was barely discernible. The absorbant above the faster-moving band was scraped off and washed with ether, evaporation of which left about 400 mg. of oil. After a week's standing in the refrigerator, white crystals were found in the oil. Filtration yielded 75 mg. of material which, when purified by recrystallization from 95% ethanol, melted sharply at 70.5-71.0° (1,2,4,5-TTBB melts at 155-156°). Gas chromatography on an SE30 on Chromosorb P column separated the new material widely from 1,2,4,5-TTBB, which has a much longer retention time. Although the new compound is stable enough to survive passage passage through a g.l.c. column at 230°, it decomposes at 300° in the heated inlet of the mass spectrometer where the 1,2,4,5-isomer is stable.

The oil remaining from the crystals had an infrared spectrum(5) and NMR spectrum in CCl_4 appropriate for IV (τ = 8.83, 8.85, 8.97, and 9.08 for methyl hydrogens; vinyl doublet, J = 1.2 cps., centered at τ = 4.06 ppm. and a methine doublet, J = 1.2 cps., centered at τ = 6.92 ppm.). Mol. wt. 281 (vapor pressure osmometer). On heating at 200° for 30 minutes, it was mostly converted to 1,2,3,5-TTBB, as shown by melting point and gas chromatography. Anal. (Schwarzkopf) cald. for $C_{22}H_{38}$:C,87.34;H,12.66. Found: C,87.59; H,12.66.

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