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# Solid State Photolysis of Triazene 1-Oxides with Naphthols. Synthesis of Azo Dyes†

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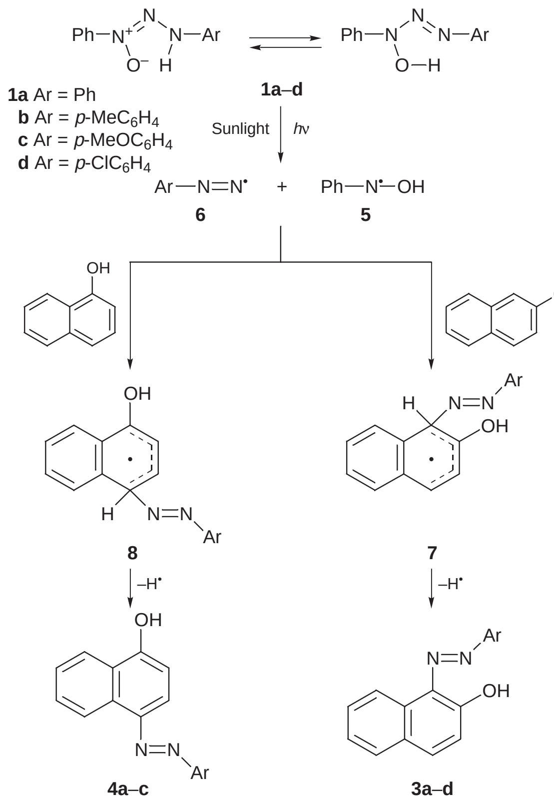
Sunlight irradiation of solid mixed crystals of the photolabile triazene 1-oxides and α- or β-naphthol afford azo dyes.

Almost all the energy received by the earth comes from the sun which is not only a cheap and continuous energy source but also has no waste product problems. As a result, solar energy applications have acquired great importance. It is well known that sunlight can be used directly in many chemical reactions and syntheses.[1]

Recently,[2] the solid state photoreactions, photoaddition, hydrogen abstraction and condensation between two different organic compounds, have been reported. Here we report our results of the solid state photolysis of mixtures of 1,3-diaryltriazene 1-oxides or α- and β-naphthols with direct sunlight.

In previous works[3,4] we have shown that the treatment of 1,3-diaryltriazene 1-oxides with oxalyl chloride in dry toluene at room temperature gave only solid arenediazonium chlorides, while their photolysis in aromatic and non-aromatic solvents, led to the formation of 2-hydroxyazobenzene, mono- and di-substituted biaryls. The aryldiazenyl radical has been postulated as an intermediate. Therefore it seemed that it was interesting to examine the possibility of the use of sunlight directly to irradiate the photolabile 1,3-diaryltriazene 1-oxides **1a**–**d** in the presence of α- and β-naphthols in the solid state hoping that azo dyes may be formed *via* coupling between the probable formed diazonium radical species and α- or β-naphthol.



**Scheme 1**

Thus, on exposure of equimolecular mixtures of the oxide and of 1-α-naphthol and 2-β-naphthol (see experimental) to sunlight, the mixtures gradually changed to deep red. The photoreactions were monitored by thin layer chromatography. After 7–10 h, the reaction mixture was dissolved in acetone and separated on a preparative thin layer chromatoplate using a 1 : 10 mixture of ethyl acetate: toluene as eluent to afford the azo dyes as the sole products. The structures of the azo dyes **3a**–**d** (83–93%) and **4a**–**c** (69–81%) were established from comparison of their melting points and their IR spectra with those of authentic samples.

The formation of the products **3a**–**d** and **4a**–**c** may arise from an initial hydrogen shift to give the tautomeric hydroxy form, which undergoes N–N bond fission forming the *N*-phenylhydroxylaminyl radical **5** and the corresponding aryldiazenyl radical **6**. The latter could attack the more active phenolic ring at the *ortho* position to give the adducts **7** and **8** which in turn may lose a hydrogen radical to afford the corresponding azo dyes **3a**–**d** and **4a**–**c**.

## Experimental

The triazene 1-oxides were prepared according to literature methods.[5] All melting points were recorded on a Galenkamp melting point apparatus and are uncorrected. Preparative TLC were carried out on air-dried 1 mm layers of silica gel Merck PF254 on plates 20 cm by 48 cm.

*Preparative Photolysis*.—Mixing of 1 mmol of triazene 1-oxide **1** with 1 mmol of α- or β-naphthol in acetone followed by evaporation gave the mixed crystals. These were finely ground in a morter, spread on petri dishes and directly exposured to sunlight. TLC examination showed that the reactions were finished within 7–10 h. The tempera-

**Table 1** Melting point and yields of **3a**–**d** and **4a**–**c**

| Compound | Yield(%) | Colour | Mp/ °C |
|---|---|---|---|
| **3a** | 91 | scarlet red | 132<br>(132–133)[a] |
| **3b** | 93 | deep red | 133<br>(133–134)[a] |
| **3c** | 83 | red | 140<br>(139–140)[b] |
| **3d** | 87 | bright red | 156<br>(155–157)[b] |
| **4a** | 73 | brown | 183<br>(182–184)[c] |
| **4b** | 69 | deep brown | 193<br>(193–194)[c] |
| **4c** | 81 | brown | 171<br>(170–172)[c] |

[a]Ref. 6. [b]Ref. 7. [c]Ref. 8.

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ture was measured as 18 to 25 °C. Chromatographic separation on silica gel with ethyl acetate: toluene (1 : 10) as eluent gave two zones. The first zone with the higher $R_f$ value gave the azo dye, and the second zone with the lower $R_f$ value (at the start) afforded a multicomponent mixture, which could neither be separated nor could individual components be identified.

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## References

1 P. Esser, B. Pohlmann and H.-D. Sharf, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2009.

2 H. Koshime and T. Matsuura, *J. Photochem. Photobiol. A: Chem.*, 1996, **100**, 85.

3 S. K. Mohamed, M. A.-M. Gomaa and A. M. Nour El-Din, *J. Chem. Res. (S)*, 1997, 166.

4 A. M. Nour El-Din, S. K. Mohamed and D. Doepp, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 131.

5 E. Bamberger, *Ber.*, 1896, **29**, 102; E. Bamberger and A. Stiegelmann, *ibid.*, 1899, **32**, 3554.

6 R. P. Lastovsk and I. Zhur, *J. Gen. Chem. USSR (Engl. Transl.)*, 1948, **18**, 921.

7 J. W. Raymond, Le Fevre and H. T. Liddicoet, *J. Chem. Soc.*, 1951, 2743.

8 R. Hempel, H. Viola, J. Morgenstern and R. Mayer, *J. Prakt. Chem.*, 1976, **6**, 983.