A Novel Bridged Ferrocene Derivative[1]

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Summary Photolysis of ferrocenylsulphonyl azide in hydrocarbon solvents using 3500 Å radiation yields the novel [2]ferrocenophane (IV) in good yield; this product is not formed on thermolysis of the azide.

MUCH effort has been devoted to the stabilisation of electron deficient intermediates by transition metals.[2] We have investigated the photolysis and thermolysis of ferrocenylsulphonyl azide (I) in a variety of solvents and report the ready cyclisation of the photochemically generated nitrene (II) in benzene. Compound (I), m.p. 43°, was prepared in 76% yield from the corresponding sulphonyl chloride with NaN_3 in acetone, and had *m/e* 291 (M^+) and i.r. bands at 2100 ($-N_3$) and 1360 and 1135 cm.$^{-1}$ ($-SO_2-$).† Photolysis of (I) in benzene under nitrogen at room temperature using 3500 Å light was complete in 3 hr. and gave ferrocenyl sulphonamide (III)[3] (14%), m.p. 171—172°, and a reddish-brown product (67%), m.p. 170—171°, which was characterised as [2]ferrocenophanethiazine 1,1-dioxide (IV) on the basis of the following evidence. The mass spectrum showed a molecular ion at *m/e* 263 and the analytical data confirmed the formula $C_{10}H_9FeNO_2S$. While λ_{max} (EtOH) 470 nm. (ϵ 309) is suggestive of cyclopentadienyl rings joined by a two-atom bridge,[4] the n.m.r. spectrum ($CDCl_3$) was definitive: it consisted of two pairs of triplets, and a broad singlet at τ 2·67. One pair of triplets was centred at

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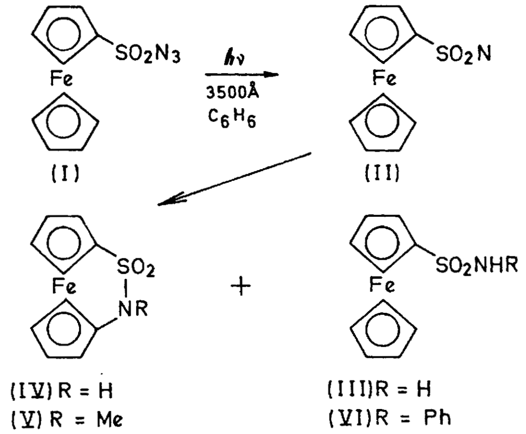
† All new compounds have been fully characterised.

τ 5·89 and 5·70 (J 2 Hz) and the other at τ 4·40 and 4·25 (J 2 Hz). These are A_2B_2 patterns associated with the monosubstituted cyclopentadienyl rings, the downfield pair being assigned to the ring bearing the sulphonyl group. The singlet (NH) at τ 2·67 disappeared on exchange with D_2O. The integral ratio was 2 : 2 : 2 : 2 : 1 as required by (IV). Methylation of (IV) with dimethyl sulphate and NaOH gave the *N*-methyl derivative (V) (73%), m.p. 176—178°; n.m.r. spectrum: two pairs of A_2B_2 triplets at τ 4·55, 5·02 and 5·59, 5·76 (J 2 Hz), respectively, and a singlet (*N*-CH_3) at τ 6·97, in the ratio of 2:2:2:2:3. The spectrum was unaffected by D_2O. No product of inter molecular arylation, ferrocenylsulphonylanilide (VI), m.p. 188—190°, was formed in the photolysis. Compound (IV) was also obtained in 13 and 43% yields, respectively, from the photolysis of (I) in cyclohexane and cyclohexene.



A number of sulphonyl nitrenes have been shown to cyclise to the corresponding sultams[5] but in all cases the cyclisation has been *thermally* induced and, as such, reasonably ascribable to the singlet nitrene.[6] On the other hand, thermolysis of (I) in benzene gives mainly the hydrogen abstraction product (III) with no detectable quantities of (IV), though other experiments show (IV) to be stable under the conditions of the thermolysis. This suggests that the sulphonyl nitrene is complexed with the metal in the thermolyses (the decomposition of methanesulphonyl azide in aromatic solvents in the presence of an iron carbonyl leads to an appreciable increase in the amount of hydrogen-abstraction product compared with the reaction in the absence of metal[7]). It is not clear whether the cyclisation involves a singlet or a triplet nitrene. Attempts to use sensitised photolyses as a probe of the spin state of the intermediate did not clarify the picture.‡ The hypothesis that the thermolysis involves a metal–nitrene complex while the photolysis involves a free sulphonyl nitrene is being tested further.

We thank the National Research Council of Canada for financial assistance and the Public Health Service for a grant (to R.A.A.).

(*Received, October,* 13*th*, 1969; *Com.* 1552.)

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‡ Photolyses in the presence of sensitisers suggest, but do not require, the intermediacy of a triplet nitrene. The picture is complicated further by the fact that ferrocene is a very efficient triplet quencher as well as a sensitiser.[8]

[1] Presented at the IVth International Conference on Organometallic Chemistry, Bristol, 1969, Abstract G. 4.

[2] For a recent critical discussion, see M. L. H. Green, in "Organometallic Chemistry, Vol. II. The Transition Elements," 3rd edn., Methuen, London, 1968.

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