Tetrahedron Letters No.26, pp. 2947-2951, 1966. Pergamon Press Ltd.
Printed in Great Britain.

COMPARATIVE STUDIES OF ELECTRON-IMPACT AND THERMOLYTIC FRAGMENTATION. I. AROMATIC ANHYDRIDES

M. P. Cava, M. J. Mitchell, D. C. DeJongh, and R. Y. Van Fossen
Department of Chemistry, Wayne State University
Detroit, Michigan 48202

(Received 15 April 1966)

Recent reports on the generation of aryne intermediates by the thermolysis of phthalic anhydride[1] and pyrazine-2,3-dicarboxylic anhydride[2] prompt us to disclose some of our own work which, though independently initiated, has progressed along similar lines.

The mass spectrum of phthalic anhydride has an intense peak at m/e 76 (Eq. 1), resulting from the loss of carbon dioxide and carbon monoxide, in that order. The m/e 76 peak corresponds to $[C_6H_4]^{+\cdot}$, which fragments further by elimination of acetylene to produce a fragment of m/e 50, $[C_4H_2]^{+\cdot}$; the m/e 76 peak has been attributed to benzyne[1] and, indeed, thermolysis of a solution of phthalic anhydride in benzene has been reported to lead primarily to products attributable to the reaction of benzyne with benzene.[1] In addition, biphenylene was shown by gas chromatographic analysis and mass spectroscopic analysis to be a minor constituent (ca. 1%) of the hydrocarbon portion of the hydrolysate.[1] In our own work, phthalic anhydride vapor was pyrolyzed in a stream of nitrogen at 50 mm. over a glowing Nichrome coil at ca. 800° and the pyrolysate was trapped on a cold finger kept at -78°. In this way, biphenylene was obtained in substantial yield [10-15%, based on unrecovered anhydride (33% recovery)], together with smaller amounts of higher molecular weight hydrocarbons.

Tetrachlorophthalic anhydride behaves similarly on electron impact, except that a fragment corresponding to the m/e 50 fragment in the spectrum of phthalic anhydride is not observed (Eq. 2). In addition, chlorine is lost by $[C_6Cl_4]^{+\cdot}$ and there are peaks in the mass spectrum corresponding to the doubly-charged ions $[C_6Cl_4]^{2+}$

$[C_6Cl_3]^{2+}$, $[C_6Cl_2]^{2+}$, and $[C_6Cl]^{2+}$. Thermolysis of tetrachlorophthalic anhydride vapor at 800° in a similar manner (hot wire, nitrogen stream, 15 mm. pressure) affords two products, (a) hexachlorobenzene (VIa, 34% yield), which is probably formed by the addition of elemental chlorine to tetrachlorobenzyne, and (b) octachlorobiphenylene (VII, 30% yield), yellowish-green needles, m.p. 292-294° (sealed tube, decomp.; sublimes at 290°/760 mm.); λ_{max}^{diox} 225 mμ (log ε 4.23), 243 (4.06), 268sh (4.10), 279 (4.45), 290 (5.15), 354 (3.05), 375 (3.21), 393 (3.26), 428 (2.91), 452 (2.87). Mol. wt. (mass spectr.) 424; calcd. 424 (for C^{12} and Cl^{35} only). Octachlorobiphenylene is the first example of a perhalogenated biphenylene to be reported.

Tetrabromophthalic anhydride also loses carbon dioxide, carbon monoxide, and halogen on electron impact (Eq. 3) and the mass spectrum contains doubly-charged peaks attributable to $[C_7BrO]^{2+}$, $[C_6Br_4]^{2+}$, $[C_6Br_3]^{2+}$, $[C_6Br_2]^{2+}$, and $[C_6Br]^{2+}$. However, in contrast to the tetrachloro anhydride, the tetrabromo anhydride does not give the halogenated biphenylene on thermolysis but gives only hexabromobenzene (VIb), formed in 20% yield [based on unrecovered anhydride (31% recovery)]. Hexabromobenzene is probably formed by the addition of bromine to tetrabromobenzyne and, in fact, copious quantities of bromine are liberated during thermolysis of the anhydride.

Pyridine-2,3-dicarboxylic anhydride fragments on electron impact in a manner analogous to that of phthalic anhydride (Eq. 4). The resulting fragment of m/e 77 eliminates hydrogen cyanide and this elimination is similar to the loss of hydrogen cyanide from the molecular ion of pyridine.[3] On thermolysis in an unpacked porcelain tube in a stream of nitrogen at 600° and 12 mm. pressure, pyridine-2,3-dicarboxylic anhydride is completely degraded to give a mixture of an unsaturated nitrile (8.4% yield), hydrogen cyanide, and gaseous uncondensable products.

The unsaturated nitrile is a colorless oil, m.p. 4-6°, which polymerizes rapidly at room temperature. We assign to the nitrile the structure of β-ethynylacrylonitrile (VIII) on the basis of the following evidence: (a) Hydrogenation of the unsaturated nitrile at atmospheric pressure in the presence of 10% palladium-on-charcoal gives valeronitrile (shown to be identical with authentic material by VPC, IR, and mass spectroscopy); (b) the IR spectrum of the unsaturated nitrile contains bands at 3.02 μ (ethynyl CH stretching vibration) 3.32 (ethylenic CH stretching vibration) and a group of bands at 4.29, 4.41, 4.50, and 4.75 due to acetylenic and nitrile absorption; (c) the UV spectrum contains maxima at 242 and 252 mμ; (d) the NMR spectrum contains peaks at δ 3.5 ppm (singlet, 1 acetylenic proton), 5.8 and 6.2 (2 vinyl protons) (all peaks including the peak due to the TMS standard, were unusually broad, probably because of free-radical polymerization of the nitrile); and (e) the mass spectrum of the unsaturated nitrile contains a parent peak at $\underline{m/e}$ 77 which loses hydrogen cyanide to give a fragment at $\underline{m/e}$ 50. Copious quantities of hydrogen cyanide are actually formed in the thermolysis of pyridine-2,3-dicarboxylic anhydride, presumably through decomposition of β-ethynylacrylonitrile (VIII).

Further comparative studies on the electron-impact and thermolytic fragmentation of aromatic anhydrides and other types of aromatic carbonyl compounds are now in progress and will be reported in due course.

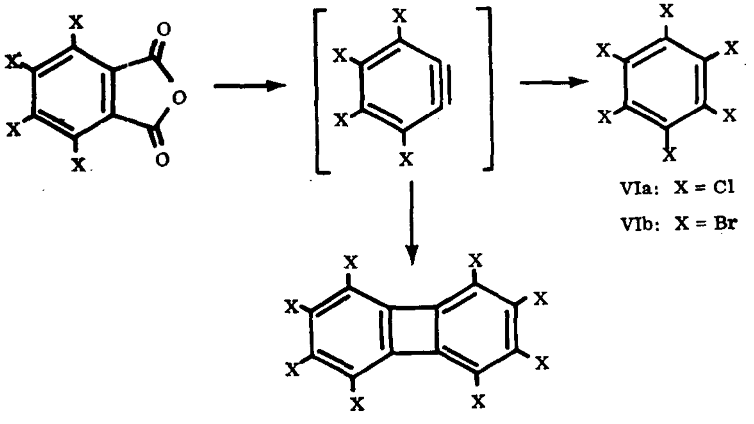
$$\begin{array}{ccccc} \lbrack C_8H_4O_3\rbrack^{+\cdot} & \xrightarrow{-CO_2} & \lbrack C_7H_4O\rbrack^{+\cdot} & \xrightarrow[m^*]{-CO} & \\ M^{+\cdot},\ \underline{m/e}\ 148\ (33\%)^{\dagger} & & (I)\ \underline{m/e}\ 104\ (100\%) & & \\ \lbrack C_6H_4\rbrack^{+\cdot} & \xrightarrow{-C_2H_2} & \lbrack C_4H_2\rbrack^{+\cdot} & & \\ (II)\ \underline{m/e}\ 76\ (95.5\%) & & \underline{m/e}\ 50\ (61\%) & & \end{array} \qquad (1)$$

$$\begin{array}{ccccccc} \lbrack C_8Cl_4O_3\rbrack^{+\cdot} & \xrightarrow{-CO_2} & \lbrack C_7Cl_4O\rbrack^{+\cdot} & \xrightarrow{-CO} & \lbrack C_6Cl_4\rbrack^{+\cdot} & \xrightarrow{-Cl^{\cdot}} & \\ M^{+\cdot}\ (68\%)^{\dagger} & & (100\%) & & (68\%) & & \\ \lbrack C_6Cl_3\rbrack^{+} & \xrightarrow{-Cl^{\cdot}} & \lbrack C_6Cl_2\rbrack^{+\cdot} & \xrightarrow{-Cl^{\cdot}} & \lbrack C_6Cl\rbrack^{+} & & \\ (26.6\%) & & (41.5\%) & & (54.3\%) & & \end{array} \qquad (2)$$

[†] The percentage figures are relative intensities. The symbol m* refers to a metastable peak formed in the transitions shown [I → II (Eq. 1), $M^{+\cdot}$ → III → IV (Eq. 3), etc.]. Mass spectra were obtained at 70 eV and 18 μA on an Atlas CH4 Spectrometer.

$$\begin{tikzcd}
\begin{array}{c}[C_8Br_4O_3]^{+\cdot}\\ M^{+\cdot}\ (100\%)\end{array} \arrow[r, "-CO_2", "m^{*}"'] & \begin{array}{c}[C_7Br_4O]^{+\cdot}\\ (III)\ (86.5\%)\end{array} \arrow[r, "-CO", "m^{*}"'] \arrow[d, "-Br^{\cdot}"'] & \begin{array}{c}[C_6Br_4]^{+\cdot}\\ (IV)\ (32.2\%)\end{array} \arrow[d, "-Br^{\cdot}"'] \\
 & \begin{array}{c}[C_7Br_3O]^{+\cdot}\\ (26.8\%)\end{array} \arrow[r, "-CO"] & \begin{array}{c}[C_6Br_3]^{+}\\ (28.6\%)\end{array} \arrow[d, "-Br^{\cdot}"'] \\
 & \begin{array}{c}[C_6Br]^{+}\\ (23.3\%)\end{array} & \begin{array}{c}[C_6Br_2]^{+\cdot}\\ (49.2\%)\end{array} \arrow[l, "-Br^{\cdot}"']
\end{tikzcd} \qquad (3)$$

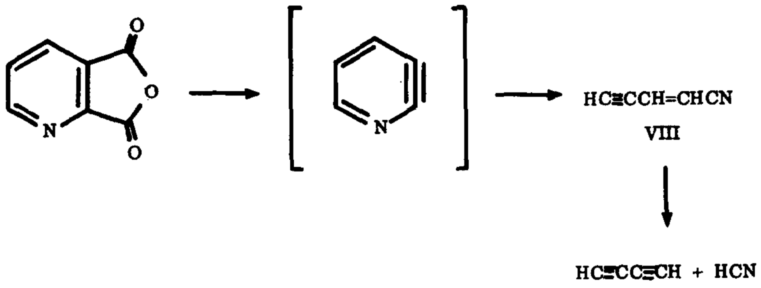
$$\begin{tikzcd}
\begin{array}{c}[C_7H_3NO_3]^{+\cdot}\\ M^{+\cdot},\ \underline{m/e}\ 149\ (13.6\%)\end{array} \arrow[r, "-CO_2"] & \begin{array}{c}[C_6H_3NO]^{+\cdot}\\ (V)\ \underline{m/e}\ 105\ (100\%)\end{array} \arrow[r, "-CO", "m^{*}"'] & {} \\
\begin{array}{c}[C_5H_3N]^{+\cdot}\\ \underline{m/e}\ 77\ (100\%)\end{array} \arrow[r, "-HCN"] & \begin{array}{c}[C_4H_2]^{+\cdot}\\ \underline{m/e}\ 50\ (70.5\%)\end{array} &
\end{tikzcd} \qquad (4)$$



VIa: X = Cl

VIb: X = Br

VII: X = Cl



$HC\equiv CCH=CHCN$

VIII

$HC\equiv CC\equiv CH + HCN$

Acknowledgement. The Atlas CH4 Mass Spectrometer was purchased with funds from a Research Instruments Grant of the National Science Foundation. We are also indebted to the National Science Foundation for grant GP-4931 in partial support of this work.

REFERENCES

1. E. K. Fields and S. Meyerson, Chem. Comm., 474 (1965).
2. R. F. C. Brown, W. D. Crow, and R. K. Solly, Chem. Ind. (London), 343 (1966).
3. Catalog of Mass Spectra Data, Amer. Petroleum Inst., Project 44. Carnegie Inst. Tech., Pittsburgh, Pa., spectrum No. 617.