Tetrahedron Letters No. 19, pp.658-662, 1961. Pergamon Press Ltd. Printed in Great Britain.

A TETRA-t-BUTYLBENZENE

Edward M. Arnett, Michael E. Strem and R.A. Friedel[1]

Department of Chemistry, University of Pittsburgh,

Pittsburgh 13, Pennsylvania

(Received 18 September 1961; in revised form 9 October 1961)

THERE has been considerable speculation about the properties that might be expected of aromatic compounds substituted with large groups in positions ortho to each other. In particular, <u>o</u>-di-t-butylbenzene has been the subject of some discussion[2,3] and of several synthetic attempts which have so far been unsuccessful.[4,5] We have attempted to approach this problem through the cyclization of appropriate acetylenic compounds with organometallic catalysts. While we were engaged in this work Hübel and Hoogzand[6] mentioned the preparation of 1,2,4-tri-t-butylbenzene using an organo-cobalt carbonyl complex. We describe below the formation of a compound which is in all probability 1,2,4,5-tetra-t-butylbenzene from the reaction of mono-t-butyl acetylene with the mono-adduct of di-t-butyl acetylene and dicobalt octacarbonyl. Independent experiments which will be described elsewhere

---

[1] U.S. Bureau of Mines, Bruceton, Pennsylvania.

[2] H.C. Brown and K.L. Nelson, <u>J.Amer.Chem.Soc</u>. <u>75</u>, 24 (1953).

[3] H.C. Brown, D. Gintis and L. Domash, <u>J.Amer.Chem.Soc</u>. <u>78</u>, 5387 (1956).

[4] E.M. Arnett, <u>J.Org.Chem</u>. 25, 324 (1960).

[5] L.R.C. Barclay, N.D. Hall and J.W. MacLean, <u>Tetrahedron Letters</u> No. 7, 243 (1961).

[6] W. Hubel and C. Hoogzand, <u>Chem.Ber</u>. <u>93</u>, 103 (1960).

indicate that *o*-di-t-butylbenzene may also be made in the same fashion. It is interesting that although 1,2,4,5-tetra-t-butylbenzene must be highly strained, its spectral properties do not indicate that its aromatic character has been dramatically affected.

The mono-adduct[7,8] of di-*t*-butylacetylene[9] and dicobalt octacarbonyl was prepared by mixing the two compounds at room temperature in Skellysolve F as solvent. Within 1½ hr the expected two equivalents of carbon monoxide had been evolved and upon removal of solvent a red-brown solid was obtained which was purified by sublimation (103°/1.5 mm) to give an 81.3% yield of ruby needles decomposing at 220° (uncorr.) in a sealed tube. In accordance with the formula $[(CH_3)_3C\text{-}C{\equiv}C\text{-}C(CH_3)_3]Co_2(CO)_6$ the infra-red spectrum showed the usual t-butyl bands and also the three terminal carbonyl bands at 4.83, 4.92 and 4.98μ which are customary for acetylenic mono-adducts of dicobalt octacarbonyl.[7,8] The 5.38μ band for the bridging carbonyl groups in $Co_2(CO)_8$ was absent. [(Schwarzkopf. Found: C, 45.54, 45.53; H, 4.24, 4.47; Co, 27.82, 28.13. Calc. for $C_{16}H_{18}O_6Co_2$: C, 45.30; H, 4.28; Co, 27.75].

The mono-adduct described above was refluxed with six equivalents of mono-t-butylacetylene (b.p. 35°) in Skellysolve C at 95° under a Dry-Ice condenser attached to a gas burette. After 6 hr the theoretical amount (two equivalents) of carbon monoxide had been evolved; at this point the bulk of the solvent was removed by distillation. The concentrated liquor was chromatographed on alumina and eluted with Skellysolve F. The first band to be discharged was a brown one which owed its color to unreacted

---

[7] H. Greenfield, Ph.D. Thesis, University of Pittsburgh (1955).

[8] H. Greenfield, H.W. Sternberg, R.A. Friedel, J.H. Wotiz, R. Markby and I. Wender, *J.Amer.Chem.Soc.* **78**, 120 (1956).

[9] G.F. Hennion and T.F. Branigan, Jr., *J.Amer.Chem.Soc.* **68**, 1202 (1946).

mono-adduct as shown by infra-red analysis. Immediately following this was a purple fraction whose color may have been due to a cobalt carbonyl tri-adduct although this was not demonstrated. Evaporation of solvent from these two fractions precipitated white crystals melting at 159.6° (uncorr.) in a sealed tube (on a Fisher-Johns block they sublimed). Gas chromatography showed the presence of a single component. Determination of the molecular weight by low-ionization voltage mass spectrum showed a main peak at mass 302, which could correspond to a tetra-t-butylbenzene, and a second smaller peak at 15 mass units less indicating fragmentation of a methyl group from the original molecule. [(Schwarzkopf). Found: C, 87.21, 87.51; H, 12.78, 12.82. Calc. for $C_{22}H_{38}$: C, 87.34; H, 12.66] The yield was 18.5% after recrystallization from methanol.

The compound then is most likely a tetrabutylbenzene and, by virtue of the synthetic route, is probably one of the three possible tetra-t-butylbenzenes. Evidence that it is the 1,2,4,5-isomer rather than the 1,2,3,4- or the 1,2,3,5-compounds rests mostly on the following spectral observations

The NMR spectrum showed only two sharp peaks in approximately the proper ratio of 18:1. This not only supports the fact that the aliphatic hydrogens are all in t-butyl groups but argues for the compound being the most symmetrical of the three isomers. Examination of the NMR results for the three tetramethylbenzenes shows the 1,2,4,5-isomer to be the only one with two simple unsplit peaks.

The ultra-violet spectrum (Cary-14 using cyclohexane as solvent) showed a single rounded peak at 273 mμ (ϵ = 363). The disappearance of fine structure is typical of highly strained aromatic systems. In Table 1 are presented the important bands and extinction coefficients for the three tetramethylbenzenes and 1,2,4,5-tetra-i-propylbenzene. It is seen that

1,2,4,5-tetramethylbenzene has an outstandingly stronger absorbance at all three bands than do the other two tetramethyl isomers. The corresponding tetra-i-propylbenzene has three bands in the same position but all of them, especially the one at 271.5 mμ, are reduced in absorbance. The single band of the tetra-t-butyl compound does not have as great an intensity as the bands of 1,2,4,5-tetra-i-propylbenzene and the fact that the single band in tetra-t-butylbenzene absorbs more strongly than do any of the bands for 1,2,3,4- or 1,2,3,5-tetramethylbenzenes is strong circumstantial evidence for the compound being 1,2,4,5-tetra-t-butylbenzene.

Table 1

Substituted benzene	λ, mμ	ε
1,2,3,4-Tetramethyl	268 272 277	292 216 211
1,2,3,5-Tetramethyl	268.5 273.5 277	273 230 207
1,2,4,5-Tetramethyl	269 272 278	625 568 666
1,2,4,5-Tetra-i-propyl	268 271.5 277	594 436 654
Tetra-t-butyl	273	363

Interpretation of the infra-red data is made rather tenuous by the scarcity of literature on tetra-substituted benzenes; however, the following tabulation of long wavelength bands gives permissive evidence for the 1,2,4,5-structure and argues against the 1,2,3,4-arrangement. The frequency for out-of-plane aromatic C-H vibrations in poly-substituted benzenes is supposed to be relatively insensitive to the nature of groups attached to the nucleus and mainly determined by the substitution pattern.[10] If the longest wavelength band for the compounds in Table 2 may be assigned to this vibration, the position of the bands for our compound appears to support the 1,2,4,5-arrangement. However, at present, assignments for such highly substituted systems are risky.[10] The rest of the spectrum showed the expected bands including the usual ones for t-butyl groups.

Table 2

Substituted benzene	Long wavelength band (cm^{-1})
1,2,3,4-Tetramethyl (in CS_2)	730 (w-m) 805 (vs)
1,2,3,5-Tetramethyl (in isooctane)	706 (s) 738 (m) 850 (vs)
1,2,4,5-Tetramethyl (in isooctane)	868 (vs)
1,2,4,5-Tetrafluoro (film)	852 (vs) 870 (vs)
Tetra-t-butyl (in CCl_4)	888 (m)

Acknowledgements - We are grateful to the National Science Foundation for a grant NSF-G-14583 supporting this work. We wish to express our great appreciation to Dr. B. Blaustein, Mr. A. G. Sharkey, Jr., Miss Janet Shultz and Mr. Sol Metlin, all of the U.S. Bureau of Mines, for assistance in this work. We thank Dr. A.A. Bothner-By of Mellon Institute for obtaining and interpreting the NMR spectrum.

---

[10] L.J. Bellamy, The Infra-red Spectra of Complex Molecules (2nd Ed.) p.79. John Wiley, New York, (1958).