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FLUORENE-9-SPIROCYCLOPROPANE FROM FLUOREN-9-ONE AZINE.

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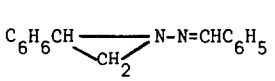
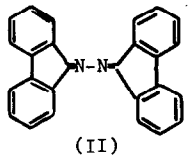
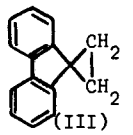
The reaction of benzalazine with dimethyloxosulphonium methylide gives 1-benzaldimino-2-phenyl aziridine (I).[1,2] Equimolar amounts of fluoren-9-one azine (II)+ and dimethyloxosulphonium methylide, reacted together by the method of Corey and Chaykovsky,[3] gave back 85% of the azine but with excess dimethyloxosulphonium methylide fluorene-9-spiro-cyclopropane (III) was obtained in 70% yield, m.p. 70-70.5°C (Lit.[4] 71.5°C), picrate m.p. 138.5 - 139°C (Lit.[4] 139.5°C). N.m.r. ($CDCl_3$, δ p.p.m.): 1.33 (singlet, 4H); 6.63-7.70 (multiplet, 8H).



(I)



(II)

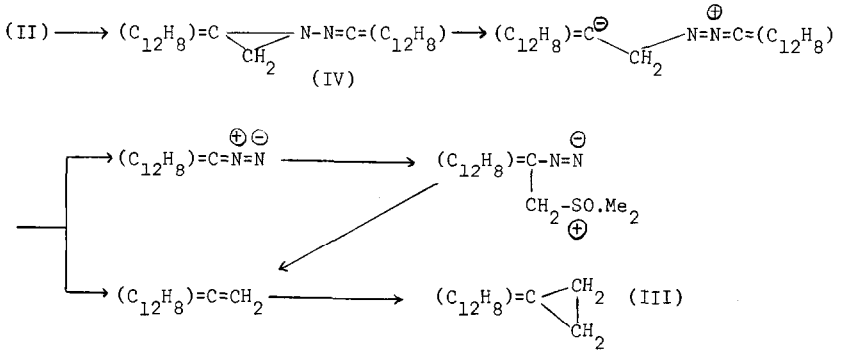


(III)

The reaction of benzophenone and sodium methylsulphinyl methide at elevated temperatures has given a 1% yield of 1,1-diphenylcyclopropane.[5] When fluoren-9-one azine (II) and sodium methylsulphinyl methide were mixed together at room temperature no reaction took place over three days but the cyclopropane (III) formed rapidly when the ylide precursor, trimethyloxosulphonium iodide, was added to this mixture.

Since the yield of the cyclopropane (III) is greater than 50% both fluorene moieties of the azine molecule must lead to this product. The mechanism proposed for this reaction is shown below. 1,2-Addition of the ylide leads to the aziridine (IV) which, by elimination of 9-diazofluorene, yields 9-methylenefluorene. More 9-methylenefluorene is then produced by reaction of the 9-diazofluorene with ylide, or by prior formation of the carbene, fluorenylidene, followed by combination of this with ylide. The olefin then reacts with excess ylide to give the cyclopropane (III).

+ Prepared in 90% yield from fluoren-9-one, hydrazine hydrate, and conc. H_2SO_4 (1 drop) in dimethylsulphoxide at 90°C for 1 hr.



Support for this mechanism is provided by the preparation of (III) from either 9-diazofluorene or 9-methylenefluorene, in 35% and 100% yield respectively, when these compounds react with dimethyloxosulphonium methylide.

The cyclopropane (III) may also be obtained, in 60% yield, by reacting the azine (II) with dimethylsulphonium methylide, the mechanism for this reaction being, no doubt, similar to that proposed for the previous reaction.

The reactivity of 9-methylenefluorene towards both ylides can be compared with that of 1,1-diphenylethylene which is reported to react only with dimethylsulphonium methylide yielding 1,1-diphenyl cyclopropane.[3]

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