Photoisomerization of 1,2,4-Trifluorobenzene

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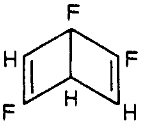
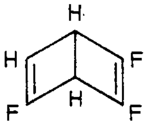
Summary Two photoproducts from the photoisomerization of 1,2,4-trifluorobenzene, probably of excited singlet origin, have been isolated and characterized as being trifluorinated "Dewar benzenes."

IN a previous study,[1] it was reported that in excitation of 1,2,4-trifluorobenzene(I) with 254 nm radiation the sum of fluorescent and phosphorescent quantum yields did not exceed 0·07. We now report that irradiation of (I) at 253·7 nm in the vapour phase, gives small quantum yields ($2{\cdot}0 \times 10^{-4}$—10^{-3}, depending on conditions) of only two major products, (II) and (III).

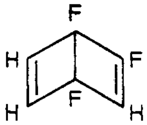
Separation and analyses were done by temperature-programmed g.c. using a 3·3 m DIDP column and helium carrier. (II) and (III) each shows its molecular ion at *m/e* 132 ($C_6H_3F_3^+$) in the mass spectra. The u.v. absorption spectra of (II) and (III) indicate no maxima at $\lambda > 210$ nm (ϵ_{210} *ca.* 300). The i.r. spectra of the vapours showed bands at 3120 (=C–H), 3018 (C–bridgehead H), 1645 (HC=CF), and 1325 cm^{-1} (=C–F) for compound (II), and bands at 3120 (=C–H), 3008 (C–bridgehead H), 1760 (FC=CF), 1650 (HC=CF), and 1319 cm^{-1} (=C–F) in the case of compound (III). The ^1H n.m.r. spectrum of (II) displayed three signals of equal intensity at τ 6·3 (bridgehead H), 4·3, and 4·7 p.p.m. (FC=C*H*); while that of (III) had three signals at τ 4·6 (FC=C*H*), 6·2, and 6·3 p.p.m. (bridgehead H). The sum of the intensities of the last two (τ 6·2 and 6·3) is exactly twice the intensity observed at τ 4·6 p.p.m.



(II)



(III)



(IV)

These spectral data, combined with the observation that both (II) and (III) revert quantitatively to (I) on heating, suggest that (II) is 1,2,5-trifluorobicyclo[2,2,0]hexa-2,5-diene and (III) is 2,3,5-trifluorobicyclo[2,2,0]hexa-2,5-diene.

A comparison of the spectral data obtained for (II) and (III) with those previously reported for hexafluorobicyclo-[2,2,0]hexa-2,5-diene (V)[2] and 1,2,4-trifluorobicyclo[2,2,0]-hexa-2,5-diene (IV),[3] both of which contain structural features in common with (II) and (III), shows good agreement and consistency in structural interpretation. It is significant that (IV) is not a photoisomer of (I) under the conditions of our study.

The activation energy for the formation of the "Dewar benzenes" from the ground-state benzene is approximately 80 kcal mol^{-1},[4] with ΔH *ca.* 51 kcal mol^{-1}. The triplet state energy of (I) is approximately 83·8 kcal mol^{-1}.[5] Thus, on an energetic basis alone the "Dewar" photoisomers could originate from either the singlet or triplet state of (I). The addition of 674 Torr of oxygen did not completely prevent the formation of (II) and (III) although it did decrease their yield, suggesting that (II) and (III) are formed from the excited singlet of (I) and not from the triplet. This cannot, however, be taken as a firm conclusion, as previous work[1] indicates the triplet of (I) to have a much shorter lifetime than the triplet of benzene and that in the case of benzene the oxygen quenching rate constant is approximately ten times greater for the singlet than for the triplet.[6]

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