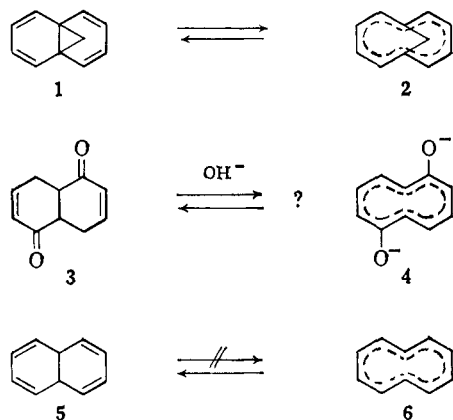


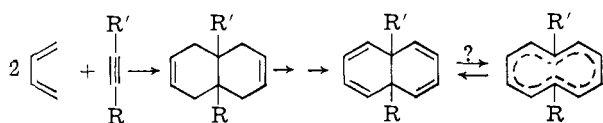
9,10-Dihydronaphthalene and Cyclodecapentaene<sup>1,2</sup>

Sir:

Recently there has been considerable interest in the possible aromaticity of the ten  $\pi$ -electron system, cyclodecapentaene. The general synthetic approach through 9,10-dihydronaphthalene or a derivative is especially appealing because transannular reactions during elimination are avoided and because of the possibility of an equilibrium with the corresponding cyclodecapentaene. Three syntheses have been published which utilize this approach, with one success,<sup>3</sup> one possible,<sup>4</sup> and one failure.<sup>5</sup>



We, too, have been engaged in pursuing the cyclodecapentaene system through 9,10-dihydronaphthalene along the lines outlined in ref. 3 and 5. In addition it has been our desire to prepare 9,10-disubstituted dihydronaphthalenes to prevent disproportionation reactions leading to naphthalene<sup>5</sup> or rearrangements leading to 1,2-dihydronaphthalene.<sup>5</sup> Our method of attack involves the reaction of an appropriately substituted acetylene with two moles of butadiene to provide 9,10-disubstituted  $\Delta^{2,6}$ -hexalins. Bromination and subsequent dehydrobromination leads to the required dihydronaphthalene.



This procedure has now been partially successful, even though no cyclodecapentaene was produced, with acetylenedicarboxylic acid as dieneophile in the Diels-Alder reaction.<sup>6</sup> The anhydride 7 isolated in this reaction was reduced with lithium aluminum hydride in tetrahydrofuran to the diol 8, 86–96%, m.p. 130–134°.<sup>7</sup> Conversion of the diol to the tetrahydrofuran 9 was effected by a trace of toluenesulfonic acid in refluxing toluene with the aid of a water separator, 65–87%, b.p. 69–71° (0.7 mm.),  $n_D^{25}$  1.5195.

(1) This research is supported by National Science Foundation Grant GP-260.

(2) This work was discussed at the Southwestern Regional Meeting of the American Chemical Society, Houston, Texas, Dec. 5–7, 1963, and at the Tenth Oklahoma Tetrasectonal Meeting, Ponca City, Okla., March 14, 1964.

(3) E. Vogel and H. D. Roth, *Angew. Chem.*, **76**, 145 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 228 (1964).

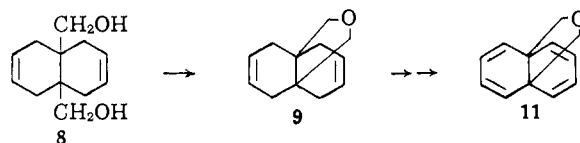
(4) W. S. Johnson, J. D. Bass, and K. L. Williamson, *Tetrahedron*, **19**, 861 (1963).

(5) E. E. van Tamelen and B. Pappas, *J. Am. Chem. Soc.*, **85**, 3296 (1963).

(6) K. Alder and K. H. Backendorf, *Ber.*, **71**, 2199 (1938).

(7) Satisfactory analyses have been obtained on all new compounds reported here.

Treatment of 9 with bromine in carbon tetrachloride at room temperature produced the tetrabromide, 10, 93–100%, m.p. 164–166°, which was converted to the dihydronaphthalene 11, with potassium *t*-butoxide in *t*-butyl alcohol, in only 7–10% yield, m.p. 74–75°.



Studies with models indicate that 11 could exist in the open chain form, but not without considerable angle strain. In fact, the n.m.r. spectrum<sup>8,9</sup> shows an  $A_2B_2$  multiplet (12) centered at  $\delta$  5.58 and a singlet at  $\delta$  3.93 in the ratio of 2:1 while the ultraviolet spectrum has  $\lambda_{max}$  242  $m\mu$  ( $\epsilon$  3400) which indicates that the compound is, indeed, merely the second example containing the 9,10-dihydronaphthalene skeleton.

Compound 11 formed only a monoadduct with maleic anhydride, m.p. 240–241°, infrared peaks at 1785 and 1860  $cm^{-1}$ . Both 9 and 11 produced the same 9,10-disubstituted decalin on catalytic hydrogenation, m.p. 62–64°, n.m.r. singlets at  $\delta$  1.42 and 3.60 in the ratio of 4:1. Further interesting transformations of the diester of 7 and of derivatives of the diol, 8, will be reported in a subsequent paper.

(8) Determined with a Varian Associates A-60 spectrometer in carbon tetrachloride solution. Chemical shifts in p.p.m. downfield from tetramethylsilane.

(9) The n.m.r. spectrum remained unchanged over a temperature range varying from 35 to 170°.

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## Benzynes

Sir:

We wish to report a set of experiments intended to establish the existence of 1,2-dehydrobenzene or benzyne as a free and well-defined molecular species. The mode of investigation we have used is time-resolved mass spectroscopy of the gaseous products of a decomposition reaction induced by flash photolysis.

A large number of results have shown that benzenediazonium 2-carboxylate is a precursor of benzyne in solution.<sup>1–3</sup> Chemical and spectral evidence shows that when the dry compound undergoes rapid flash-initiated decomposition, the final products are  $N_2$ ,  $CO_2$ , and biphenylene. The evidence inclines one to believe that benzyne is the first-formed gaseous organic product.<sup>4</sup> Moreover, mass 76 has been detected as a parent, together with several other masses including 152, among the products of the thermal decomposition of *o*-diiodobenzene, and the appearance potential of mass 76 is consistent with its assignment as benzyne.<sup>5</sup> The ease with which it decomposes and the simplicity of its pattern of products make the diazonium carboxylate an ideal starting material for virtually any experiment which monitors a transient

(1) M. Stiles, R. G. Miller, and U. Burckhardt, *J. Am. Chem. Soc.*, **85**, 1792 (1963).

(2) R. Huisgen and R. Knorr, *Tetrahedron Letters*, 1017 (1963).

(3) G. Wittig in "Congress Lectures, XIXth International Congress of Pure and Applied Chemistry," Butterworths, London, 1963, p. 173.

(4) R. S. Berry, G. N. Spokes, and M. Stiles, *J. Am. Chem. Soc.*, **82**, 5240 (1960); *ibid.*, **84**, 3570 (1962).

(5) I. P. Fisher and F. P. Lossing, *ibid.*, **85**, 1018 (1963).