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The Preparation of Perhalogenopentafulvalenes utilising a Palladium Catalyst

EDWARD W. ABEL and GRAHAM M. PRING

Department of Chemistry, University of Exeter, Exeter EX4 4QD, U.K.

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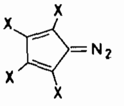
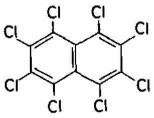
We have recently been interested in tetrahalogenodiazocyclopentadienes (I and II) as sources of perhalogenocyclopentadienyl ligands. We have observed that heating (I) in the absence of solvent gave a small yield of octachloronaphthalene in an explosive reaction releasing nitrogen (150 °C).

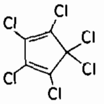


I: X = Cl
II : X = Br



III

The temperature at which this reaction occurred was considerably reduced in the presence of iron(II) iodide, to the melting point of (I) (109 °C). An explosion has previously been reported when (I) was heated with triphenylphosphine above 90 °C, but no products were isolated [1]. There is a precedent for the formation of octachloronaphthalene (III), with its six-membered rings, from such a five membered ring precursor in the thermal dechlorination of hexachlorocyclopentadiene (IV) at 700 °C/0.1 mmHg [2].



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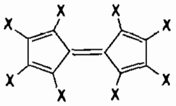


V : X = Cl
VI : X = Br

The repeat of this dechlorination at 500 °C/0.1 mmHg over iron wool however gave octachloropentafulvalene (V) [2], and it is the pentafulvalenes which we have obtained from the tetrahalogenodiazocyclopentadienes (I and II) under moderate conditions utilising bis(μ-chloro-π-allylpalladium) as a catalyst. Octachlorofulvalene (V) and octabromofulvalene (VI) have been prepared previously by the reductive coupling and dehalogenation of the corresponding hexahalogenocyclopentadiene [3–5]. In the case of the bromide the product was rapidly decomposed in the preparation conditions, resulting in yields of 5–7% [5].

Although fulvalene itself has been spectroscopically characterised in the photolysis of diazocyclopentadiene in a solid fluorocarbon–ether matrix at 77 K [6a] and in a solid nitrogen matrix [6b], there has been no previous report of the preparation and isolation of fulvalenes via diazocyclopentadienes. McBee *et al.* have noted that the catalysed decomposition of tetrachlorodiazocyclopentadiene (I) in the presence of alkynes gives not the expected spiro[2.4]heptatrienes, but spiro[4.4]nonatetraenes and tetrachlorocyclopentadienone azine. No fulvalene was reported [7].

Experimental

All reagents were prepared by literature methods: hexabromocyclopentadiene from hexachlorocyclopentadiene by halogen exchange [5, 8], the tetrahalogenodiazocyclopentadienes from the appropriate hexahalogenocyclopentadiene, [9] (Cl) [10] (Br), and bis(μ-chloro-π-allylpalladium) from palladium(II) chloride and 3-chloropropene [11]. Reactions were carried out routinely under nitrogen.

Formation of Octachloronaphthalene

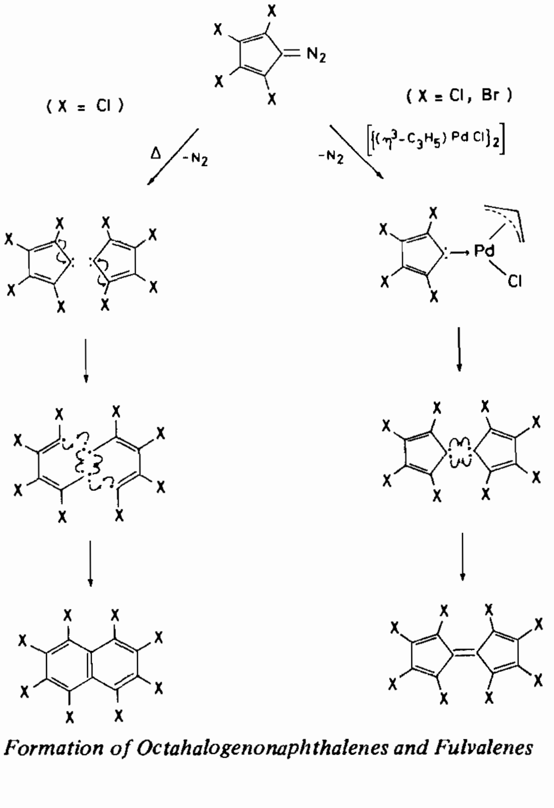
Tetrachlorodiazocyclopentadiene (I) was slowly heated under nitrogen in a glass tube. At a temperature of 150 °C an explosive reaction occurred covering the walls of the tube with dark residue. Extraction with hexane and chromatography on grade II alumina gave octachloronaphthalene (III) as almost white needles. The product was characterised by comparison of U.V. and mass spectra, and by a mixed melting point (196 °C), with an authentic sample. Repeating the experiment in the presence of intimately mixed iron(II) iodide reduced the explosion temperature to 109 °C, and gave a comparable yield of the octachloronaphthalene.

Catalytic Syntheses of Perhalogenopentafulvalenes

A small amount (~0.1 g) of bis(μ-chloro-π-allylpalladium) was stirred in hexane (10 cm^3) at 0 °C for ten minutes before a solution of the tetrahalogenodiazocyclopentadiene (I or II) at 0 °C was added. The orange mixture was then stirred, gradual darkening took place with the formation of the fulvalene on the vessel walls. The progress of the reaction was conveniently followed by observing the disappearance of the ν(NN) peak at 2100 cm^{-1} in the infrared spectrum. Best yields and products were obtained if the temperature was maintained at 0 °C, reaction times being 40 and 100 hours respectively for (V) and (VI). Upon completion, octachlorofulvalene (V) was recrystallized from hot hexane (77% yield). *Anal.* Calcd. for $C_{10}Cl_8$: C, 29.7; H, 0.00: Cl, 70.2%. Found: C, 29.6; H, <0.2; Cl, 69.1%. Octabromofulvalene (VI) was chromatographed on a short, wide grade II alumina column in a 1:1 hexane–chloroform solution (39% yield). *Anal.* Calcd. for $C_{10}Br_8$; C, 15.8%. Found C, 15.4%. Both products were also characterised by their mass spectra, and the excellent agreement of their infrared and ultraviolet spectra with literature data [5].

Discussion

Diazocyclopentadienes, by loss of nitrogen, are known precursors of carbenes, and reactions of tetrachloro- and tetrabromocyclopentadienylidene with olefins, acetylenes, benzene, carbon tetrachloride *etc.*, have been reported [7, 10, 12, 13]. The formation of naphthalene and fulvalenes respectively from the non-palladium and palladium routes are illustrated in the scheme below. The naphthalene appears to be a result of concerted carbene ring opening and bond formation, and the fulvalenes via initial complexation of the carbene to the organopalladium catalyst.

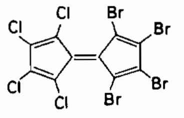


Formation of Octahalogenonaphthalenes and Fulvalenes

The mass spectra of the perhalogenonaphthalene and fulvalenes show considerable similarities, especially in their preference to lose even numbers of halogen atoms, presumably due to the simultaneous breaking of corresponding pairs of carbon–halogen bonds in the two rings of each compound [14, 15].

The perhalogenofulvalenes do not melt upon heating, but undergo polymerization at 200 °C (chloro) and 170 °C (bromo). We find an average value of 15 units for the yellow chloro polymer [16] by molecular weight determination, though high pressure liquid chromatography shows that several products are present.

Our described catalytic method of fulvalene preparation has been utilized to prepare a mixed halogen-substituted pentafulvalene, 2,3,4,5-tetrabromo-$2^1,3^1,4^1,5^1$-tetrachloropentafulvalene (VII), from an equimolar mixture of (I) and (II).



VII

The mass spectrum of the product mixure showed the products $C_{10}Br_8$, $C_{10}Br_4Cl_4$ and $C_{10}Cl_8$ in approximately the expected ratio 1:2:1. In addition to the known absorption maxima of $C_{10}Br_8$ and $C_{10}Cl_8$, the ultraviolet spectrum of the mixture showed a new peak in cyclohexane at 401 nm due to (VII). We have been unable to separate a pure sample of the unsymmetrical fulvalene, even with high performance liquid chromatography. This was largely due to the formation of charge transfer complexes in many solvents, where perhalogenofulvalenes act as strong, but sterically hindered π-acceptors [16, 17].

Acknowledgements

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