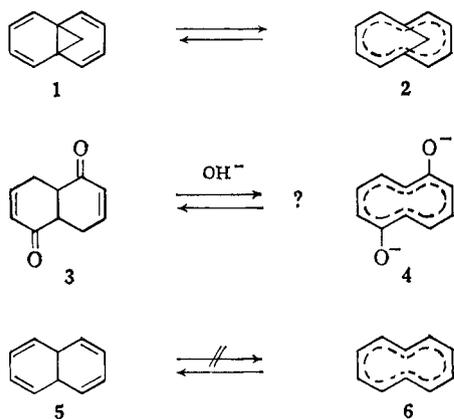


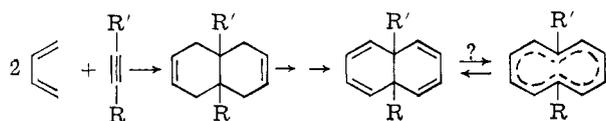
9,10-Dihydronaphthalene and Cyclodecapentaene<sup>1,2</sup>

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 Tetrastetional 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).

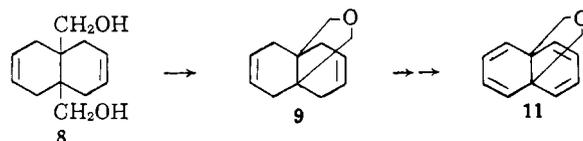
(4) W. S. Johnson, J. D. Bass, and K. L. Williamson, *Tetrahedron*, **19**, 861 (1963).

(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°.

DEPARTMENT OF CHEMISTRY  
THE UNIVERSITY OF OKLAHOMA  
NORMAN, OKLAHOMA

JORDAN J. BLOOMFIELD  
W. T. QUINLIN

RECEIVED MAY 11, 1964

## 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).

physical property. For these reasons, we have elected to study the mass spectrum of its decomposition products as a function of time.

The apparatus consisted of a Bendix time-of-flight mass spectrometer with a silica sample tube mounted axially "upstream" from the ionizing electron beam. A pinhole (diameter about 40  $\mu$ , in mica) approximately 1 mm. from the electron beam separated the two chambers. About 8 in. beyond the spectrometer the sample tube joined a conventional vacuum system. The sample tube was also equipped, through a buffer chamber, with a silicone rubber septum for injection of samples. A flash tube, Tesla-triggered, could be placed next to the sample tube. The tube was supplied by a 1.5- $\mu$ f. capacitor charged to 12 kv.; the time constant of the capacitor was 1  $\mu$ sec.

The oscilloscope output of the mass spectrometer was fed into half of a Type G differential preamplifier in a Tektronix 533 oscilloscope. The other side of the preamplifier received as its signal a single slow (2 or 5 msec.) sawtooth, triggered by the discharge of the flash lamp. The oscilloscope itself was triggered by the spectrometer at the beginning of each of its very rapid sweeps of the mass spectrum. The repetition frequency was adjusted to 20 kc. Thus, the oscilloscope showed a continual display of superposed mass spectra on a single base line, *except* for the 2 or 5 msec. following the flash discharge. During this interval, each sweep was displaced vertically from that preceding it, so that a sequence of 20 or more individual mass spectra could be observed. A conventional Tektronix camera with Polaroid back recorded the spectra. Signal-to-noise ratio was typically 3 or 4 to 1 (or more) for major peaks.

Samples (0.5 to 2.5 mg.) of benzenediazonium 2-carboxylate were injected in water or occasionally methanol solution, the solvent was pumped away, the pure solid was flashed, and the time-resolved mass spectrum was recorded. The spectrometer background could be recorded before photolysis by triggering the sawtooth manually; mass spectra of products after photolysis and calibration spectra of known substances were obtained in the same way.

The mass spectra show a very distinct evolution. There first occurs an interval of 200–300  $\mu$ sec. during which only the background is present. This level is ordinarily the oscilloscope line width except at masses 18 and 28, which are slightly above the line width. The delay is due to the distance between the solid precursor and the pinhole, and to any induction period in decomposition. Then, within the 50  $\mu$ sec. time resolution of our system, *masses 28, 44, and 76 appear simultaneously, at or near their maximum intensities.* Mass 152 appears at the same time but at an intensity less than one-fourth of its maximum. There are, naturally, several other peaks, which depend on the ionizing voltage. Most of pattern thereafter also depends on the ionizing voltage and on the sample size. Mass 152 most frequently rises to approach its maximum intensity about 200–250  $\mu$ sec. after the first appearance of masses 28, 44, and 76; this maximum persists for more than the duration of the sawtooth sweep. The rise time of 152 is closely matched by the disappearance time of 76, usually 250–300  $\mu$ sec. but occasionally longer.

It proved very helpful to compare mass spectra obtained with different ionizing voltages. Spectra at 50–55 v. show many masses between 76 and 152; mass 76 decays to a nonzero intensity. Comparisons showed that mass 76 is a cracking product of mass 152. Other peaks, especially 26, 50, 51, and 61–64, decrease to background in the same time that 76 goes to its limiting value. With an ionizing energy of 42 v., the intensities of all masses between 76 and 152 were reduced almost to background, while 76 and 152 remained relatively high. At 35 v., the only peaks which cannot be attributed to background, N<sub>2</sub>, or CO<sub>2</sub> are 152, 77, 76, and, less intense, 50 and a trace of 26.

The cracking pattern associated with mass 76, determined at 50-v. ionizing energy, from the first 200  $\mu$ sec. after appearance for masses above 18 is as follows (relative intensities in parentheses): 25 (2), 26 (8–9), 27 (4–8), 37 (3), 38 (6), 39 (10), 40 (3), 50 (9–4), 51 (4–3), 52 (2), 61 (2), 62 (6), 63 (2), 64 (1), 74 (3), 75 (4), 76 (9), and traces of 77 and 78.

At this point we can consider the foregoing results in light of the evidence cited in the second paragraph. We infer that the peak at mass 152 is due to biphenylene, and that masses 28 and 44 are due to N<sub>2</sub> and CO<sub>2</sub>, respectively. We infer also that the biphenylene, which appears much more slowly than diffusion alone would indicate, is formed as a gas. We infer from the rates of appearance of 152 and disappearance of 76 that the former is a product of dimerization of the latter. We infer, finally, that mass 76 is due to the transient benzyne molecule, and that no other species besides nitrogen, carbon dioxide, biphenylene, and benzyne are present in significant concentration in the gas phase.

The length of time in which the benzyne mass is observable is the same, within experimental uncertainty, as that during which a transient continuous absorption spectrum is detectable.<sup>4</sup> This agreement, together with the absence of other transient parent masses, is strong confirming evidence for the assignment of the spectrum to benzyne.

**Acknowledgments.**—We wish to thank Mr. Douglas Cornell and Mr. Walter Krol for helping to tame the apparatus. The Bendix time-of-flight mass spectrometer was obtained by the Chemistry Department of Yale University with a grant from the National Science Foundation. The work was supported in part by a grant from the Division of Chemical Sciences, United States Air Force Office of Scientific Research.

(6) Alfred P. Sloan Fellow; correspondence should be addressed to Department of Chemistry, University of Chicago, Chicago 37, Ill.

(7) National Science Foundation Undergraduate Research Participant.

(8) National Institutes of Health Predoctoral Fellow.

DEPARTMENT OF CHEMISTRY  
YALE UNIVERSITY  
NEW HAVEN, CONNECTICUT

R. STEPHEN BERRY<sup>6</sup>  
JON CLARDY<sup>7</sup>  
MARGARET E. SCHAFER<sup>8</sup>

RECEIVED MAY 7, 1964

### Endogenous Formation of $\Delta^{5,7,24}$ -Cholestatrien-3 $\beta$ -ol<sup>1</sup>

Sir:

The over-all mechanism of cholesterol biosynthesis is known and the reaction sequence between mevalonate

(1) Agents Affecting Lipid Metabolism. Part X. Part IX: M. Kraml, J. F. Bagli, and D. Dvornik, *Biochem. Biophys. Res. Commun.*, **16**, 455 (1964).