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Photochemical Reaction of 9-Bromo-Fluorene

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With a view to examining the photochemical behaviour of some typical aromatic halogenated compounds, irradiation of 9-bromo-fluorene was done in benzene and toluene which led to produce two fluorenone derivatives in each case.

INTRODUCTION

Consequent to the discovery that one of the sereoisomers (gammexane) from the group of hexachlorocyclohexanes obtained by chlorination of benzene is an excellent insecticide, and later observations that photochemical reactions of organic halides can be employed for the synthesis of naturally occurring compounds such as tetracyclines, considerable interest has been shown in the past few years both in the photohalogenation of organic halides. With this view, photochemical reactions of 9-bromo-fluorene was done in different solvents.

EXPERIMENTAL

Preparation of 9-bromo-fluorene (I): 9-bromo-fluorene (I) was prepared by reacting bromine (80 g) with flourene(8.3 g) according to the procedure detailed in literature (I). Yield 6 g, m.p. 103°C (Lit. m.p. 103–104°C).

Irradiation of 9-bromo-fluorene (I) in benzene: A solution of 250 mg of 9-bromo fluorene (I) in 60 mL benzene was irradiated in a 250 mL flask made of quartz glass fitted with a guard tube (air not excluded) using light from 125 W medium pressure mercury arc kept at a distance of 15 cm from the flask. After 4 h, the solvent was removed and photolysate was put on a column of silica gel (10 g, slurry packed in pet. ether). Elution with 100 mL pet. ether gave 250 mg of a solid residue, TLC test indicated it to be a mixture of two compounds (benzene-pet. ether-chloroform-ethyl acetate, 12 : 6 : 1 : 1, R_f 0.67 and 0.6).

The mixture was rechromatographed over silica gel (10 g, slurry packed in pet. ether). Elution with 100 mL of pet. ether furnished first in very minute quantity a yellow solid, m.p. 210°C. This contained bromine as revealed by elemental test and was not further investigated.

Subsequent elutions with 509 mL of pet. ether yielded a solid residue. TLC on this indicated it to be a mixture of two compounds (benzene-pet. ether-ethyl acetate-chloroform, 12 : 6 : 1 : 1, R_f 0.67 and 0.6). Later elution with 100 mL of solvent furnished 80 mg of second light yellow crystals, m.p. 150°C (III or IIIa). This did not give test for bromine. Its phenyl hydrozone melted at 120°C. λ_{max}(MeOH) 261, 297 nm; ν_{max} (nujol) 1720 cm^{-1} (s), 160 cm^{-1} (s).

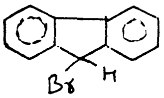
Irradiation of 9-bromo-fluorene (I) in toluene: A solution of 300 mg of 9-bromo-fluorene (I) in thiophene free toluene was irradiated for a total period of 24 h under similar conditions as done in case of irradiation of (I) in benzene.

Finally toluene was removed under reduced pressure and residue was chromatographed over silica gel (15 g, slurry packed in pet. ether). Column was allowed to stand for 3–4 h, after feeding the reaction mixture. Elution with pet. ether (1 L) gave 15 mg of starting material (I). Further elution with 100 mL pet. ether gave 60 mg of light yellow solid (II or IIa) which after cyrstallization from benzene-pet. ether melted at 205°C. This showed single spot on TLC (benzene-pet. ether-ethyl acetate-chloroform, 12 : 6 : 1 : 1, R_f 0.67). This contained bromine as shown by elemental detection test. Its dinitrophenyl hydrazone melted at 160°C; ν_{max} (nujol) 1725 cm^{-1} (s).

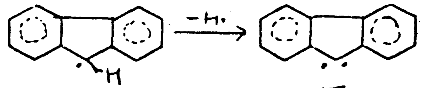
Irradiation of 9-bromo-fluorene (I) in each dry methanol and cylohexene under similar conditions showed no reaction. A parallel reactibn of (I) in the dark, in benzene or toluene, when carried out for 16 h, showed no change.

RESULTS AND DISCUSSION

With a view to examine the photochemical behaviour of some typical aromatic halogenated compounds irradiation of 9-bromo-fluorene was done which appeared to be of interest as the initial C—Br bond cleavage in this substrate under photochemical conditions was anticipated to produce resonance stabilized radicals in which radical character would extend over to the aromatic rings. A competitive pathway for radical (Ia) formed from (I) would perhaps be to generation of the respective carbene (Ib).



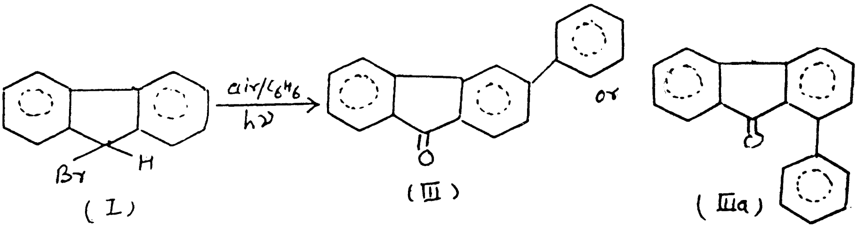
(I)



(Ia) (Ib)

To examine the behaviour of mono- radical (Ia) generated under photo-chemical conditions, the photolysis of 9-bromo-fluorene (I) was studied intially in benzene and then in toluene without excluding air. (When photolysis of (I) was done in nitrogen atmosphere, a complex inseparable mixture of many compounds was formed. Photo conversion did not appear to be smooth.)

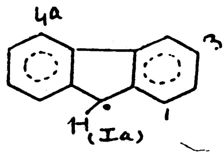
When a solution of 9-bromo-fluorene in benzene was irradiated with unfiltered light from 125 watt medium pressure mercury vapour lamp for 4 h and the resulting dark coloured mixture was chromatographed over silica gel; elution first with pet. ether gave a light yellow crystalline compound (in minute quantity), m.p. 210°C. This contained bromine as revealed by elemental detection test. Later elution with pet. ether furnished 80 mg of other yellow crystalline product, m.p. 160°C (III or IIIa). This did not contain bromine. Its IR spectrum revealed a strong



(I) (III) (IIIa)

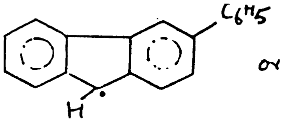
band at 1720 cm^{-1} indicative of fluorenone (2). No other bands were seen in the functional group region of the IR spectrum. In U.V. it absorbed at 261 mμ and 297 mμ. Its NMR spectrum (80 Mc, $CDCl_3$) showed the presence of only aromatic proton resonance clustered in the region δ 7.90–7.20. The mass spectrometric molecular weight of (III or IIIa) was seen as 256 and the presence of attached phenyl group in (III or IIIa) was revealed through intense peaks at m/e 179 $[M^+-77(C_6H_5)]$ and m/e 77 (due to supplementary fragment, C_6H_5). The mechanism of formation of III (or IIIa) from I supports the initial C_9—Br bond cleavage in (I) leading to radical (Ia) suggesting it to be fluorenone derivative having phenyl nuclear substituent.

Mechanistically, the first formed radical (Ia) from (I) will have three preferred nuclear postions (1, 3 and 4a) for the attachment fo new phenyl moiety (which comes from solvent benzene).



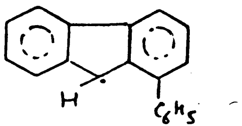
(Ia)

The attack at 4a is less likely in comparison to the available 3 and 1 positions in (Ia) due to steric reasons. Such a link up of benzene ring at C_3 or C_1 (in Ia) with loss of a hydrogen molecule (two hydrogen radicals) should lead to mono radicals (IV) and (IVa).



(IV)

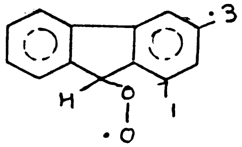
or



(IVa)

Timing and manner of oxidation at C_9 (which occurs in the photoformation of above fluorenone derivative (III or IIIa)) which takes place with aerial oxidation in solution would perhaps be that it occurs on the 9-carbene (derived from IV or IVa) through further loss of a hydrogen radical. But for the reaction of a carbene with oxygen to occur, it is imperative that carbene is in its triplet excited state since singlet carbenes are not known to react with oxygen (3).

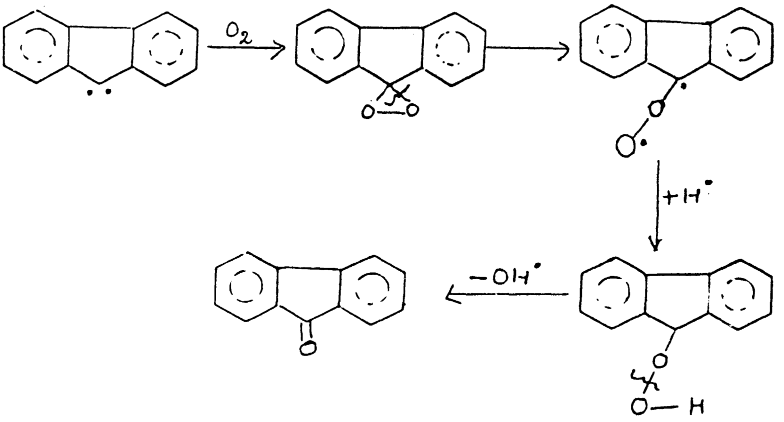
A more plausible way to the ketone (III or IIIa) from mono radical (IV or IVa) shall involve intermediacy of mone radical (A) from (IV or IVa) through addition of oxygen.



(A)

Radical (A) then through a hydrogen transfer (from C_9 to terminal oxygen atom) with concomitant O—O bond fission should produce 9-ketone (III or IIIa). The distinction with structural expressions (III or IIIa) for the derived product is however at the moment uncertain.

An alternative pathway for photo conversion of (I) into (III) (or IIIa) in benzene and air might be through the formation first of fluorenone (from I) which in its triplet excited state (which is a diradical state) adds on benzene at C_3 or C_1 in the manner of (IV) or (IVa). Such a course, however, is excluded since fluorenone is not known to display such modes of additon. It is further added that presently no unsubstituted fluorenone was detected in the photolysis mixture.

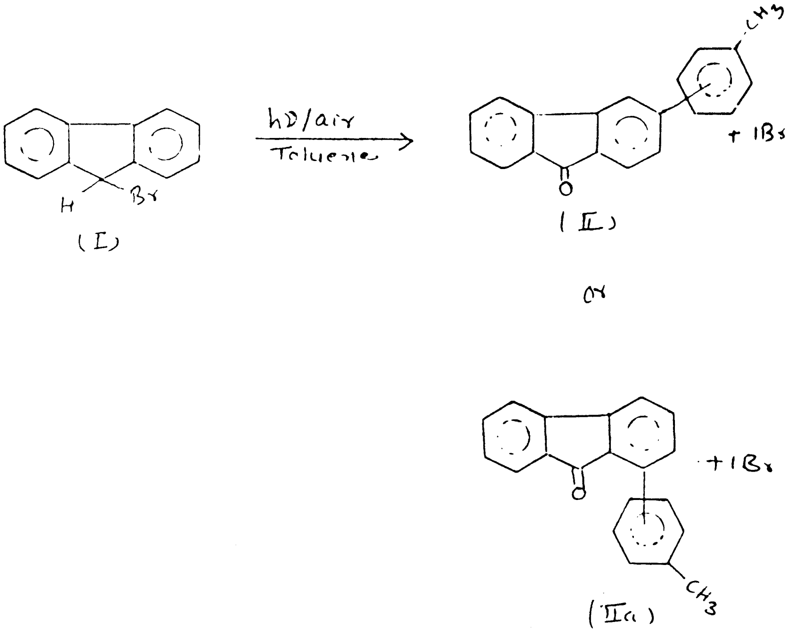


Irradiation of 9-bromo-fluorene (300 mg) was done in thiophene free toluene in quartz glass reactor for 24 h using a 125 W medium pressure mercury vapour lamp. Chromatographic work up of photolysate (silica gel) using pet. ether gave first 60 mg of bromine containing light yellow cyrstalline material, m.p. 205°C. A second crystalline compound (*ca.* 50 mg) which came later from the chromatogram (with pet. ether) melted at 150°C. This also gave a positive test for bromine.

The compound with m.p. 205°C is formed from (I) through addition of elements of toluene (the highest peak in the spectrum was located at m/e 350. The compound revealed a strong band around 1720 cm^{-1} in its functional group region of its IR spectrum which is characteristic of a fluorenone derivative (2). Its 80 Mc NMR spectrum ($CDCl_3$) showed the presence of an aromatic methyl group through a sharp singlet at δ 1.80. Other features of NMR spectrum were the aromatic proton resonances located in the region δ 8.50–7.00; in this region at the extreme left end, the presence of unresolved multiplet (between δ 8.5–8.25) is suggestive of excessive deshielding of (two) aromatic protons (due to the promixity of carbonyl group).

The compound with m.p. 205°C thus displayed features similar to that of (III) or (IIIa) derived from 9-bromo-fluorene (I) and benzene, with additional bromine atoms. So gross structure (II) or (IIa) is suggested. The postion of bromine atom in it is not ascertained yet.

Second crystalline compound, with m.p. 150°C, showed intense band around 1725 cm^{-1} in its IR spectrum indicative of the presence of fluorenone moiety in



this; no other bands were seen in the functional group region of its IR spectrum. Its mass spectrum revealed highest peak at m/e 259 (which was also the base peak of the spectrum) corresponding to loss of tolyl group (91 mass units). 80 Mc NMR spectrum ($CDCl_3$) of this compound showed bands similar to that of compound (II) or (IIa). This data alludes to the gross structure (II) or (IIa) for this compound also. The point of attachment of bromine atom in this remains as yet inconclusive.

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