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THE PYROLYSIS OF HOMOPHTHALIC ANHYDRIDE.
SIMPLE SYNTHESIS OF BENZOCYCLOBUTENONE AND FULVENEALLENE.

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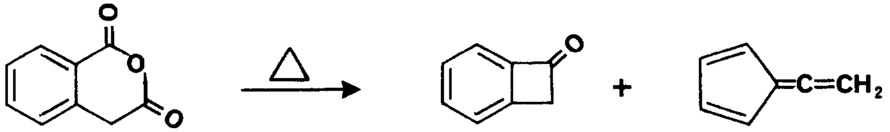
We wish to record the thermolysis of homophthalic anhydride (1), a process which provides a ready synthesis of either benzocyclobutenone (2) or fulveneallene (3). Pyrolysis at two mm by subliming 1 (2.7-3.0 g during a period of 1-2.5 hr) in a stream of nitrogen (22 ml/min at 690 mm) over a hot nichrome wire[1] results in the formation of two products, benzocyclobutenone (2) and fulveneallene (3). The products are collected in a cold trap at -78° while unreacted 1 solidifies directly above the pyrolysis zone. When the cold trap is warmed to -25° at 1 mm, 3 readily distills to a second -78° cold trap. The yields of pyrolysis products as a function of temperature are shown in the Figure. Ketone 2 is isolated pure in greater than 40% yield over the temperature range 515-545°. At 570° fulveneallene (3) is isolated pure in 71% yield. In all cases the material balance is excellent and little carbonization occurs. The pyrolysis of 1 offers a convenient, one-step preparation of either benzocyclobutenone (2) or the interesting hydrocarbon, fulveneallene (3), and is a considerable improvement over other methods.[2]



1 2 3

The above process finds analogy in the mass spectrum of anhydride 1 and provides a parallel between the electron impact and thermally induced fragmentation of organic molecules.[3] The partial 70 eV mass spectrum of 1 shows, m/e (relative abundance): 162 (19) $[\overset{+}{\mathrm{M}\cdot}]$, 118 (100) $[\overset{+}{\mathrm{M}\cdot}-\mathrm{CO}_2]$ and m/e 90 (96) $[\mathrm{C}_7\overset{+}{\mathrm{H}_6\cdot}]$. These peaks account for 46% of the total ion current. The 15 eV spectrum consists of only two peaks, 162 (21) and 118 (100). The thermal decomposition of 1 is also clearly related to the pyrolysis of indan-1,2-dione, which also produces 2 and 3 as the major products.[4, 5]

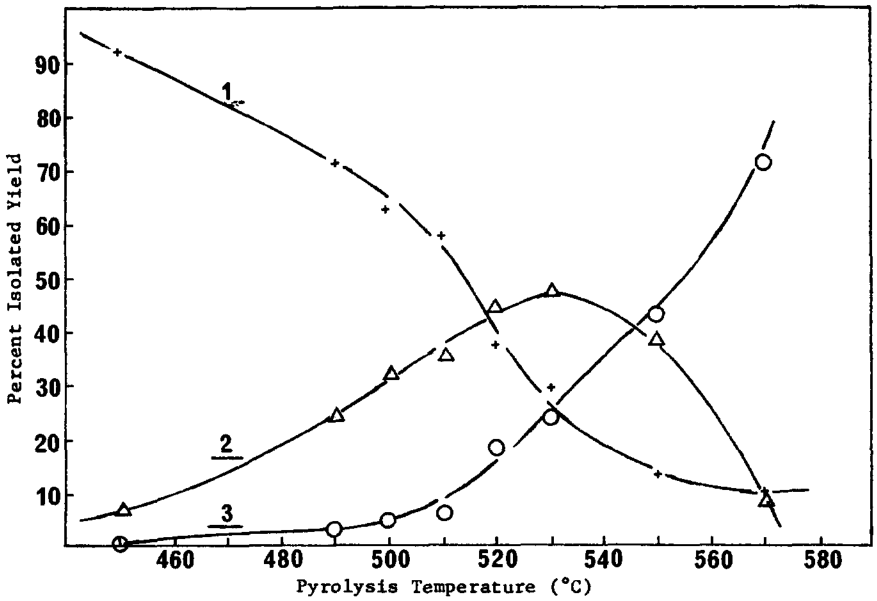
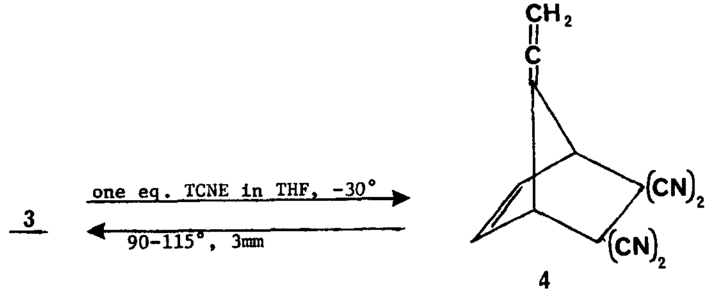


Figure. Pyrolysis of Homophthalic Anhydride (1).

Ketone 2 was identified by comparison of its gc retention time, ir and nmr spectra with those of an authentic sample prepared by the oxidation of benzocyclobutenol.[6] Physical and spectral properties of 3 agreed with the reported values.[4, 7] Fulveneallene 3 was also converted to its tetracyanoethylene adduct 4, obtained pure in 45% yield after repeated recrystallization from acetone-water. The mp, ir, 60 MHz nmr and mass spectra of 4 agreed with the reported values.[7] However the 100 MHz nmr spectrum of 4 revealed that the singlet at $\delta 5.4$ in the 60 MHz spectrum is actually an AB quartet (the chemical shift between the two protons being 7.2 cps and $J=12$ cps) arising from the geminal coupling of the two non-equivalent terminal methylene protons.

We have also found that adduct 4 constitues a stable, solid derivative of the unstable 3 from which 3 can be easily regenerated in good yield. Thus when neat adduct 4 is heated at 90-115° and three mm pure fulveneallene 3 is readily collected in a -78° cold trap. The overall process 3→4→3 proceeds in a 75% yield; adduct 4 need not be purified for this purpose.



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REFERENCES

1. For a complete description of the pyrolysis apparatus, see R. Y. Van Fossen, Ph.D. thesis, Wayne State University, Detroit, 1970.

2. Benzocyclobutenone (2) has been prepared by a multi-step sequence beginning with α,α'-dibromo-*o*-xylene[6] and by the pyrolysis of indan-1, 2-dione.[4] Fulveneallene (3) has been prepared by the pyrolysis of benzyl fluoride,[7] phenyldiazomethane[7] and indan-1, 2-dione.[4] Our yields are much better in all cases in which a direct comparison of absolute yields is possible. Furthermore, starting anhydride 1 is commercially available.

3. For a recent summary, see T. W. Bentley and R. A. W. Johnstone in "Advances in Physical Organic Chemistry," Vol. 8, V. Gold, Ed., Academic Press, New York; 1970, pp. 236-241.

4. E. Hedaya and M. E. Kent, J. Amer. Chem. Soc., 92, 2149 (1970).

5. Pyrolysis of indan-1, 2-dione produces low yields of benzocyclopropene and ethynylcyclopentadiene in addition to 2 and 3.[4] We did not detect either of these in the nmr of our hydrocarbon fraction.

6. M. P. Cava, D. Mangold and K. Muth, J. Org. Chem., 29, 2947 (1964); M. P. Cava and K. Muth, J. Amer. Chem. Soc., 82, 652 (1960).

7. P. Schissel, M. E. Kent, D. J. McAdoo and E. Hedaya, J. Amer. Chem. Soc., 92, 2147 (1970).