

Photoisomerisation Reactions of 5,6,7,8-Tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene: Tetrafluorobenzene in Mass Spectrometry¹

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THE reaction between tetrafluorobenzene and benzene² produces 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene (I) in high yield. In view of the current interest in the photochemistry of olefins and aromatic compounds,³ and the recent publication of the photoisomerisations of compounds related to (I),⁴ we now report some of our results for the photoisomerisation of compound (I).

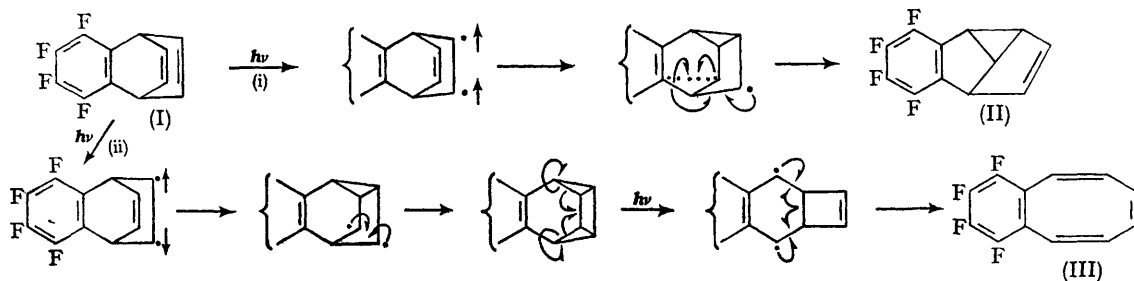
The irradiation of a 1% solution of (I) for 5 hr. in pentane containing acetone (4%), using a Hanovia medium-pressure quartz lamp gave a 66% conversion to (II), together with a trace of (III). Compound (III) was also obtained in 56% conversion together with 17% of (II) after 100 hr. in similar experiments in which no sensitiser was present. Both (II) and (III) were shown to be primary products, since (III) was not produced from (II) in the presence of a photosensitiser, and (II) was not produced from (III), either in the presence or absence of a sensitiser.

The structure of (III) was shown to be tetrafluorobenzocyclo-octatetraene. Elemental analysis and molecular weight determination (mass spectrometric) showed the compound to be isomeric with starting material. Catalytic hydrogenation with 10% palladium on carbon in ethanol led to the uptake of 3 mol. of hydrogen, and this was confirmed by mass spectrometry. The u.v. spectrum of (III) shows λ_{\max} 236.5 m μ (ϵ 9280) which compares well with the spectrum of benzocyclo-octatetraene.⁵ Structurally significant peaks in the infrared spectrum are: 3010, 1650, 1640,

1620, 1520, 1012, and 742 cm.⁻¹. The ¹H n.m.r. spectrum shows a complex multiplet from τ 3.35—4.5. The mass spectrum shows the expected loss of acetylene from the molecular ion to give the stable tetrafluoronaphthalene ion.

The structure of (II) (which is formally related to that obtained with hex-3-yne and benzene^{3a}) was also established by spectroscopic studies. That (II) is isomeric with (I) and (III) was shown by analysis and molecular weight determination (mass spectrometric). Difficulty was experienced in determining the number of double bonds, but catalytic hydrogenation with 10% palladium on carbon in benzene led to the slow uptake of 1 mol. of hydrogen. The presence of one double bond was confirmed by the isolation of a stable, crystalline, 1:1 adduct with phenyl azide. The ultraviolet spectrum of (II) is similar to that of (I), the expected λ_{\max} at 219 m μ being obscured by the benzenoid absorption. The infrared spectrum showed the following significant peaks: 3060, 3040, 2980, 2935, 1640, 1500, and 750 cm.⁻¹. The ¹H n.m.r. spectrum showed multiplets at: τ 4.37 (1 proton), 4.75 (1 proton), 5.93 (1 proton), 6.73 (2 protons), and 7.23 (1 proton); and the ¹⁹F n.m.r. spectrum showed multiplets at: ϕ 146.2 (1 fluorine), 149.8 (1 fluorine), and 159.8 (2 fluorines). Whereas semibullvalene undergoes rapid Cope rearrangements,^{4a} (II) cannot.

Although at low temperatures the molecular ion peak and expected fragmentation was observed in the mass spectrum of (II), this was completely



absent when the sample was directly inserted into the ion chamber at $\sim 80^\circ$. The molecular ion peak observed was at m/e 374, and an accurate mass measurement showed that this ion corresponds to $[C_{18}H_6F_8]^+$. An ion at m/e 148 is present in this spectrum but absent in the former spectrum. These results lead us to suggest that (II) can fragment to give tetrafluorobenzynes, and that this attacks (II) to yield eventually the ion at m/e 374.

Our photoisomerisation results are most easily explained by assuming that compound (II) arises from the triplet state, and (III) from the singlet state. Self sensitisation and intersystem crossing could account for the slow production of (II) in our photolyses in the absence of a photosensitiser. The scheme shows possible mechanisms which could account for the production of (II) and (III).

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