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CYCLODECAPENTAENE-DIHYDRONAPHTHALENE CHEMISTRY. 9,10-DIHYDRO-9,10-ETHANONAPHTHALENE[1]

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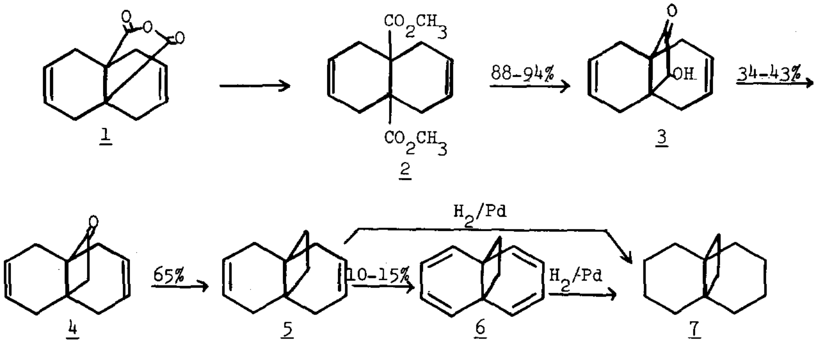
We have been engaged in attempts to prepare 9,10-dihydronaphthalene derivatives which might be in tautomeric equilibrium with the corresponding cyclodecapentaene.[2] Vogel has recently described the synthesis of the title compound.[3] This communication describes an alternate route which has the advantage that the functional groups present on the bridge in 3 or 4 will allow substituted ethano- or etheno- derivatives to be prepared.



The anhydride, 1,[4] was heated in refluxing methanol for two days. The resulting half-ester was converted to the acid chloride with phosphorus pentachloride in refluxing benzene.[5] Following removal of the benzene and phosphorus oxychloride, diester 2 was prepared by treatment with methanol. Cyclization of the diester to the acyloin, 3, was accomplished by 1:1 sodium-potassium alloy in refluxing benzene.[6,7] The acyloin, dissolved in toluene, was reduced by amalgamated (technical grade) zinc in 6N hydrochloric acid during a ten hour reflux period, to produce the ketone, 4; m.p. 80.8-82.0°; IR, 1771 cm^{-1}; semicarbazone, 235.0-235.5°(dec.). The ketone was reduced by the Huang-Minlon modification of the Wolff-Kishner reduction[8] to the diene, 5, n_D^{25} 1.5116. Hydrogenation of the diene afforded the saturated hydrocarbon, 7, n_D^{25} 1.4954; nmr (CCl_4) singlets at 1.39 (4H) and 1.64 ppm (1H)[7,9].

The diene was treated with bromine in chloroform, and after evaporation of the solvent, the crude mixture was dehydrobrominated with potassium tert-butoxide in dimethyl sulfoxide, to produce 9,10-dihydro-9,10-ethanonaphthalene, 6, in poor yield. We have also used the procedure described by Vogel.[3] The tetraene was separated from the reaction mixture by column chromatography on silicic acid. The nmr spectrum, Fig. 1, is very similar to that of the previously prepared oxydimethylene bridged naphthalene.[2] The UV spectrum in 95% ethanol shows $\lambda\lambda_{max}$, 233 mμ(ε 4.2 x 10^3); 284 mμ (ε 2.2 x 10^3) with a shoulder at 225 mμ(ε 3.9 x 10^3); n_D^{25} 1.5451.

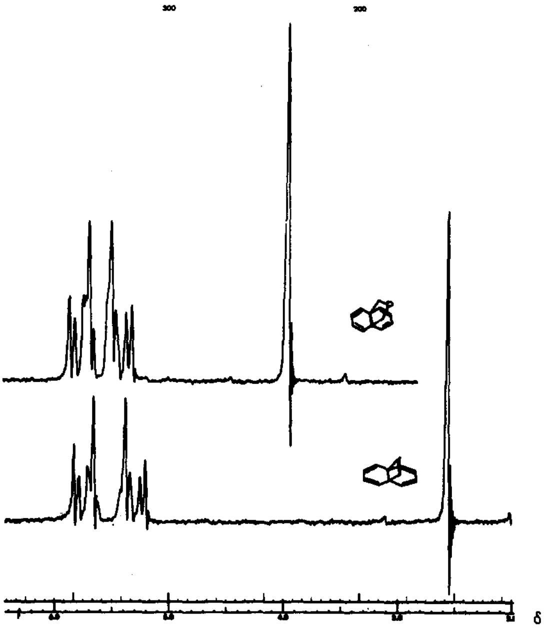


Fig. 1. NMR spectra of 9,10-dihydro-9,10-bridged naphthalenes.

The tetraene apparently cannot exist in equilibrium with the corresponding bridged cyclodecapentaene. When the tetraene was heated in hexachlorobutadiene at 150-152° in a sealed nmr tube, the distinctive nmr pattern of naphthalene gradually emerged ($t_{1/2}$ 7 ± 2 hrs.), and ethylene was produced. The ethylene (nmr, singlet at 5.33 ppm) was further identified as its dibromide which showed a singlet at 3.62 ppm.[7,10]

BIBLIOGRAPHY AND FOOTNOTES

1) This work was supported by National Science Foundation Grants GP-260 and GP-4439.
2) J. J. Bloomfield and W. T. Quinlin, J. Am. Chem. Soc., 86, 2738 (1964).
3) E. Vogel, W. Maier and J. Eimer, Tetrahedron Letters, 655 (1966). This paper was purposely delayed in revision until Professor Vogel's work, which was completed well before our independent synthesis, was published.
4) K. Alder and K. H. Backendorf, Ber., 71, 2199 (1938).
5) cf. G. Snatzke and G. Zanati, Ann., 684, 62 (1965), these authors claim that the acid chloride could not be prepared.
6) J. J. Bloomfield and J.R.S. Irelan, J. Org. Chem., In Press.
7) Satisfactory analyses have been obtained for the new compounds reported. The nmr spectra are reported in ppm downfield from internal tetramethylsilane. An A60, purchased with the aid of NSF funds, Grant GP-830, was used.
8) Huang-Minlon, J. Am. Chem. Soc., 68, 2487 (1946).
9) This compound is a member of a class of tricyclic molecules in which all three rings share a common bridge. We have coined the trivial name "Propelleranes" to describe these molecules in our laboratory.
10) The Varian Spectra Catalog #1, Varian Associates, 1962, gives 3.63 for dibromoethane in chloroform.