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SOLID PHASE PHOTOLYSIS:
PHOTOCLEAVAGE OF A STERICALLY HINDERED AZOXYBENZENE INTO ARYLDIAZONIUM AND PHENOXIDE IONS

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Recent and very elegant work by Bunce[1,2] on the photolysis of azoxybenzene (1a), o,o'-azoxytoluene (1b) and other 2,2'-substituted azoxybenzenes in solution has demonstrated the necessity of modifying the usual textbook mechanism[3] of azoxyarene photoisomerization (as given by sequence 1→2→3→7).

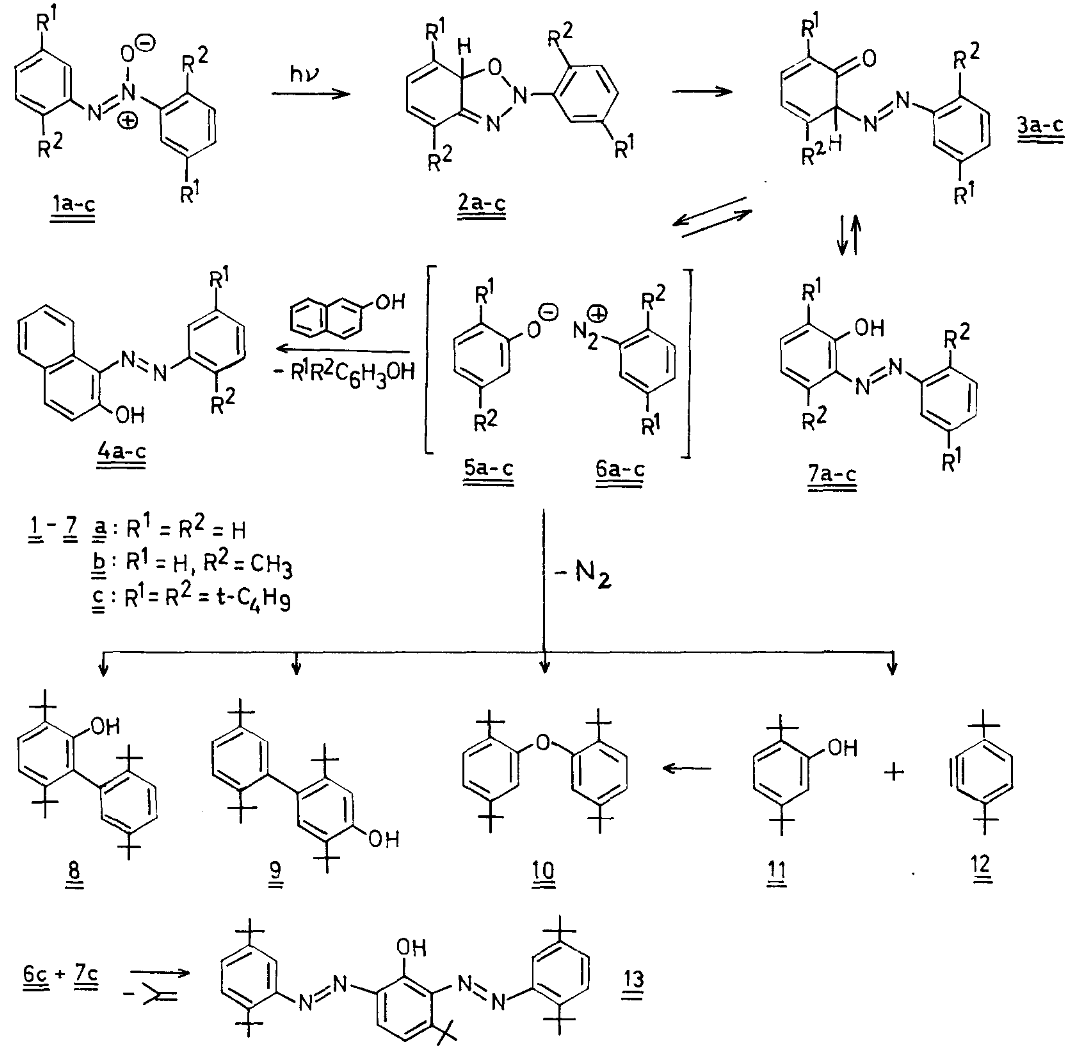
It had been shown in particular[2] that the primary intermediate 2 is rearranged preferentially to 7 (probably via 3) in solvents exhibiting some basicity through the presence of lone pairs, e. g. in ethanol, whereas cleavage of 3 into the ion pair [5,6] becomes important in solvents not containing lone pairs, e. g. in benzene. [5,6] may either undergo azo coupling to the "normal" product 7 or, after escape from the ion pair [5,6], the diazonium ion 6 may give rise to o-hydroxy bisazocompounds by secondary reaction with 7. When azoxybenzenes such as 1a,b and others are photolyzed in benzene solution in the presence of 2-naphthol, o-hydroxy arylazonaphthalenes are obtained along with liberation of the phenol corresponding to 5[1,2].

We wish to report that expulsion of diazonium ions may also be observed upon irradiation of crystalline trans-2,5,2',5'-tetra-tert-butylazoxybenzene (1c).

Sterically hindered azoxybenzenes as 1c should in general be very well suited for the investigation of the photochemistry of azoxybenzenes for the following reasons:

a) The non-coplanarity of the azoxy linkage and the benzene rings facilitates vertical attack of the azoxy oxygen on the more distant ring, thus enhanced light sensitivity compared to sterically less hindered analogues (as 1a,b), may be expected for compound 1c.

b) The tendency to expel a diazonium ion should be enhanced, and the re-coupling of the diazonium phenoxide ion pair should be retarded.



Initially colourless dilute hydrocarbon solutions of 1c[4] rapidly turn deeply yellow upon exposure to dim daylight, and crystalline 1c has to be stored in brown glass vials to prevent discolouring. From photolysis (high pressure mercury burner, light of ⩽280 nm filtered off) of 1c to 40% conversion in hexane under nitrogen 26%[5] 3,6,2',5'-tetra-tert-butyl-2-hydroxyazobenzene (7c)[6], m. p. 215°C, 2% of the cis-isomer of 1c, m. p. 186°C and 20% of a compound isomeric to starting material, m. p. 186°C (dec.) have been obtained along with some hitherto unidentified low yield products. The constitution of an α,ß-unsaturated tetra-tert-butyl-phenylazocyclopentadiene aldehyde may tentatively be assigned to the new isomer on the basis of its spectral data [IR: C=O 1660/1670 cm^{-1}, formyl-CH 2720/2820 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ = 7,52 ppm (vinyl-H) and 9.79 ppm (CHO)] .

Irradiation of powdered crystals of 1c, spread either on a polished metal sheet or on the porous glass plate of a specially designed Büchner funnel (to allow trapping of volatile products) was carried out with Osram Ultra-Vitalux 300 W lamps (combinations of high pressure mercury vapour burners and tungsten filaments) at 40 - 50°C (temperature maintained by IR output of lamps) to 25-50% conversion of starting material. In addition to 2% 7c, 18-38% of the bisazo compound 13, m. p. 152°C, were obtained. Also, four nitrogen-free products could be isolated: 3% 3,6,2',5'-tetra-tert-butyl-2-hydroxybiphenyl (8), m. p. 85°C; 13% 2,5,2',5'-tetra-tert-butyl-4-hydroxybiphenyl (9), m. p. 169°C; 2 - 14% 2,5,2',5'-tetra-tert-butyl-diphenyl ether (10), m. p. 164°C; 1% 2,5-di-tert-butylphenol (11)[7], m. p. 116°C. All new compounds gave correct elemental analyses, their spectral data were in accord with the structures shown.

When a finely powdered mixture of 4,7 mmoles of 1c, 21 mmoles of 2-naphthol and 5,0 g sodium bicarbonate was irradiated to 44% conversion of 1c, a 16% yield of 2,5-di-tert-butylphenylazo-2-naphthol (4c)[6] m. p. 130°C, was obtained along with 31% 13, 15% 8 and 2% 10. Thus trapping of 6c is possible also under the conditions used in this investigation.

All products formed in the solid phase photolysis experiments clearly demonstrate the importance of the diazonium ion expulsion pathway for the solid phase photorearrangement of 1c. Since only 2% 7c are found, neither the "normal" azocoupling pathway to form 7c via [5c, 6c] and **3c** nor the direct rearrangement of **3c** (for which a base would be required according to Bunce[2]) can be of importance for solid phase photolysis of **1c**.

Furthermore, the four nitrogen-free products, albeit in moderate or low yield, demonstrate the retarded azo coupling in the diazonium phenoxide ion pair [**5c**,**6c**]. The ether **10** may well be formed by addition of **11** to the aryne **12** or arise from direct substitution of the diazonium group in **6c** by the phenoxide **5c**, and the biphenyls **8** and **9** may well be envisaged as formed in Gomberg-Bachmann arylation of **11** by **6c**[8].

From the viewpoint of conversion of starting material, the solid phase photodecomposition reported here has to be regarded as quite efficient although the crystals become rapidly covered by more strongly light absorbing products during the course of photolysis.

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References and Footnotes:

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5) All yields given are minimum yields from extensive chromatographic separations.

6) This compound has also been obtained by Prof. N. J. Bunce from irradiation of **1c** in ethanol and benzene solution (private communication).

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