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Photochemistry of 3*H*-Indazoles in Protic Media. Benzyl Cations via Protonation of 2-Methylene-3,5-cyclohexadienylidenes

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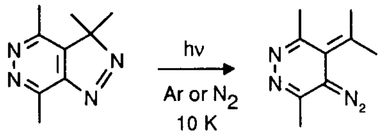
Abstract: Photolysis of 3,3-disubstituted 3*H*-indazoles in protic media (ROH) gives rise to benzyl ethers, in addition to hydrocarbons (derivatives of benzocyclopropene, styrene, and fluorene) which are also found in aprotic solvents. In the presence of ROD, the benzyl ethers are formed with incorporation of deuterium into the *ortho* position, pointing to protonation of 2-methylene-3,5-cyclohexadienylidenes. Laser flash photolysis of 3*H*-indazoles generates diazo compounds and benzyl cations as transient intermediates.

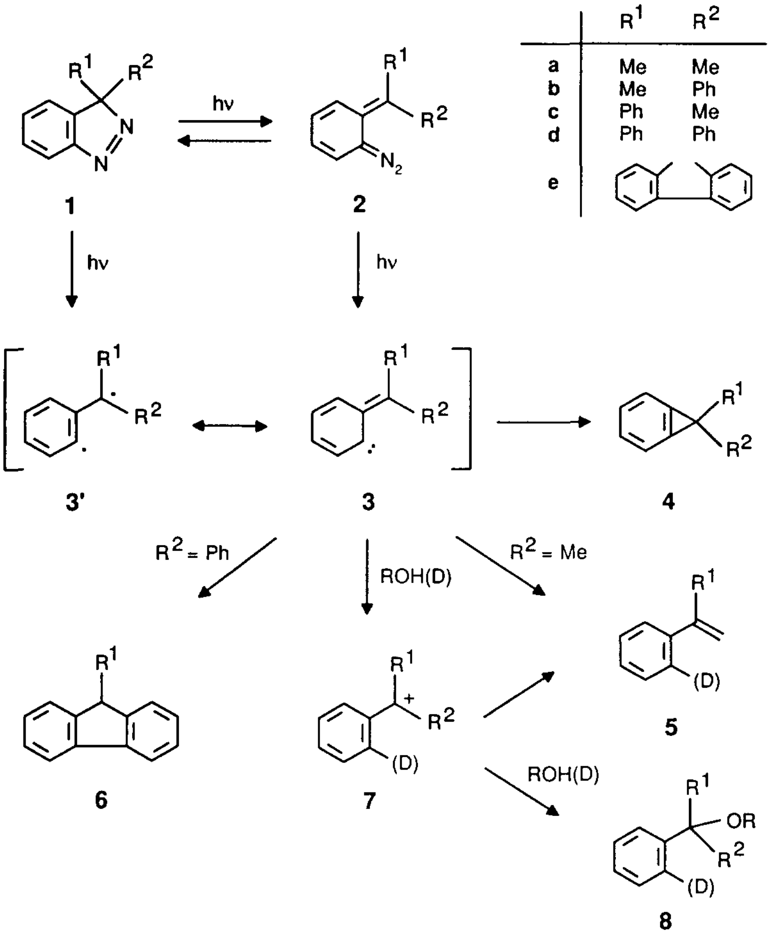
The photochemistry of 3*H*-indazoles[1] was developed by Anet[2] and by Closs[3]. Extrusion of nitrogen from **1** (R^1 and/or R^2 = Me) afforded benzocyclopropenes **4** and styrenes **5**. In the case of R^1 and/or R^2 = Ph, fluorenes **6** were obtained instead of benzocyclopropenes.[4-6] The formation of these products was explained in terms of diradicals **3'** which undergo cyclization and hydrogen transfer. The diradicals **3'** were trapped with 1,3-butadiene, and the triplet state of **3'** was detected by ESR spectroscopy at 77 K.[3] The role of intermediate diazo compounds **2** was explored recently when 3,3,4,7-tetramethylpyrazolo[3,4-*d*]pyridazine **9** was shown to give **10** on irradiation in gas matrices at 10 K.[7] Further photolysis converted **10** into analogs of **4** and **5**.



9 **10**

Our continuing interest in O-H insertion reactions of carbenes[8] prompted us to study the photolysis of 3*H*-indazoles in protic solvents. If the singlet state of 2-methylene-3,5-cyclohexadienylidenes **3** is trapped by alcohols, electrophilic attack of the carbene at the oxygen of ROH (ylide mechanism) should introduce an alkoxy group into the *ortho* position whereas transfer of a proton (carbocation mechanism) should eventually lead to benzyl ethers **8**.

When 3,3-dimethyl-3*H*-indazole (**1a**)[9] was irradiated (medium pressure mercury arc, pyrex vessel, 15°C) in methanol, 1,1-dimethylbenzocyclopropene (**4a**), α-methylstyrene (**5a**), and 2-methoxy-2-phenylpropane (**8a**) were formed in the ratio of 28:45:27. Photolysis of **1a** in MeOD afforded **8a** with incorporation of 0.97 D and **5a** with incorporation of 0.57 D (MS). In both products, the deuterium was located exclusively at the *ortho* position of the benzene ring. These results suggest that protonation of the carbene **3a** (deuteration by ROD) competes with ring closure (→ **4a**) and hydrogen shift (→ **5a**, no deuteration). The cumyl cation **7a** undergoes nucleophilic capture (→ **8a**) and deprotonation (→ **5a**). Thus the alkene **5a**, arising from both **3a** and **7a**, is partially deuterated.



In the weakly nucleophilic solvent hexafluoroisopropanol (HFIP), the cumyl cation **7a** can be detected spectroscopically.[10] Laser flash photolysis (LFP) of **1a** in HFIP was found to generate a transient whose absorption (λ_{max} = 325 nm) and reaction rates (k_{HFIP} = $4.8\pm0.3\cdot10^4$ s^{-1}, k_{MeOH} = $3.4\pm0.3\cdot10^6$ $M^{-1}s^{-1}$) are in good agreement with previous data for **7a**.[10] We also observed a broad transient absorption around 410 nm whose rate of decay (k_{HFIP} = $1.6\cdot10^6$ s^{-1}) was not affected by the addition of methanol (Fig. 1). By means of matrix spectroscopy (Ar,10K), the 410 nm absorption was correlated with an IR band at 2040 cm^{-1} and is hence assigned to the diazo compound **2a**.[11] The relative optical densities of the 325 and 410 nm absorptions were found to depend on the laser dose (Fig. 2). High light intensities favor the formation of **7a** while **2a** prevails at low light intensities; i.e., **7a** arises, at least in part, by two consecutive photochemical steps, **1a** → **2a** → **3a**, followed by protonation of **3a**.[12]

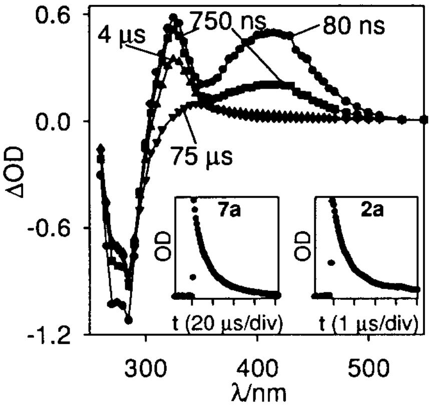


Fig. 1. Time-dependent absorption spectra obtained after laser excitation (248 nm, 20 ns, 110 mJ/pulse) of **1a** (0.44 mM) in oxygen-saturated HFIP. Insets: Decay of **7a** (at 325 nm) and of **2a** (at 410 nm).

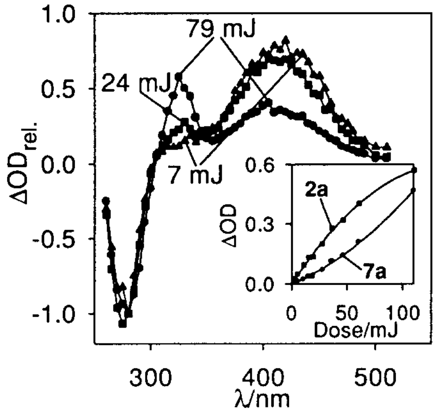
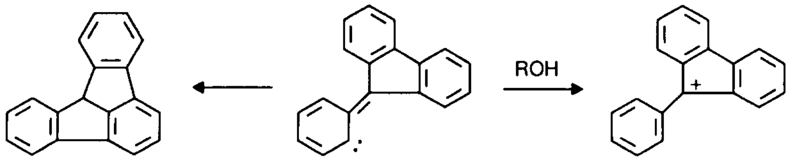


Fig. 2. Laser-dose dpendent absorptions of **7a** (325 nm) and **2a** (410 nm), recorded 70 ns after LFP of **1a** (0.24 mM), as in Fig. 1. Inset: Yields of **2a** and of **7a** as a function of the laser dose (mJ/pulse).

Similar observations were made with **1b**(=**1c**) which gave **5c**, **6b**, and **8b** (32:59:9) on photolysis in methanol. Triplet sensitization (benzophenone) had only a small effect on product distribution (19:68:13). In MeOD, **8b** was obtained with complete deuteration of one *ortho* position while only 0.24 D was found in **5c**. Employing LFP of **1b** in trifluoroethanol (TFE), we observed the transient absorption spectrum of **7b** (λ_{max} = 430 nm, k_{TFE} = $1.5 \cdot 10^5$ s^{-1}).[13] In contrast, photolysis of **1d**[14] in TFE afforded 9-phenylfluorene (**6d**) as the only product. The cation **7d** was neither trapped by ROH nor detected by time-resolved spectroscopy. It appears that the cyclization of **3d** to give **6d** proceeds too rapidly for protonation to compete. The experience with **1d** suggests that photolysis of **1b** generates a mixture of **3b** and **3c** of which only **3c** is captured intermolecularly. On the other hand, LFP of **1e**[4] in TFE gave rise to the transient absorption spectrum of the 9-phenyl-9-fluorenyl cation **7e** (λ_{max} = 490 nm, k_{TFE} = $2.0 \cdot 10^4$ s^{-1}).[15] We assume that the cyclization of **3e** is retarded, due to the substantial strain of the resulting fluoradene **11**. Thus protonation is reestablished as a competitive reaction path for **3e**.



11 **3e** **7e**

In summary, we have shown that light-induced ring opening of 3*H*-indazoles **1** is followed by photolysis of the diazo compounds **2**. The spectroscopic detection of **2** as a transient intermediate *in solution* complements the results of a recent matrix study.[7] A variety of 2-methylene-3,5-cyclohexadienylidenes **3** react with alcohols by way of proton transfer to the divalent carbon, as demonstrated by means of deuterium labels. Protonation of **3** competes with 1,3-cyclization to give benzocyclopropenes **4** and 1,4-H shift leading to alkenes **5** but is inferior in rate to 1,5-cyclization yielding fluorenes **6**. The carbocations **7**, resulting from protonation of **3**, undergo nucleophilic capture (→ **8**) and elimination (→ **5**). LFP of appropriate 3*H*-indazoles in protic media generates cumyl (**7a**), 1,1-diphenylethyl (**7b**), and 9-phenyl-9-fluorenyl (**7e**) cations whose absorption spectra and kinetics are in accordance with data from the literature.

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(12) Since **7a** has been generated by LFP of **5a** in HFIP, it might be argued that **5a** rather than **3a** is protonated in the present experiments. However, excitation of **5a** under our conditions is unlikely, owing to an excess of the strongly absorbing **1a**. In fact, addition of an equimolar amount of **5a** prior to LFP of **1a** did not enhance the yield (OD) of **7a**.

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(14) Addition of benzyne to diphenyldiazomethane, in a procedure similar to that described for diazofluorene,[4b] gave 4% of **1d**, m.p. 82-84 °C, ^{13}C NMR (CD_3COCD_3): δ = 102.27, 122.71, 125.33, 128.33, 128.78, 129.36, 130.11, 130.99, 139.11, 144.26, 157.51. $C_{19}H_{14}N_2$ (270.3): calcd. C 84.24, H 5.22, N 10.36; found C 84.52, H 5.23, N 10.35.

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