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DETECTION BY INFRARED SPECTROSCOPY OF BENZYNE FORMED BY FLASH VACUUM PYROLYSIS AND TRAPPED IN AN ARGON MATRIX

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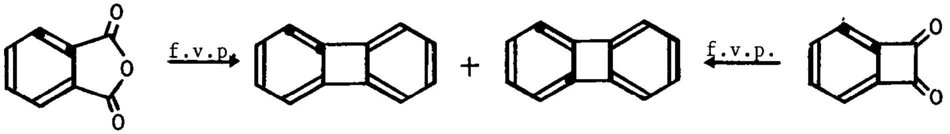
Summary: Benzyne has been detected in the argon matrices obtained from pyrolyses of isobenzofuran-1,3-dione (1), 2,3-benzodioxin-1,4-dione (2), benzocyclobutenedione (3), 2,2-dimethyl-5-(octahydro-1',2',4'-methano-3'<u>H</u>-cyclobuta[cd]pentalen-3'-ylidene)-1,3-dioxan-4,6-dione (8) and 5,5'-(pentacyclo[$5.3.0^{2,6}.0^{4,10}.0^{5,8}$]decane-3",9"-diylidene)bis(2,2-dimethyl-1,3-dioxan-4,6-dione) (9). At both 650° and 700° compound (3) yields only benzyne while (8) yields ketenes and benzyne. It is suggested that compounds (1), (2) and (3) undergo concerted fragmentation to benzyne while (8) and (9) give ketene intermediates which fragment to benzyne.

Previous techniques for generating benzyne under conditions suitable for physical observation have involved photolysis. R.S. Berry and coworkers studied the ultraviolet spectrum of the gaseous products resulting from flash photolysis of films of 2-diazoniabenzoate and 2-iodophenylmercuric iodide.[1] The time-dependent mass spectrum of the gaseous photolysis products of 2-diazoniabenzoate has also been investigated.[2] O.L. Chapman and coworkers have published the infrared spectrum of benzyne produced by <u>in situ</u> photolysis of benzocyclobutenedione, phthaloyl peroxide or of 2-diazobenzofuranone in an argon matrix.[3]

The formation of benzyne in the gas phase by flash vacuum pyrolysis (f.v.p.) of phthalic anhydride (1),[4] phthaloyl peroxide (2),[5] benzocyclobutenedione (3)[6,7] and compound (8)[8] has previously been inferred from the isolation of biphenylene and triphenylene. These compounds are formed in moderate yields and are accompanied by oxygen-containing compounds. We wish to report that benzyne can be detected by infrared spectroscopy in argon matrices of pyrolysates of compounds (1), (2), (3), (8) and (9).[9]

F.v.p. of [3a,4-$^{13}C_2$]isobenzofuran-1,3-dione (1*) diluted to 5% $^{13}C_2$ with unlabelled compound and of [2a,3-$^{13}C_2$]benzocyclobutenedione (3*) diluted to 7.5% $^{13}C_2$ yielded biphenylene which contained approximately equal amounts of [1,8b-$^{13}C_2$]biphenylene (4) and [1,4a-$^{13}C_2$]-biphenylene (5).[11]



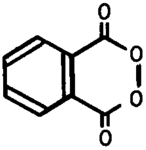
(1) unlabelled
(1*) labelled

(4)

(5)

(3) unlabelled
(3*) labelled

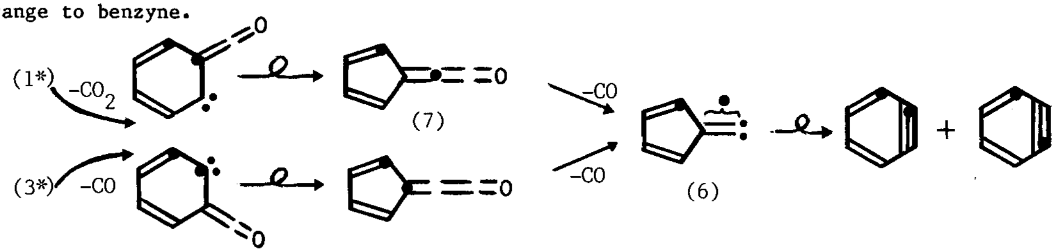
This skeletal rearrangement had been predicted by us on the basis of a reversible rearrangement of benzyne to cyclopentadienylidenecarbene (6). The benzyne may be formed by concerted loss of CO_2 and CO from (1) or of two molecules of CO from (3).



(2)

(6)

An alternative hypothesis proposed by Prof. C. Wentrup (Brisbane) involved decarboxylation or decarbonylation and a Wolff type rearrangement leading to cyclopentadienylideneethenone (7).[11] Decarbonylation of (7) would lead to cyclopentadienylidenecarbene (6) which would rearrange to benzyne.



We show in this paper that the infrared spectra of the pyrolysis products of phthalic anhydride (950°, spectrum (a)), phthaloyl peroxide (620°) or benzocyclobutenedione (650°; 700°, spectrum (b)) when trapped in an argon matrix show the presence of benzyne but do not show absorption attributable to ketenes.

Cyclopentadienylideneethenone (7) was first proposed by us as an intermediate formed on pyrolysis of compound (8).[8] The ketene (7) was postulated to yield carbene (6) which rearranged to benzyne. We now show that pyrolysis of compounds (8) (650°, spectrum (c); 700°. See also below) and (9) (600°, spectrum (d)) yield benzyne and in addition propose that ketene intermediates, the structures of which are not defined, are formed.

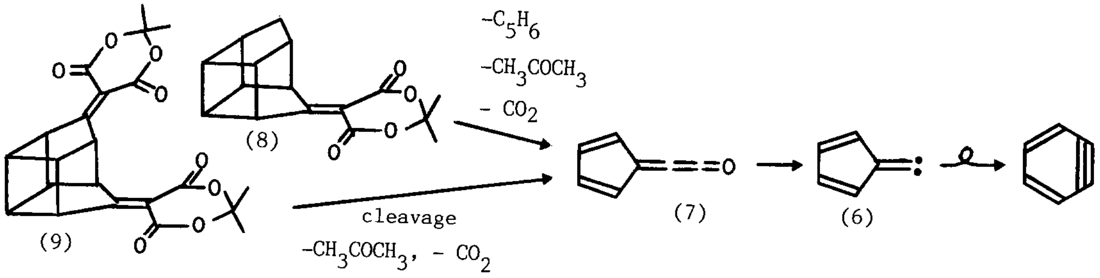


Figure 1. (Opposite page) Infrared spectra of the pyrolysates in an argon matrix; (a) phthalic anhydride (pyrolysis temp. 950°C), (b) benzocyclobutenedione (700°), (c) compound (8) (650°), (d) compound (9) (600°). Argon matrices were deposited on CsI plates cooled in a closed cycle CTI-Cryogenic Model 21 refrigerator at approx. 9.5K and spectra were recorded with a Perkin Elmer 180 infrared spectrophotometer. The pyrolysis apparatus consisted of a 400 mm × 20 mm i.d. silica tube with 90° bends at the entrance and exit and heated with an external furnace. The exit was joined through a 10 mm Pyrex tap to the deposition port. In a typical experiment 15 mmol of argon and the pyrolysate from 20 µmol of precursor were deposited during 1h. The furnace temperature was monitored with a chromel-alumel thermocouple. Spectrum (d) was scanned over the region 1800 to 2060 cm^{-1} and showed no appreciable absorption but the region was recorded on a different scale and is not reproduced.


a
b
c
d
400
600
800
1000
1200
1400
1600
1800
2000
2200
WAVENUMBER / cm -1
% ABSORPTION

The infrared spectra of four pyrolysates are shown in Figure 1. All four spectra show bands attributable to benzyne at 469, 736 and 849 cm^{-1}, and the two more intense spectra also show the weaker bands at 1038, 1053 amd 1451 cm^{-1}. The absorptions in spectra (a) and (b) from pyrolysates of phthalic anhydride and benzocyclobutenedione respectively can all be assigned to CO_2, CO, benzyne and unreacted precursor. The spectrum of the pyrolysate of phthaloyl peroxide was recorded on a different scale and is not reproduced here, but showed benzyne absorption bands strongly as well as bands attributable to CO_2, CO and phthalic anhydride.

The absorptions in spectra (c) and (d) from pyrolysates of (8) and (9) respectively show the presence of CO_2, CO, acetone and benzyne and in spectrum (c), cyclopentadiene. In addition, spectra (c) and (d) show a strong band at 2226 cm^{-1} with a shoulder at 2203 cm^{-1} and a complex band centred at 2090 cm^{-1} which are attributed to ketenes.

Further spectra were obtained of the products of pyrolysis of (8) at 500, 550, 600, 650 and 700°. At the lowest temperature the 2226 cm^{-1} band was very weak and the 2090 cm^{-1} band strong. With increasing pyrolysis temperature there was a reversal of these intensities and also an increase in the intensity of the CO band at 2139 cm^{-1}. Weaker bands showing the same temperature variation as the 2226 and 2090 cm^{-1} bands were also observed. We attribute these bands to two ketene type compounds and further work is in progress to identify them.

Our results show that phthalic anhydride, phthaloyl peroxide and benzocyclobutenedione probably undergo concerted fragmentation to give benzyne. The similarity between the ketene regions of spectra (c) and (d) is interpreted as meaning that compounds (8) and (9) fragment to yield common ketene intermediates which further fragment to benzyne.

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