Photorearrangement of an Unsymmetric Azo-compound

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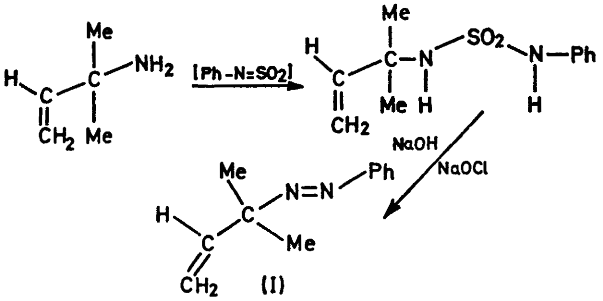
Summary Direct irradiation of an unsymmetric dimethylphenylallylazo compound leads to a new isomeric azo-compound.

ALTHOUGH the photochemistry of symmetric azo-compounds has received a considerable amount of attention in the past ten years,[1] it has only recently been recognized that the photochemistry of unsymmetric azo-compounds may be markedly different from that of their symmetric counterparts.[2] In particular, it has been proposed that alkylphenylazo compounds photodecompose by one-bond scission leading to a Ph–N=N· radical.[2] We report a photo-study of the unsymmetric dimethylphenylallylazo compound (I). Our observations of a photorearrangement of (I) to the new azo-compound (II) are compatible with the notion that Ph–N=N· radicals are generated during photolysis of (I).



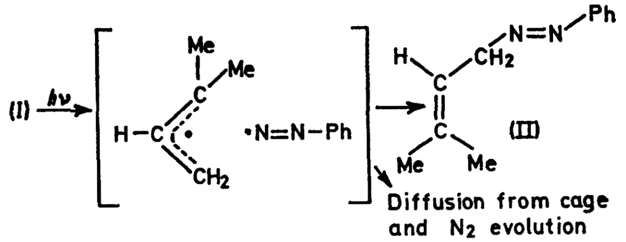
SCHEME 1

The azo compound (I) was synthesized by the route outlined in Scheme 1. *N*-Sulphonylaniline[3] was trapped with 3-amino-3-methylbut-1-ene to produce the unsymmetric sulphamide which was converted into the azo-compound by treatment with NaOCl and NaOH at 40°;[4] λ_{max} 263 (ϵ 8500) and 412 (ϵ 128), δ 1·5 (s, 6H), 4·9—6·4 (m, 3H), and 7·2—7·8 (m, 5H).†

Photolysis (436 nm) of (I) (0·05) in benzene, toluene, or cyclohexene yields a new azo-compound (II) which may be purified by preparative t.l.c.; λ_{max} 271 (ϵ 8400) and 402 (ϵ 95), the n.m.r. spectrum is consistent with the proposed structure [δ 1·7—1·9 (m, 6H), 4·5—4·7 (d, 2H), 5·2—5·6 (m, 1H), and 7·2—7·7 (m, 5H)]. (II) is air sensitive but may be stored indefinitely at −20° under nitrogen. The mass spectrum of (II) is virtually identical to that of (I) except that (II) shows a parent peak at *m/e* 174·1151 (calc. for $C_{11}H_{14}N_2$, 174·1156) whereas (I) showed no molecular ion.

In addition to the new azo-compound (II) which is isolated by t.l.c. in *ca.* 20% yield, a complex mixture of hydrocarbon products is formed (apparently from reactions of phenyl radicals and dimethylallyl radicals with each other and with the solvent). *E.g.*, in benzene the major hydrocarbon products are biphenyl and dimethylallyl radical coupling products. Photolysis of (I) (0·5M) in cyclohexene (1M) in the nitroxide scavenger, 2,2,6,6-tetramethylpiperidino-oxy-radical, did not suppress the formation of (II).

The formation of the rearranged azo-compound from photolysis of (I) contrasts with the photochemical behaviour of the symmetric azo-analogues. Azobenzenes undergo only *trans–cis* photoisomerization,[5] and the symmetric dimethylallylazo analogue of (I) is reported to photodecompose to give only free-radical coupling products,[6] no rearranged azo compound being found.



SCHEME 2

Our observations may be accommodated by the reaction mechanism outlined in Scheme 2. The formation of (II) in the presence of nitroxide and in the excellent proton-

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† (I) prepared in this way is identical to that prepared by the synthesis reported (J. E. Baldwin, *J. Amer. Chem. Soc.*, 1971, **93**, 78

donor solvent, cyclohexene, strongly suggests that the rearrangement is occurring *via* a caged radical pair. Additional support for the one-bond scission, internal return mechanism is provided by CIDNP studies which show that formation of (II) occurs from combination of the dimethylallylphenyldiazenyl radical pair.‡ These studies also show that appreciable return of the radical pair to the original azo compound (I) is occurring.

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