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ONE-STEP SYNTHESES OF FULVENE AND FULVENALLENE: THERMOLYSIS OF α-COUMARANONE, PHTHALIDE, AND BENZOCYCLOPROPENE

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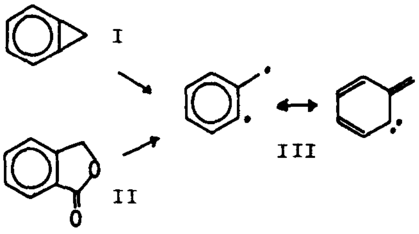
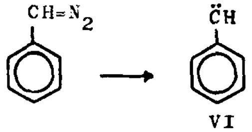
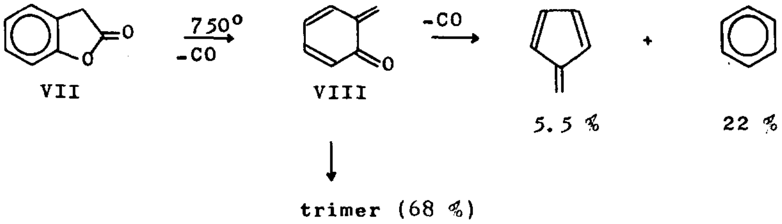
We wish to report that gas-phase thermolyses of benzocyclopropene (I) and phthalide (II) in a flow-system yields identical products, namely fulvenallene (IV),[1] ethynylcyclopentadiene (V),[1] benzene, and toluene, most probably through the common intermediate (III).[1,2] The volatile products, isolated by vacuum line distillation, had the compositions indicated:[3]

Precursor	T°C/Pmm	Products, relative yields				
		 IV	 V	$\emptyset CH_3$	$\emptyset H$	I
 I II III	515/10^{-2}	14.2	≤ 0.75	-	-	85
	590/10^{-1}	81	≤ 2	~2	~0	15
	800/10^{-2}	74	16	3	3	0
	760/10^{-2}	70	12	8	5	-
	850/10^{-2}	71	16	8	2	-
	1000/10^{-2}	9.6	25	34	32	-
 VI	590/10^{-1}	14	4.7	20	61	-
	655/10^{-1}	30	15	17.5	40	-
	800/10^{-2}	27	18	18	36	-
	850/10^{-2}	25	31	16	27	-
IV+V (1:2.6; repyrolysed twice)	1000/10^{-2}	24	76			
IV+V (1:2.6; repyrolysed 4 times)	1000/10^{-2}	20	80			

The thermolysis of I commenced at 500° with 15% conversion, largely to IV. IV is therefore considered the primary Wolff-type[4] rearrangement product of the intermediate III. Phenylcarbene (VI) from phenyldiazomethane under similar conditions gives relatively more ethynylcyclopentadiene,[5] but the preponderance of fulvenallene at moderate temperatures suggests a reaction pathway similar to that of III.[2b,5d,6]

Benzocyclopropene also gave very low yields of involatile products consisting of anthracene, phenanthrene, and stilbene. Anthracene and stilbene are also formed from phenylcarbene[5b,c] but do not require the rearrangement III ⟶ VI, since benzocyclopropenes are known to dimerise both head-to-head and head-to-tail under mild conditions.[7] Dimerization of III to anthracene has previously been suggested.[8]

α-Coumaranone (VII), an isomer of phthalide, gave at temperatures $>$ 700° and 10^{-3}-10^{-1} mm entirely different thermolysis products: CO, fulvene, benzene,[9] and a trimer[10] of the intermediate[11] VIII:



On-line distillation of the pyrolysate gives a solution of pure fulvene in benzene which, despite the low yield, presents the most convenient way to obtain small quantities of fulvene for chemical reactions (α-coumaranone is commercially available). The pyrolysis yield increased with the temperature (at 800°: 88% benzene + fulvene) but at the same time the ratio of fulvene to benzene decreased (3:97).

The thermolytic difference between α-coumaranone and phthalide is readily explained by the estimated thermochemistry.[12]

References and Notes

1. (a) These products have previously been obtained by the related thermolyses of indane-1,2-dione,[1b] benzocyclobutenone,[1b] homophthalic anhydride,[1c] indazole,[1d] 1,2-diethynylcyclopropane,[1e] and bicyclo[3.2.0]hepta-1,4,6-triene.[1e,f] (b) E. Hedaya and M.E. Kent, J. Amer. Chem. Soc. 92, 2149 (1970); (c) R.J. Spangler and J.H. Kim, Tetrahedron Lett. 1972, 1249; (d) W.D. Crow and M.N. Paddon-Row, Tetrahedron Lett. 1972, 3207; (e) R.G. Bergman, Accounts Chem. Res. 6, 25 (1973); (f) T.J. Henry and R.G. Bergman, J. Amer. Chem. Soc. 94, 5103 (1972).

2. (a) U.E. Wiersum (personal communication) has also observed the formation of fulvenallene from phthalide.[2b] (b) U.E. Wiersum and T. Niewenhuis, Tetrahedron Lett. 1973 (in the press).

3. The degree of conversion of phthalide was low: at 760° 95% starting material was recovered; at 900° 80%. Two other minor products were phenylacetylene and benzaldehyde (at 850°/0.15 mm: 0.35 and 7 %, resp., of the volatile fraction (identified by VPC/IR,UV,MS)).

4. Cf. C. Wentrup and W.D. Crow, Tetrahedron 26, 3965 (1970); O. Süs, H. Steppan and R. Dietrich, Liebig's Ann. Chem. 617, 20 (1958), and earlier papers.

5. (a) Relative yields reported by Hedaya at al.[5b] are different from ours,[5c] but the same trend is strongly apparent. For a discussion see 5(d). (b) P. Schissel, M.E. Kent, D.J. McAdoo and E. Hedaya, J. Amer. Chem. Soc. 92, 2147 (1970); (c) C. Wentrup and K. Wilczek, Helv. Chim. Acta 53, 1459 (1970); (d) C. Wentrup, Tetrahedron (submitted for publication).

6. A Similar conclusion has been reached by Dr. Wiersum: H.J. Hageman and U.E. Wiersum, Chem. in Britain 9, 206 (1973); and private correspondance with Dr. Wiersum.

7. B. Halton, Chem. Rev. 73, 113 (1973), and references therein.

8. H. Schüler and E. Lutz, Z. Naturforsch. 16a, 57 (1961).

9. Fulvene itself isomerised only slowly to benzene above 800°: pyrolysis of a 12% solution of fulvene in benzene at 810° decreased the fulvene content by 2 %; at 950° by 7.5 % (cf. also ref.[1f]). It appears therefore that benzene is formed directly in the α-coumaranone pyrolysis.[12]
10. m.p. 184-85° (col. plates from ether/petrolether). Anal. calc. for C_7H_6O: C, 79.22; H, 5.70 %. Found: C, 79.43; H, 5.68 %. Mass spectrum: M^+ 318 (in the crude product some tetramer and pentamer was also apparent in the mass spectrum).
11. Cf. O.L. Chapman and C.L. McIntosh, Chem. Commun. 1971, 383; H.E. Holmquist, J. Org. Chem. 34, 4164 (1969).
12. C. Wentrup, following publication.