

SHORT
COMMUNICATIONS

New Photochemical Reaction in the Series of Diazofuranones

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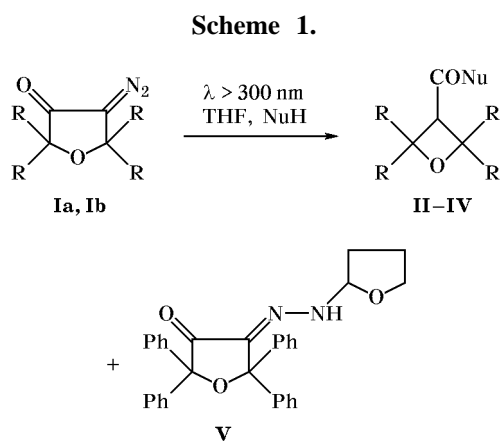
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Direct photolysis under short-wave UV irradiation ($\lambda > 210$ nm) of 2,2,5,5-tetraalkyl-4-diazotetrahydrofuran-3-ones **I** (Alk = Me, Et, etc.) in aqueous dioxane usually gives exclusively products of the Wolff rearrangement, oxetanecarboxylic acids and their derivatives; their yields are close to quantitative (90–95% and more) [1, 2]. 3-Diazo-2,2,5,5-tetraphenyltetrahydrofuran-3-one (**Ia**) behaves similarly, though short-wave irradiation of this compound in water-saturated benzene gives the corresponding oxetanecarboxylic acid **IIa** in no more than 60% yield [2].

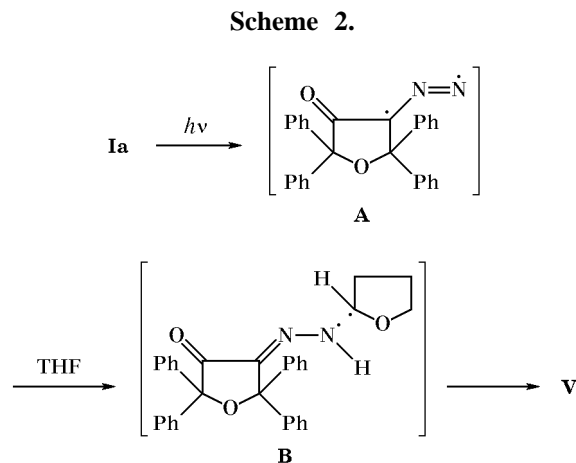
While studying photochemical transformations of diazo ketones of the tetrahydrofuran series under long-wave UV irradiation ($\lambda > 300$ nm) in THF, we have found that direct photolysis of 4-diazo-2,2,5,5-tetraphenyltetrahydrofuran-3-one (**Ia**) in the presence of various nucleophiles (H_2O , MeON, Et_2NH ; 1:10) results in formation of a mixture of usual Wolff rearrangement products (compounds **IIa–IVa**) and adduct **V** of the initial diazo ketone with THF (Scheme 1).



R = Ph (a), Me (b); **II**, Nu = OH; **III**, Nu = OMe;
IV, Nu = NEt_2 .

Compound **V** may be regarded as product of insertion of the terminal nitrogen atom of the diazo group into the α -C–H bond of tetrahydrofuran. The ratio of products **IIa–IVa** and **V** depends on the nucleophile and is approximately 1:1 in the presence of H_2O and 2.5:1 in the presence of diethylamine; the overall yield approaches 85–87%.

It should be noted that no diazo ketone adduct with THF was formed in the photolysis of tetramethyl-substituted diazo ketone **Ib** under the same conditions. In this case, only the corresponding Wolff rearrangement products **IIIb–IVb** were obtained. We presume that diazo ketone **Ia** in the excited state (**A**) abstracts hydrogen atom from the α -position of tetrahydrofuran molecule to give radical pair **B**. Recombination of the latter leads to product **V** (Scheme 2).



Carbene insertion into the α -C–H bond of tetrahydrofuran has already been reported to occur, e.g., in the photolysis of diazocyclopentadiene derivatives [3]. Nevertheless, the above transformation of diazo

ketone **Ia** is likely to be the first example of analogous reaction of diazo compounds in the excited state [4], in which the nitrogen atoms of the diazo group are retained in the final products. Taking into account that diazo compounds in the excited state can undergo the same intra- and intermolecular transformations as those typical of carbenes, thus obscuring purely carbene processes [5], the discovered reaction may appear a convenient and efficient tool for studying and identification of primary processes in the photolysis of diazo compounds. Presumably, under certain conditions, tetrahydrofuran and related substrates are capable of acting as an efficient trap of excited states of diazo carbonyl compounds.

Photolysis of diazoketones Ia and Ib. Photolytic decomposition of diazo ketones **Ia** and **Ib** was carried out with the use of a medium-pressure mercury lamp in a setup [6] equipped with a Pyrex jacket for irradiation with long-wave UV light ($\lambda > 300$ nm). A solution of 2.4 mmol of diazo ketone **Ia** or **Ib** and 2.4–5 mmol of appropriate nucleophile in 80 ml of THF (freshly distilled over metallic sodium) was irradiated with UV light at 20–25°C under vigorous stirring until the theoretical amount of nitrogen evolved and the initial diazo ketone disappeared from the reaction mixture (according to the TLC data; 4–6 h). The solvent and excess nucleophile were removed under reduced pressure (first, at a residual pressure of 10–15 mm and then at 1–2 mm) at 25–30°C. The residue was recrystallized from appropriate solvent or purified by column chromatography on silica gel using mixtures of petroleum ether, benzene, and diethyl ether at various ratios as eluent.

Photolysis of diazo ketone Ia in THF/H₂O. The reaction was carried out with 1 g (2.4 mmol) of diazo ketone **Ia** and 0.4 g (2.4 mmol) of water in tetrahydrofuran following the general procedure. The residue was recrystallized from diethyl ether, and subsequent chromatographic separation on silica gel (30 g, eluent benzene) gave 0.37 g (38%) of 2,2,4,4-tetraphenyl-oxetane-3-carboxylic acid **IIa** and 0.58 g (49%) of insertion product **V**.

Photolysis of diazo ketone Ia in the presence of diethylamine. The reaction was carried out with 1 g (2.4 mmol) of diazo ketone **Ia** and 0.5 ml (5 mmol) of diethylamine in tetrahydrofuran. Chromatographic separation of the product mixture on 60 g of silica gel (eluent benzene–petroleum ether, 1:10) gave in the order of elution: 0.1 g (10%) of initial diazo ketone **Ia**, 0.6 g (54%) of *N,N*-diethyl-2,2,4,4-tetraphenyl-oxetane-3-carboxamide (**IVa**), and 0.26 g (22%) of insertion product **V**.

2,2,4,4-Tetraphenyl-oxetane-3-carboxylic acid (IIa). mp 235–236°C [2].

2,2,4,4-Tetramethyl-oxetane-3-carboxylic acid (IIb). mp 115–116°C (from ethanol) [1]. ¹H NMR spectrum (CDCl₃), δ , ppm: 1.51 s (6H, CH₃), 1.53 s (6H, CH₃), 3.36 s (1H, CH), 10.05 br.s (1H, OH). ¹³C NMR spectrum (CDCl₃), δ_C , ppm: 26.30 (CH₃), 32.34 (CH₃), 56.10 (CH), 78.61 (C², C⁴), 174.87 (COOH).

Methyl 2,2,4,4-tetraphenyl-oxetane-3-carboxylate (IIIa). mp 158–160°C (from methanol) [2]. ¹H NMR spectrum (CDCl₃), δ , ppm: 3.13 s (3H, CH₃), 5.05 (1H, CH), 7.02 t (2H, *p*-H, $J = 7.25$ Hz), 7.13 d.d (2H, *p*-H, $J = 7.25$, 8.0 Hz), 7.14 d.d (4H, *m*-H, $J = 7.25$, 8.0 Hz), 7.44 d (4H, *o*-H, $J = 8.0$ Hz), 7.49 d (4H, *o*-H, $J = 8.0$ Hz). ¹³C NMR spectrum (CDCl₃), δ_C , ppm: 51.13 (CH), 61.02 (OCH₃), 84.62 (C², C⁴), 124.94 and 125.22 (C^o), 126.71 and 126.73 (C^p), 127.70 and 127.83 (C^m), 143.13 and 146.41 (Cⁱ), 168.51 (C=O).

Methyl 2,2,4,4-tetramethyl-oxetane-3-carboxylate (IIIb). bp 53–54°C (4 mm) [1]. ¹H NMR spectrum (CDCl₃), δ , ppm: 1.42 s (6H, CH₃), 1.44 s (6H, CH₃), 3.23 s (1H, CH), 3.66 s (3H, OCH₃).

***N,N*-Diethyl-2,2,4,4-tetraphenyl-oxetane-3-carboxamide (IVa).** mp 148–150°C (from benzene). ¹H NMR spectrum (CDCl₃), δ , ppm: 0.59 t (6H, CH₃, $J = 7.13$ Hz), 3.04 q (2H, CH₂, $J = 7.15$ Hz), 3.39 q (2H, CH₂, $J = 7.15$ Hz), 6.99 t (2H, *p*-H, $J = 7.1$ Hz), 7.07 t (2H, *p*-H, $J = 7.1$ Hz), 7.11 d.d (4H, *m*-H, $J = 7.09$, 8.0 Hz), 7.20 d.d (4H, *m*-H, $J = 7.15$, 8.0 Hz), 7.35 d (4H, *o*-H, $J = 7.95$ Hz), 7.42 d (4H, *o*-H, $J = 7.95$ Hz). ¹³C NMR spectrum (CDCl₃), δ_C , ppm: 12.20 and 15.37 (CH₃); 40.41 and 41.92 (CH₂); 56.26 (CH); 85.10 (C², C⁴); 125.27, 125.33, 127.40, and 127.79 (C^o, C^m); 126.31 and 126.53 (C^p); 143.62 and 147.01 (Cⁱ); 165.44 (C=O). Found, %: C 83.37, 83.40; H 6.83, 6.81; N 3.16, 3.15. C₃₂H₃₁NO₂. Calculated, %: C 83.3; H 6.72; N 3.04.

***N,N*-Diethyl-2,2,4,4-tetramethyl-oxetane-3-carboxamide (IVb).** bp 89–90°C (4 mm). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.10 t (3H, CH₂CH₃), 1.25 t (3H, CH₂CH₃), 1.50 s (6H, CH₃), 1.52 s (6H, CH₃), 3.20 q (4H, CH₂), 3.50 s (1H, CH). Found, %: C 67.11, 67.09; H 10.25, 10.29. C₁₂H₂₃NO₂. Calculated, %: C 67.61; H 10.80.

2,2,5,5-Tetraphenyltetrahydrofuran-2,3-dione 3-(2-tetrahydrofuryl)hydrazone (V). mp 150–151°C (from benzene). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.86 m, 1.93 m, 2.04 m, and 2.12 m (4H, CH₂CH₂); 3.83 d.q (2H, OCH₂, $J = 25$, 7.5, 7.1 Hz); 5.39 d.t (1H, CHNH, $J = 6.0$, 3.9 Hz); 7.13–7.37 m (20H,

H_{arom}); 11.93 d (1H, NH, $J = 5.6$ Hz). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: 24.9 and 30.3 (CH₂CH₂); 67.9 (OCH₂); 84.8 and 87.1 (C², C⁵); 90.8 (CHN); 127.06, 127.16, 127.27, 127.34, 127.49, 127.54, 127.61, 127.64, 127.89, 127.96 (C_{arom}); 134.88 (C=N); 141.47, 141.66, 144.87, 145.25 (C_{arom}); 195.02 (C=O). Found, %: C 79.15, 78.97; H 5.69, 5.98; N 5.77, 5.79. C₃₂H₂₈N₂O₃. Calculated, %: C 78.69; H 5.74; N 5.74.

The ¹H and ¹³C NMR spectra were measured on a Bruker AM-500 spectrometer at 500 and 125 MHz, respectively, relative to tetramethylsilane as internal reference.

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