# Photochemical Behavior of 1,3-Diaryltriazene 1-Oxides

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Photolysis of the 1,3-dipolar unsymmetrical 1,3-triazene 1-oxides in aromatic and nonaromatic solvents led to their decomposition. 2-Hydroxyazobenzene, mono- and disubstituted biaryls were produced.

Our interest in the study of the chemical and physical reactivity[1,2] of the 1,3-dipolar 1,3-triazene 1-oxides towards different reagents led us to investigate their photochemical behavior in different organic solvents to obtain further information on the nature and reactivity of this system. Previously,[1,2] we have indicated that, the unsymmetrical 1, 3-diaryltriazene 1-oxides did not undergo neither 1,3-dipolar cycloaddition reactions nor the nucleophilic reaction with the electron-defficient double-bonded compounds like tetracyanoethylene (TCNE). Instead, charge-transfer complexes were formed. On the other hand, their thermolysis in heterocyclic solvents, pyridine and quinoline, led to their decomposition. Beside the products produced from the decomposition of the 1,3-diaryltriazene 1-oxides, arylated products were formed.[2] In all cases, a radical pathway mechanism was proposed.

## Results and Discussion

Irradiation of stirred solutions of 1,3-triazene 1-oxides **1a—d** in aromatic (benzene) and nonaromatic solvents (ethanol and cyclohexane), using a 125-W high-pressure mercury lamp, and chromatographic separation of the residue, gave the products, 2-hydroxyazobenzene **2** (in ethanol), *p,p'*-disubstituted biaryl derivatives **4a—d** along with **2** (in cyclohexane), and **4a—d**, *p*-substituted biaryls **5a—c** along with **2** and **4a—d** (in benzene) (see Fig. 1).

The structures of the photo-products in Fig. 1 were assigned on the basis of satisfactory analytical and physical data listed in Table 1, in addition to that of spectral analysis tabulated in Table 2. Moreover, compounds **2**, **4a—d**, and **5a—c** were established from comparison of their spectral ($^1$H NMR, IR, and MS) data and mixed melting points with those of authentic samples.

The formation of these different products may be interpreted as an initial cleavage of the 1,3-triazene 1-oxides **1a—d** with the formation of the corresponding *N*-phenylhydroxyaminyl and aryl radicals, the latter being formed via the aryldiazenyl radical (Ar–N=N$^\bullet$). Coupling of these two radicals yields nitrosobenzene and the unstable diazene Ar–N=N–H **6**, which can lose either hydrogen giving the diazenyl radical or nitrogen forming the corresponding arenes **3a—d**.

Formation of the unstable intermediate diazene **6a—d** was also proposed by Schulz et al.[3—6] who discussed the formation of various products from the thermolysis of 1-(*t*-butylazo)cyclohexyl hydroperoxide via formation of intermediate diazene.

*N*-Phenylhydroxylaminyl radical undergoes dimerization followed by loss of a molecule of water giving azoxybenzene, which was photochemically rearranged to 2-hydroxyazobenzene **2** via the primary intermediate **7**.[7,8] This photorearrangement is considered to be an intramolecular reaction resulting in the attachment of the azoxy oxygen atom to an ortho-position of the more distant aromatic ring. The transfer is believed[9,10] to be an aromatic substitution in which oxygen atoms attacks the ortho-carbon atom directly rather than first abstracting the ortho-hydrogen atom. The primary intermediate **7** had been proven to rearrange preferentially to **2** probably via **8** in solvents exhibiting some basicity through the presence of lone pairs, e.g. in ethanol, whereas cleavage of **8** into the ion pair **9** and **10** becomes important in solvents not containing lone pairs e.g. benzene. The ion pair **9** and **10** might undergo azo coupling to the normal product **2**.

It is important to take into consideration that the polarity of the solvent used has a great influence on the yield of 2-hydroxyazobenzene. The yield in ethanol is higher than that in benzene and cyclohexane as listed in Table 3. These results are in agreement with those reported by Bunce et al.[9]

On the other hand, aryl radicals abstract hydrogen from hydrogen donor solvents forming arenes and/or react with the aromatic solvent benzene and form $\sigma$-complex which may be oxidized by aryl radicals before disproportionation to afford the products **5a—c**. Dimerization of aryl radicals results in the formation of the biaryls **4a—d** (Fig. 2).

Identical results were obtained on irradiation of diaryltriazenes in nonaromatic solvents which afforded biaryls, diarylamine and aryl amines; arylation of benzene occured when benzene was used as solvent in photolysis.[11]

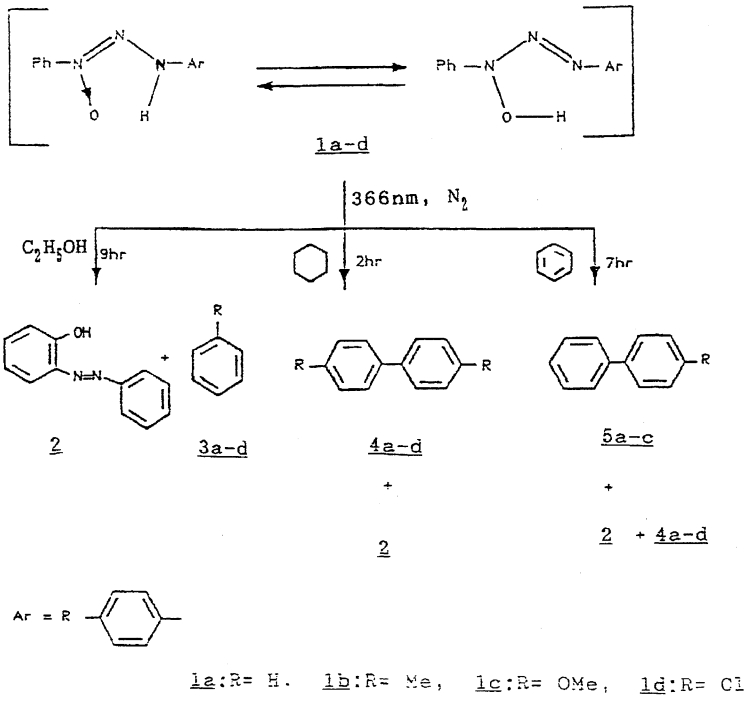


Fig. 1.

Table 1. Analytical and Physical Data of Products **2**, **4a—d**, and **5a—c**

| Compd | R | Solvent of crystallization | Mp °C (lit) | $R_f$ | Color | Molecular formula (mol.wt.) | Analysis/% Found (Calcd) C | H | N |
|---|---|---|---|---|---|---|---|---|---|
| **2** | | Ethanol | 79 (78—80)[a] | 0.83 | Orange-red | $C_{12}H_{10}N_2O$ (198.20) | 72.73 (72.71 | 5.28 5.08 | 14.10 14.13) |
| **4a** | –H | Petroleum ether | 68—70 (69—72)[b] | 0.93 | White | $C_{12}H_{10}$ (154.20) | 93.42 (93.46 | 6.58 6.54 | — —) |
| **4b** | $-CH_3$ | Cyclohexane | 119—120 | 0.91 | White | $C_{14}H_{14}$ (182.252) | 92.23 (92.26 | 7.43 7.74 | — —) |
| **4c** | $-OCH_3$ | Petroleum ether | 178—180 | 0.93 | White | $C_{14}H_{14}O_2$ (214.252) | 78.47 (78.48 | 6.62 6.58 | — —) |
| **4d** | –Cl | Cyclohexane | | 0.94 | White | $C_{12}H_8Cl_2$ (223.184) | 64.13 (64.57 | 3.70 3.61 | — —) |
| **5a** | $-CH_3$ | Cyclohexane | 44—45 | 0.93 | White | $C_{13}H_{12}$ (168.196) | 92.84 (92.82 | 7.06 7.19 | — —) |
| **5b** | $-OCH_3$ | Ethanol/ water | 87—88 (90)[b] | 0.95 | White | $C_{13}H_{12}O$ (184.196) | 84.69 (84.75 | 6.58 6.56 | — —) |
| **5c** | –Cl | Ethanol/ water | 74—75 (73)[b] | 0.922 | White | $C_{12}H_9Cl$ (188.692) | 76.31 (76.38 | 4.86 4.81 | — —) |

a) Ref. 15. b) Ref. 16.

## Experimental

Melting points were taken with a microscope/Reichert Thermovar and Griffin melting point apparatus and uncorrected. UV-vis spectra were recorded on a Perkin–Elmer 554 and Pye Unicam SP8-200 UV-vis spectrophotometers using 1.0 cm stoppered silica cells. IR Spectra were recorded on Shimadzu 470 and Perkin–Elmer 283 spectrophotometers. $^1$H NMR spectra were determined with JNM-PMX (60 MHz) JEOL and Bruker WM300 (300 MHz) instruments using TMS as an internal standard. Mass spectra were recorded on a Varian MAT 311A (EI-Mode at 70 eV). Elemental analyses were performed by the microanalytical unit at Duisburg University, FRG, using Carlo Erba Strumentazione elemental analyzer Modell 1106. Preparative TLC were carried out on air-dry 1 mm layers of silica gel Merck PF 254 on plates 20 cm by 48 cm were employed. The chromatograms were examined by UV irradiation at 254 nm. The triazene 1-oxides **1a—d** were prepared according to the literature.[12]

**Irradiation in Ethanol:** The reaction vessel is a cylindrical Pyrex tube (o.d., 8 cm; length excluding joints 25 cm), which is fitted with a 60/50 ground socket, two side arms with 14/14 standard joints, and at the center of its lower end, a sintered glass plate (diameter 2 cm; porosity No. 2) through which nitrogen can be introduced. One side arm is stoppered, and the other carries

Table 2. The $^1$H NMR, IR, and Mass Spectral Data of Compounds **2**, **4a—d**, and **5a—c**

| Compd | R | IR (KBr, $cm^{-1}$) | $^1$H NMR ($\delta$, TMS) | MS $m/z$ (rel intensity) |
|---|---|---|---|---|
| **2** | –H | 3350 (OH); 3030 (Ar–CH); 1590 (–N=N–) | 7.33—8.66 (m, 9H) Ar–H; 13.33 (s, 1H) OH | 198 ($M^+$; 46), 169 (20), 121 (30), 93 (43), 77 (46) |
| **4a** | –H | 3020 (br, Ar–CH); 1595 (–C=C–) | 7.3—7.9 (m, 10H) Ar–H | 154 ($M^+$; 63), 153 (100), 115 (22), 77 (57), 64 (39) |
| **4b** | –Me | 3010 (br, Ar–CH); 2900 (br, aliph-CH) | 7.2—7.8 (m, 8H) Ar–H; 2.5 (s, 6H) 2Me | 182 ($M^+$; 100), 167 (85), 152 (25), 91 (17), 76 (18) |
| **4c** | –OMe | 3030 (br, Ar–CH); 2885 (br, aliph-CH) | 3.86 (s, 6H) 2OMe; 6.9—7.23 (d, 4H) Ar–H; 7.5—7.8 (d, 4H) Ar–H | 214 ($M^+$; 76), 199 (78), 171 (43), 128 (27), 77 (5) |
| **4d** | –Cl | 3015 (br, Ar–CH); 1600 (–C=C–); 770 (C–Cl) | 6.96—7.21 (d,4H) Ar–H; 7.55—7.83 (d, 4H) Ar–H | 223 ($M^+$; 52), 222 (82), 152 (78), 93 (11), 75 (20) |
| **5a** | –Me | 3010 (br, Ar–CH); 2900 (br, aliph-CH); 1600 (–C=C–). | 7.3—7.9 (m, 9H) Ar–H; 2.5 (s, 3H) Me | 168 ($M^+$; 46), 167 (100), 154 (99), 91 (17), 76 (53) |
| **5b** | –OMe | 3020 (Ar–CH); 2910-2925 (br, aliph-CH), 1285 (–C–O); 1600 (–C=C–) | 3.8 (s, 3H) OMe; 7.1—7.7 (m, 9H) Ar–H | 184 ($M^+$; 52), 169 (33), 141 (26), 115 (19), 77 (1) |
| **5c** | –Cl | 3020 (br, Ar–CH) 1590 (–C=C–); 760 (C–Cl). | 7.33—7.8 (m, 9H) Ar–H | 188 ($M^+$; 100), 152 (73), 151 (26), 127 (8) |

Table 3. Yield of Products **2**, **4a—d**, and **5a—c** in Ethanol, Cyclohexane, and Benzene Produced from **1a—d**

| Compd | R | Yield/% | | |
|---|---|---|---|---|
| | | Ethanol | Cyclohexane | Benzene |
| **2** | –H | 84.6 | 10 | 14.5 |
| **2** | $-CH_3$ | 73.5 | 8.2 | 11.95 |
| **2** | $-OCH_3$ | 80.6 | 9 | 14.6 |
| **2** | –Cl | 72.5 | 7.3 | 11.7 |
| **4a** | –H | — | 17.9 | 23.2 |
| **4b** | $-CH_3$ | — | 15.2 | 19.1 |
| **4c** | $-OCH_3$ | — | 16.3 | 18.3 |
| **4d** | –Cl | — | 14.8 | 18.0 |
| **4a** | –H | — | — | 53.4 |
| **5a** | $-CH_3$ | — | — | 53.1 |
| **5b** | $-OCH_3$ | — | — | 58 |
| **5c** | –Cl | — | — | 54.3 |

an efficient stopcock which is used to control the introduced nitrogen. A solution of triazene 1-oxide **1a—d** (1 mmol) in 200—225 ml of absolute ethanol[13,14] is placed in the reaction vessel and a gentle stream of dry nitrogen (high-purity "oxygen-free" nitrogen was used) is passed through it and adjusted to prevent leakage of reaction solution through the sintered plate, and a water-cooled immersion well made of Duran glass containing a 125-W high-pressure mercury lamp is inserted.

The solution is stirred magnetically while being irradiated. The irradiation is started and the progress of the reaction can be conveniently monitored by TLC. After about 9 h (in case of ethanol) or 2 h (in case of cyclohexane) of irradiation, the conversion of the starting material is essentially complete. The solvent is removed on a rotary evaporator under reduced pressure at approximately 30 °C. The oily residue was dissolved in a small amount of acetone and separated by preparative TLC using toluene as an eluent to afford a characteristic yellow zone. Extraction of the zone with acetone gave a residue, which was rechromatographed with the same eluent and recrystallized from the suitable solvent to give an orange-red needle crystals of compound **2** (see Table 1).

**Irradiation in Cyclohexane:** A solution of 1 mmol of triazene 1-oxide **1a—d** in 200—220 ml of dry cyclohexane[13,14] (anhydrous cyclohexane of analytical purity was used) was irradiated in the same system and under the same conditions for two hours. The reaction was monitored during irradiation by TLC. The solvent was evaporated under reduced pressure and the residue separated by preparative TLC using a 1 : 1 mixture of toluene and petroleum ether (bp 40—60 °C) as eluent to afford two zones.

The two zones were extracted with acetone and rechromatographed in another eluent as cyclohexane to separate them well. The upper zone contains compound **2** and the lower one contains compound **4**. Recrystallization from the suitable solvent afforded the pure compounds **2** and **4a—d** (see Table 1).

**Irradiation in Benzene:** A stirred solution of 1 mmol of 1, 3-diaryltriazene 1-oxide **1a—d** in 200—220 ml of anhydrous benzene[13,14] was irradiated under the same conditions as above for 5 h. The reaction progress was monitored by TLC. The solvent was removed on a rotary evaporator under reduced pressure at approximately 30 °C; and the residue was dissolved in a small amount of acetone and separated by preparative TLC using a 1 : 1 mixture of toluene and petroleum ether bp 60/80 °C as eluent. Three zones were observed upon exposure to 254 nm-UV-light after drying of the plates from the eluent. The fastest-migrating

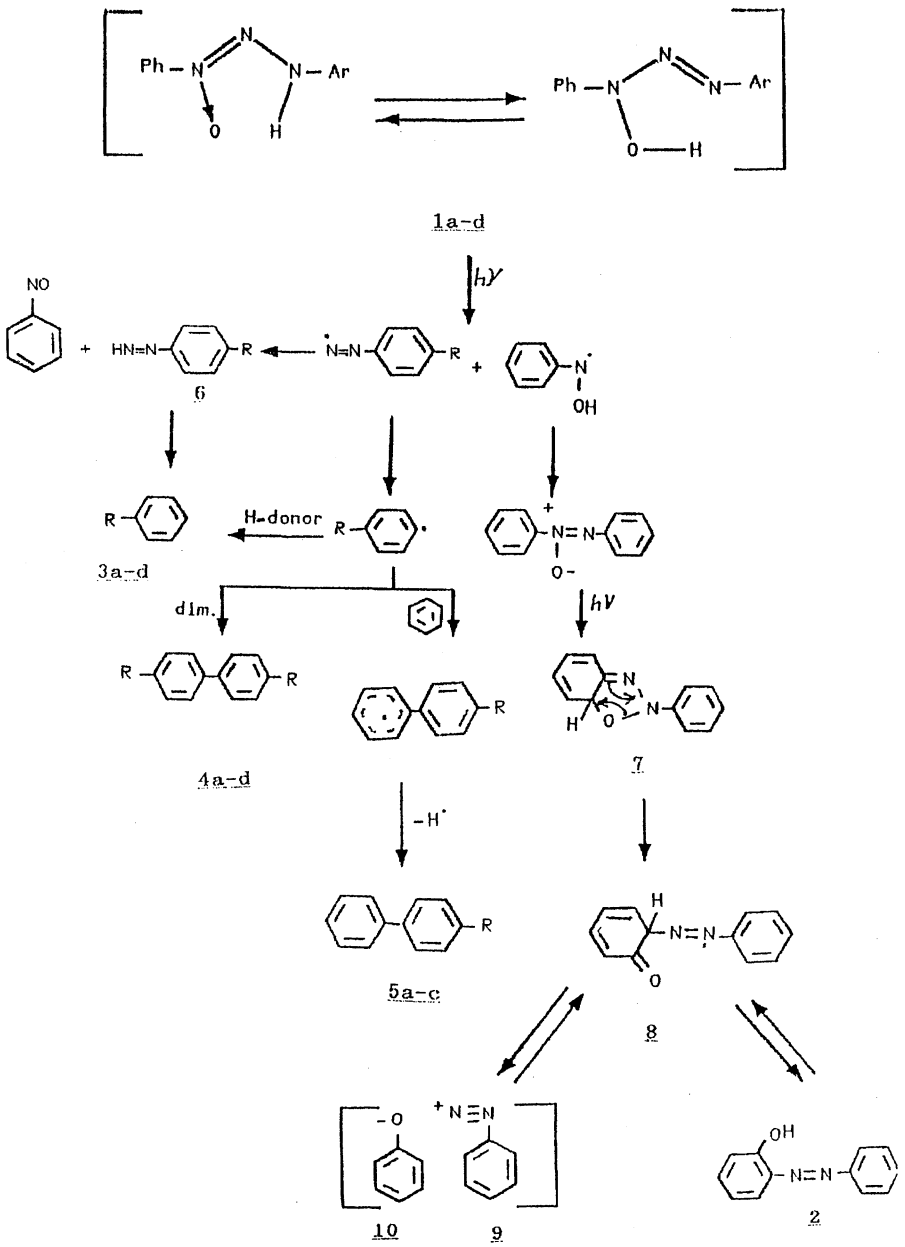


Fig. 2.

zone contains compound **5a**—**c**. It was extracted with dry acetone and rechromatographed in the same eluent. Recrystallization from the suitable solvents afforded the pure crystals **5a**—**c** as listed in Table 1. The other two slower-migrating zones were extracted with acetone and rechromatographed with cyclohexane as eluent. The upper zone was extracted and recrystallized from ethanol to afford **2** in pure orange-red needles; and the lower zone was extracted and recrystallized from the suitable solvent (see Table 1) to give the pure compound of **4a**—**d** (see Fig. 1).

The spectral data of all products were listed in Table 2 and their yields were tabulated in Table 3.

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