# A New Photochemical Source of Aryl Radicals. Photoisomerisation of Methylbiphenyls

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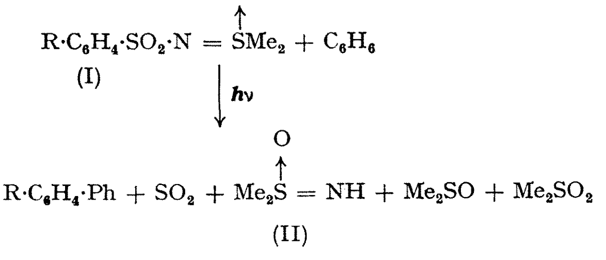
*Summary* Photolysis of *N*-arylsulphonyldimethyl sulphoximine in aromatic hydrocarbons produces aryl radicals: *o*- and *m*-methylbiphenyl undergo isomerisation upon irradiation with 2537 Å light.

IN a continuation of our studies on sulphonyl nitrenes we attempted to produce arylsulphonyl nitrenes at ambient temperatures in an aromatic solvent by the photolysis of an *N*-arylsulphonyldimethyl sulphoximine. Aryl radicals were produced instead which led to the formation of biphenyls in good yield.

Photolysis of *N*-benzenesulphonyldimethyl sulphoximine (I; R = H) in benzene (quartz vessel, 2537 Å radiation) at room temp. gave biphenyl (74·5%) with dimethyl sulphoximine (7%), dimethyl sulphoxide (0·03%), dimethyl sulphone (trace), and $SO_2$ (7%). The remaining sulphur-containing fragments have not been accounted for. No diphenyl sulphone was formed. Similarly, photolysis of (I; R = *p*-Me) in benzene gave a 79·6% yield of a mixture of 4-methylbiphenyl and biphenyl in the molar ratio of 96 : 4. Photolysis of (I; R = H) in toluene for 34 hr. gave a mixture of the methylbiphenyls (48—53%), the *o* : *m* : *p* ratio being 11·3 : 48·5 : 40·5. No biphenyl or bibenzyl was detected.



$$\underset{\text{(I)}}{\mathrm{R{\cdot}C_6H_4{\cdot}SO_2{\cdot}N}} = \mathrm{\overset{\overset{O}{\uparrow}}{S}Me_2} + \mathrm{C_6H_6} \xrightarrow{h\nu} \mathrm{R{\cdot}C_6H_4{\cdot}Ph} + \mathrm{SO_2} + \underset{\text{(II)}}{\mathrm{Me_2\overset{\overset{O}{\uparrow}}{S} = NH}} + \mathrm{Me_2SO} + \mathrm{Me_2SO_2}$$

A competitive phenylation of toluene and benzene gave a total rate ratio of 1·95. Variation of the relative ratios of the two solvents did not change ${}^{\mathrm{Me}}_{\mathrm{H}}K$ and thus no selective solvation occurs. This value is higher than that obtained (1·26—1·29) when either benzenediazonium tetrafluoroborate and pyridine[1] or benzoyl peroxide[2] are used as the source of phenyl radicals, but almost identical with the value obtained (1·99) from the photolysis of triphenylbismuth.[3] (No bibenzyl was formed in the $Ph_3Bi$ photolyses in toluene[3]). Ph· produced photochemically thus appears to be more selective (or electrophilic) than that generated thermally.

The isomer ratio in the phenylation of toluene is, at first sight, inconsistent with an attack by a phenyl radical (or by a phenyl cation). We have now found that *o*- and *m*-methylbiphenyls isomerise (see Table) under the reaction conditions to a mixture in which the *meta* predominates so that the observed isomer ratio is not necessarily a reflection of the intermediacy of a species other than a phenyl radical. It is interesting to note that no such photoisomerisation was observed with $Ph_3Bi$.[3] Isomerisation of the xylenes, mesitylene, and the di- and tri-t-butylbenzenes on irradiation is well known.[4]

TABLE

*Photoisomerization of methylbiphenyls* (2537 Å *for* 24 *hr.*)

| Starting $Me{\cdot}C_6H_4{\cdot}Ph$ | Isomer ratio (%) *o*- | *m*- | *p*- | Total yield (%) |
|---|---|---|---|---|
| *o*- | 1·70 | 64·0 | 34·5 | 50·1—58·6 |
| *m*- | 1·97 | 76·9 | 21·0 | 56·0—60·1 |
| *p*- | — | — | 100 | 87·2 |

The formation of $Me_2SO$ and $Me_2SO_2$ in the phenylation reactions can be accounted for by secondary photolysis of the initially formed $\mathrm{Me_2\overset{\overset{O}{\uparrow}}{S}{=}NH}$. Thus, irradiation (2537 Å) of a solution of the latter in $C_6H_6$ for 24 hr. gave $Me_2SO$ (10%) and $Me_2SO_2$ (0·4%): 74·5% of (II) was recovered.

The photodisproportionation of a sulphoxide has been observed.[5]

Photolysis of (I; R = H) in bromobenzene for 24 hr. gave biphenyl, and the *o*-, *m*- and *p*-bromobiphenyls in the molar ratios of 14·4 : 49·4 : 20·2 : 16·0 in very low overall yield [92% of (I) was recovered]. That this was probably not due to cleavage of (I) in this solvent was shown by irradiation of neat PhBr under otherwise identical conditions: the same four products were formed in the ratio of 4·0 : 57·0 : 23·9 : 15·1 and again the overall yield was extremely low. Seven other even more minor products were detected by gas chromatography. Photolysis of aryl bromides is known to give aryl radicals.[6]

No decomposition of (I; R = H) occurred in nitrobenzene or pyridine, the solvent probably absorbing all the radiation, or quenching excited (I) before it could decompose.

We thank the National Science Foundation for a grant.

(*Received, October 3rd*, 1969; *Com.* 1499.)

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