The Dimerization of Gaseous Benzyne

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Benzyne is the primary organic product of the photo-initiated decomposition of benzenediazonium 2-carboxylate. Its presence and its ultraviolet absorption spectrum are established by the coincident results of time-resolved optical and mass spectra. The integrated intensity of the ultraviolet absorption spectrum, and the intensity of mass peak 76, both measured as functions of time, lead to a rate constant for the dimerization of benzyne to biphenylene. The second-order constant has a value greater than or equal to 7×10^8 l./mole sec., and corresponds to a minimum reaction probability, per collision, of 7×10^{-3}.

I. Introduction

Gaseous benzyne is the primary product of photo-initiated decomposition of benzenediazonium 2-carboxylate in an evacuated tube. This is the conclusion drawn from the combined results of two types of investigation of reactions assumed to be eq. 1 and 2.

$$C_6H_4N_2CO_2(s) \xrightarrow{h\nu} C_6H_4(g) + CO_2 + N_2 \qquad (1)$$

$$2C_6H_4(g) \longrightarrow (C_6H_4)_2(g) \qquad (2)$$
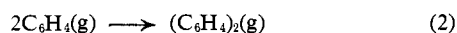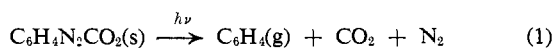
The first step was the observation of the formation of biphenylene,[3] $(C_6H_4)_2$, in the gas, presumably from reaction 2. The biphenylene spectrum, observed as a function of time, grows in intensity while a broad continuum, previously unknown, diminishes.[3] The time scale for this process is measured in tens or hundreds of microseconds. From the products formed, and from the variety of precursors giving the broad continuum, this absorption was attributed to benzyne.[4] Without further evidence of some altogether different kind, it did not seem fruitful to carry the spectroscopic study of benzyne further.

The different kind of information took shape in the second type of investigation,[5] the study of the time dependence of the mass spectrum of gaseous species in the system of reactions 1 and 2. The mass spectrum shows that the primary masses first produced are N_2, CO_2, and C_6H_4, followed by a slower growth of $C_{12}H_8$, as the C_6H_4 decays. There is no evidence for any gaseous starting material or for any partially decomposed transient like $C_6H_4CO_2$, C_6H_4CO, or C_6H_4O in this system. Moreover the C_6H_4 peak disappears as $C_{12}H_8$ grows, and the time scale for this process is the same as for the disappearance of the continuum attributed to benzyne and the growth of biphenylene absorption.

From these two sets of results, we infer that the decomposition of benzenediazonium 2-carboxylate does proceed through reactions 1 and 2 when carried out at low pressures. Moreover, we can rely with considerable confidence on the assignment of the broad absorption continuum to benzyne.

With this foundation, we can proceed to use the absorption spectrum of benzyne as a probe, and specifically to use the integrated intensity of the continuum to measure the "instantaneous" relative concentration of benzyne. From the time dependence of the relative concentration, we can infer a rate law and a lower limit for the rate constant. We cannot determine this constant precisely, both because of the uncertainties inherent in the data and because the absolute concentration of benzyne in the sample cell is never really known.

The mass spectrum can be used in essentially the same way. Unfortunately, these results are not as precise as the spectroscopic results because of instrumental limitations in addition to the uncertainties inherent in any flash photolytic experiment. Nevertheless, the mass spectrometric results are in quite good agreement with the spectroscopic rate measurements.

The results of both kinetic studies are reported here. We have also included some of the data concerning the mass spectrometric technique which were omitted from the preliminary communication.[5]

II. Experimental Section

A. Ultraviolet Spectroscopy. The flash-kinetic spectroscopy was carried out in much the same way as the previous work on the benzyne spectrum.[4] Argon-filled fused silica flash tubes were used for photolysis. Some experiments were carried out with helical lamps, (tube i.d. *ca.* 0.5 cm., helix diameters from *ca.* 3 to to 6 cm.) because these are known to deliver a large amount of light energy.[6] However, the duration of the flash from one of these helices is often as long as 200 μsec., too long for the study of biphenylene formation. The straight tubes finally used for this work dissipated essentially all their energy in 75 μsec. or less. The spectral flash lamp was an air-filled, fused silica capillary (i.d. 0.2 cm., length 5 cm.) operating on the low-pressure side of the minimum-voltage breakdown pressure. Its light pulse persisted no longer than 20 μsec.

Loading and flashing procedures were carefully standardized. All spectrographic plates (Eastman Kodak 103-0) came from the same batch. Fresh developer was used to standardize plate densities. Considerable care was taken to assure uniform illumination of the slit of the Bausch and Lomb medium quartz prism spectrograph.

The sample size was standardized at approximately 1 μmole. This size was chosen because it gave plate densities covering the most linear portion of the plate response curve.

(1) National Institutes of Health Predoctoral Fellow.
(2) Alfred P. Sloan Fellow.
(3) R. S. Berry, G. N. Spokes, and R. M. Stiles, *J. Am. Chem. Soc.*, **82**, 5240 (1960).
(4) R. S. Berry, G. N. Spokes, and R. M. Stiles, *ibid.*, **84**, 3570 (1962).
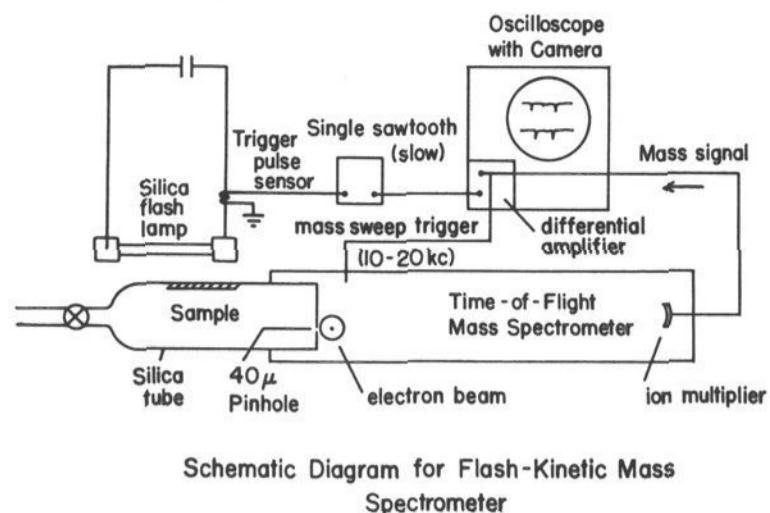(5) R. S. Berry, J. Clardy, and M. E. Schafer, *ibid.*, **86**, 2738 (1964).
(6) L. S. Nelson and J. L. Lundberg, *J. Phys. Chem.*, **63**, 433 (1959).

Figure 1. Schematic representation of the time-of-flight mass spectrometer–flash photolysis apparatus.

Figure 2. Oscilloscope records of mass spectra from flash photolysis. Upper photograph shows mass range 12–90; lower photograph, 6–160. The heavy trace at the top of each is the superposition of the undisplaced spectra before ($t = 0$) and after ($t = \infty$) the raster has completed its sweep. Note that the mass spectrum is nearly blank until 200–250 μsec. after the raster begins, i.e., after photolysis. The spectra at the earliest times represent the background. Consequently the peaks in the "$t = 0, t = \infty$" spectrum are essentially all due to stable products of the photolysis. The vertical deflection in the lower photograph was about half that of the upper photograph. This gives a longer observation time, but the peaks heights on this scale could not be measured accurately enough to give meaningful kinetic information.

Plate calibrations were made with a Jarrell-Ash seven-step neutral density filter. Optical densities of the plates, spectra, standards, and calibrations were measured with a Leeds and Northrop Knorr–Albers microdensitometer. Calibration curves of plate density vs. optical density were taken for every wave length that was included in the final extinction curves, i.e., at about 10-Å. intervals, except where there were severe interferences. Comparison and "experimental" plate densities were then converted to optical densities and the differences were taken between the corresponding values to obtain an absorption spectrum of the reacting system at a particular time. Integrated intensities were then determined by planimeter measurement.

B. Mass Spectrometry. Time-resolved mass spectrometry was carried out with a Bendix Model 12 time-of-flight mass spectrometer. It was equipped with a simple sample inlet in which the diazonium carboxylate could be photolyzed, and from which the vapor could effuse directly into the ionizing electron beam. The 40-μ orifice was less than 1 mm. from the electron beam. A sketch of the apparatus is shown in Figure 1.

The method of operation was outlined previously.[5] The details of the apparatus and procedure are described elsewhere.[7] The mass spectra showed signal-to-noise ratios of 3 or 4 to 1 for most peaks, and much higher ratios for the strongest peaks. The limitations on the measurement of mass peak heights were interference of strong peaks with the succeeding spectrum, and for weak peaks, the width of the oscilloscope trace and random intensity fluctuations. Two of the better but still typical oscillograph records are shown in Figure 2.

III. Results

A. Ultraviolet Spectroscopy. Absorption spectra of the photolyzed diazonium carboxylate were taken at times from 85 μsec. to 2 msec. after the photolysis flash, at approximately 100-μsec. intervals. During the first 500 μsec., the spectra were dominated by benzyne absorption; by about 500 μsec., the benzyne maximum was virtually gone, and only a very broad, weak, and flat absorption was detectable. This was, of course, due to the remaining benzyne absorption and to the overlapping biphenylene 2300-Å. band, broadened

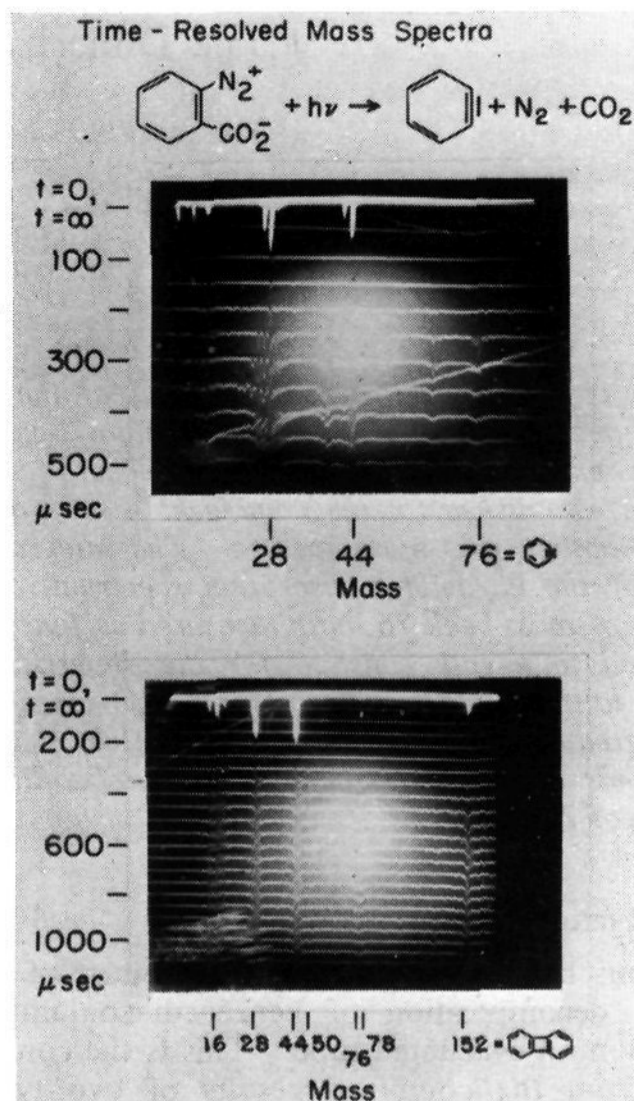(7) M. E. Schafer, Ph.D. Dissertation, Yale University, 1965.

and shifted by vibrational excitation. (Vibrational excitation was previously detected in the shift of the lower-energy transition of biphenylene,[4] but the 2390-Å. band was not heretofore examined for this phenomenon.) After 600 μsec., the biphenylene absorption grew narrower, until, at 1500 μsec., the spectrum was essentially the same as that of ordinary biphenylene vapor in the same cell at room temperature, except that at 1500 μsec. the intensity of absorption is still somewhat higher than that of the equilibrium vapor. The time development of the spectrum is shown in the series of typical spectra of Figure 3. These are the reduced absorption spectra and not simply microdensitometer traces. The raw data are much the same as those presented in the discussion of the spectrum itself.[4]

The assumption was made that the integrated intensity of any particular spectrum, $\int \log [I_0(\nu)/I(\nu)]d\nu$, is always directly proportional to the concentration of absorber, and that the proportionality factor is independent of time. Even if the absorbing gas obeys Beer's law instantaneously and at any one frequency, this assumption is strictly true only if the band contour is independent of time (i.e., the gas is in vibrational equilibrium) or if the transition probabilities are the same
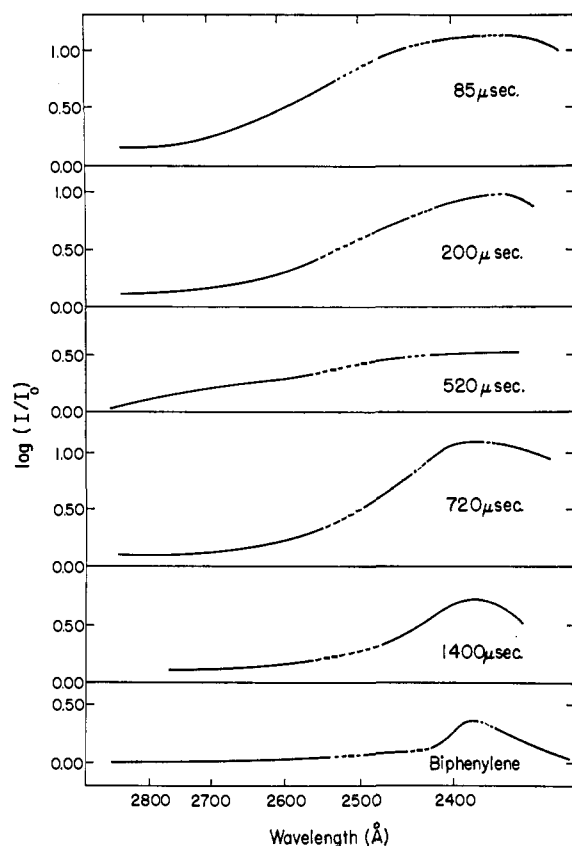
Figure 3. Time development of the ultraviolet spectrum of dimerizing benzyne. The spectrum at 85 μsec. is very similar to that reported in ref. 3. Only a few representative spectra are included in this figure. Table I contains the integrated intensities of all the spectra used in the rate determination.
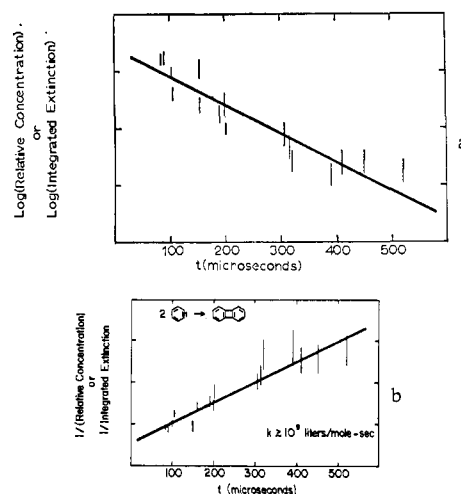

Figure 4. (a) Plot of kinetic data according to first-order kinetics, log (integrated extinction) vs. t. (b) Plot of kinetic data according to second-order kinetics (integrated extinction)$^{-1}$ vs. t. The two plots (a and b) are interpreted to suggest that second-order kinetics are the more likely. The actual second-order rate constant according to the data is $k_2 = 7 \times 10^8$ l./mole sec., with an uncertainty no greater than a factor of 2. (It is assumed that 35% of the starting material gives benzyne at $t = 0$.)

for all the pertinent vibrational states of the molecule. In general, the total integrated absorbance is

$$\int \log [I_0(\nu)/I(\nu,t)]d\nu = l\sum_j C_j(t) \int \epsilon_j(\nu)d\nu$$

where j runs over all vibrational and rotational states. In an arbitrary reacting system, the ϵ_j values may be different for different states, and the C_j values are quite definitely functions of time. In our system, we are marginally justified in assuming vibrational equilibrium, so that $C_j(t) = C_0 \exp(-E_j/kT)$. This justification comes from the analogy of the vibrational relaxation times of benzene, cyclohexane, and cyclohexene. At 369°K. and 1 atm., the vibrational relaxation time of benzene is 0.15 μsec., and those of cyclohexane and cyclohexene are smaller by tenfold.[8] The corresponding relaxation time for benzene, at the pressures we used, would be about 200 μsec., and less than 20 μsec. for cyclohexane and cyclohexene under the same conditions. As Figure 3 shows, the band contour does change somewhat at long wave lengths between 85 and 200 μsec. but relatively little between 200 and 500 μsec. Strictly, we should assume also that the integrated extinction coefficients of the populated vibrational states are nearly equal. This is not unreasonable for a molecule like benzyne because the transition is a broad continuum, probably to a strongly dissociating state. This means that this molecule will

(8) J. D. Lambert and J. S. Rowlinson, *Proc. Roy. Soc.* (London), A204, 424 (1951).

not exhibit the huge variations in ϵ_j values that sometimes occurs as a result of wildly varying Franck–Condon factors.

In the absence of any more reliable hypothesis, we have gone ahead and assumed that the proportionality factor relating benzyne concentration to integrated absorbance is time independent. The errors coming from any failure of this assumption seem to be small compared with uncertainties inherent in the flash method itself; at least this is what is suggested by the agreement of the optical and mass spectrometric results.

The base line for the spectral integration was the essentially constant level of absorption between 2700 and about 2880 Å. There is a little background, probably due to scattering. The limits of integration were 2416 to 2626 Å.; these limits exclude the region of intense biphenylene absorption. Smooth curves were drawn to connect the regions on either side of interfering lines. These regions of interference are dotted in Figure 3.

Table I contains the relative concentration c or absorbance values at various times from 85 to 520 μsec. after photolysis. These values have been plotted in Figures 4a and 4b according to first-order and second-order kinetics; that is, Figure 4a shows $-\log c$ vs. t, and Figure 4b shows c^{-1} vs. t. In both figures, a least-squares line has been drawn through the points. The average deviations are 15.3 and 11.7%, respectively, apparently rather similar. However, we feel that the deviations in the first-order plot are rather systematic, and that the points in Figure 4a tend to define a curve with positive curvature rather than a line. The points in Figure 4b appear more randomly scattered about their least-squares line. From these plots we infer that the reaction is probably second order, as one would expect on any reasonable intuitive ground.

The absorption spectrum of biphenylene did not prove to be a useful alternative probe for determination of the rate of reaction (eq. 2). In our apparatus, the longer wave length bands are only intense enough

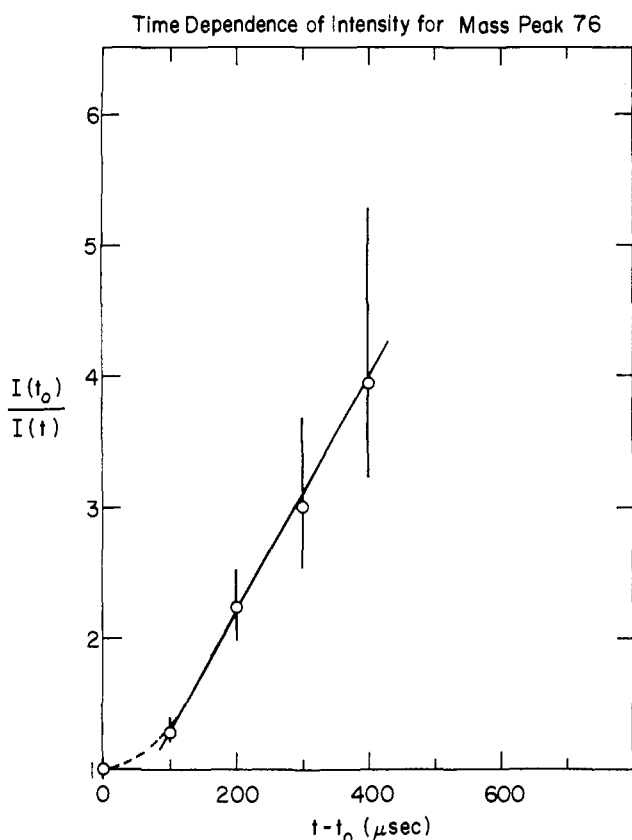## Time Dependence of Intensity for Mass Peak 76

Figure 5. Second-order kinetic plot of mass 76 peak. The first point was excluded from the line because at such short times, the peak intensity could well be anomalously high due to incomplete vibrational relaxation. This exclusion in no way affects the rate constant computed from these data, because of the uncertainties in the oscilloscope trace measurements (indicated by the error bars) and in the amount of benzyne actually present at t_0. The latter introduces an uncertainty surely no larger than a factor of 3 in the rate constant. The value determined from this plot, if 35% of the starting material gives benzyne present at t_0, is $k_2 = 9 \times 10^8$ l./mole sec.

Table I

Delay time, μsec.	Relative concn. of benzyne	1/rel. concn.	Log (rel. concn.)
85	112 ± 5	0.0090 ± 0.0004	2.05 ± 0.02
90	117 ± 5	0.0086 ± 0.0004	2.07 ± 0.02
102	98 ± 5	0.010 ± 0.001	1.99 ± 0.02
106	81 ± 5	0.012 ± 0.001	1.91 ± 0.02
152	97 ± 5	0.010 ± 0.001	1.99 ± 0.02
152	116 ± 5	0.0086 ± 0.0003	2.07 ± 0.02
155	73 ± 5	0.014 ± 0.001	1.86 ± 0.03
190	66 ± 5	0.015 ± 0.001	1.82 ± 0.03
200	70 ± 5	0.014 ± 0.001	1.85 ± 0.06
200	57 ± 5	0.018 ± 0.001	1.75 ± 0.03
305	51 ± 5	0.020 ± 0.002	1.71 ± 0.05
315	47 ± 5	0.021 ± 0.003	1.67 ± 0.05
320	38 ± 5	0.026 ± 0.004	1.58 ± 0.04
390	36 ± 5	0.028 ± 0.005	1.55 ± 0.04
410	41 ± 5	0.024 ± 0.002	1.61 ± 0.05
450	40 ± 5	0.025 ± 0.004	1.60 ± 0.05
520	36 ± 5	0.028 ± 0.005	1.56 ± 0.05

to be measured when the concentrations of benzyne is so high that triphenylene is also formed, so that the bands were not useful. The strong 2390 band overlaps the benzyne absorption much too much for it to be useful.

From the plot of Figure 4b, and with the assumption that the photolysis was about 35% efficient,[4] a rate constant was determined for the benzyne dimerization reaction 2, $k_2 = 7 \times 10^8$ l./mole sec.

If one uses the electron collision cross section of benzene,[9] 51.5 Å.^{2}, as the collision cross section for benzyne, then the initial collision frequency of benzyne with benzyne is 1.3×10^6 sec.$^{-1}$ under our conditions. This, together with the rate constant, implies that the initial rate of reactive collisions of a single benzyne is 9×10^3 sec.$^{-1}$, again under our conditions, and finally, that the probability of reaction per collision is about 6.6×10^{-3} or about 1 in 150. The uncertainty in the rate constant is probably less than a factor of two.

B. Mass Spectrometry. The mass spectrum shows the parent benzyne and biphenylene peaks and a number of fragment peaks. The cracking pattern at 200 μsec. after photolysis was presented earlier. For convenience we include here the almost identical pat-

(9) E. M. Bulewicz and P. J. Padley, *J. Chem. Phys.*, **36**, 2231 (1961).

tern at 250 μsec., and at a nominal electron-accelerating potential of 50 v.; the list gives mass number (relative intensity): 25 (3), 26 (5), 27 (4), 37 (3), 38 (4), 39 (5), 40 (3), 50 (5), 51 (4) 52 (3), 62 (3), 63 (4), 64 (3), 65 (3), 74 (3), 75 (3), 76 (5), 77 (1), and 78 (1). These masses all appear at the same time and decay together with approximately constant relative intensities. The 76 peak is frequently more intense just at its earliest appearance. This may be associated with vibrational excitation in the benzyne. If the electron-accelerating potential is a nominal 35 v., only traces of masses 26 and 50 can be attributed to benzyne.

The mass pattern of biphenylene under the same conditions shows only small quantities of 62 and 76 in addition to the parent 152, on the same scale of sensitivity as that used for benzyne. At an 80-v. electron accelerating potential, masses 26, 27, 38, 50, 57, 63, 76, and 77 can all be detected just above the background level.

Naturally masses 28 (N_2) and 44 (CO_2) are the most prominent among the peaks arising from photolysis. They appear at the same time as 76, and with their maximum intensities.

The intensity of the mass 76 peak could be measured as a function of time on a few of the oscilloscope records. Figure 5 shows the data from the best of these. The height of the error bars is due almost entirely to the width of the oscilloscope trace. At t_0, the time of first clear appearance of the mass 76 peak, the height of the peak is approximately ten times the uncertainty in the location of the base line, the center of the undisplaced oscilloscope trace. (The trace width itself is about three times the uncertainty in the location of its center.) At $t_0 - 400$ μsec., the signal height is only three times the uncertainty in the base line, or is displaced just over one trace width from the base line. This is the origin of the large error bars in Figure 5.

We can estimate the rate constant for dimerization from Figure 5. Let us neglect the point at t_0 in constructing our kinetic plot, not that doing this affects our conclusions in any significant way, but we suspect that the intensity at t_0 is anomalously high. Then the other four points lie on a much better straight line than one has any right to expect. The slope is approxi-

mately 9×10^3 sec.$^{-1}$. For this particular photolysis, the initial concentration of benzyne was estimated as 10^{-5} mole/l., so that the rate constant k_2 from the mass spectrometric data is 9×10^8 l./mole sec. This figure is almost surely within a factor of three of the true rate constant, and agrees inexplicably well with the rate determined by optical spectroscopy.

The Facile Isomerization and Dimerization of 1,2,6-Cyclononatriene

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It is demonstrated that 1,2,6-cyclononatriene (1) undergoes a facile isomerization in the liquid phase at ca. 135° to give 2,3-divinylcyclopentene (2) and also dimerizes to yield both stereoisomers of tricyclo[9.7.0.0²,¹⁰]-octadeca-5,9,11,15-tetraene, 7a and 7b. The configurational assignments of these dimers are based on the dimethyl acetylenedicarboxylate adducts isolated and on the Woodward–Hoffman generalized hypothesis for the steric course of electrocyclic transformations.

During our investigations directed toward syntheses of *cis,cis,cis*-1,4,7-cyclononatriene[1] we attempted to isomerize 1,2,6-cyclononatriene (1) with base, with acid, and thermally. The base-catalyzed isomerization of 1,2,6-cyclononatriene has been described by Gardner and co-workers.[2] Here we report on the structures of some of the products of the thermally induced reactions of 1,2,6-cyclononatriene.

Isomerization of 1. Heating 1 in a sealed tube under a nitrogen atmosphere to *ca.* 150° converts it partially to a mixture of new hydrocarbons. Starting material 1 and one of these products (2) were easily detected using g.l.p.c. analysis (isothermally at 100°), and together accounted for >98% of the material detected by g.l.p.c. at this temperature. However, by using temperature programmed g.l.p.c., it was demonstrated that higher molecular weight material was also present in the thermal reaction mixtures. Table I shows the results of
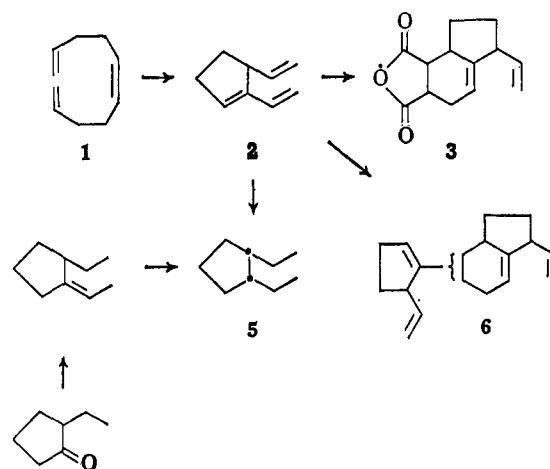

Table I. Thermal Isomerization of 1

Time, min.	Temp., °C.	Composition, % 1	2
30	150	73.9	25.9
60	150	26.4	72.5
30	175	4.3	94.3

three experiments in which the composition percentages were determined.

(1) K. G. Untch, *J. Am. Chem. Soc.*, **85**, 345 (1963).
(2) D. Devaprabhakara, C. G. Cardenas, and P. D. Gardner, *ibid.*, **85**, 1553 (1963).

Pure 2 was isolated by preparative g.l.p.c. We found by varying the heating period and temperature that highest yields of 2 resulted when 1 was heated for 40 min. at 150°. The elemental analysis and molecular weight of 2 showed it to be isomeric with 1. Its infrared spectrum exhibits absorptions at 3.23, 3.24, 3.28, 5.52, 10.07, and 11.04 μ, which are characteristic for a vinyl group, and at 6.10 and 6.30 μ which are typical for isolated and conjugated olefinic bonds. The ultraviolet spectrum of 2 shows absorptions at 228 mμ (sh, ϵ 24,200), 234 (27,000), and 241 (sh, 18,800) in cyclohexane at 2.33×10^{-5} mole/l. indicating a semi- or bicyclic diene chromophore. The n.m.r. spectrum of 2 shows three groups of absorptions: a complex set of lines between τ 3.3 and 5.3 (olefinic), a multiplet centered at *ca.* 6.6, and another set of lines between 7.3 and 8.5 with relative areas of 7.00:1.05: 3.84, respectively (theory, 7:1:4).

Since these data showed that 2 contained a conjugated diene, the thermal reaction mixture was treated with maleic anhydride. Two crystalline Diels–Alder adducts, 3, m.p. 93–94°, and 4, m.p. *ca.* 217°,[3] were isolated. Elemental analyses and molecular weight determinations showed 3 to be C_9H_{12} plus maleic anhydride and 4

(3) The melting point of 4 is variable. It was generally found near 217° (Kohler hot stage). Other samples melted at *ca.* 210°. Samples in capillary tubes melted consistently 12–13° higher than was found on the hot-stage apparatus.