Photochemical Oxidation of Hydrocarbons by Nitropyridinium Salts

Stephan Negele, Katja Wieser, and Theodor Severin*

*Institut für Pharmazie und Lebensmittelchemie der Ludwig-Maximilians-Universität München,
Sophienstrasse 10, D-80333 München, Germany*

Received September 2, 1997

Aliphatic and alicyclic hydrocarbon compounds can be oxidized by photoactivated 4-nitropyridinium salts **(1)**. Reaction of **1** with indan, tetralin, 2-ethylnaphthalene, or cyclohexane leads to the formation of indanone, tetralone, 2-acetylnaphthalene, cyclohexanol, and cyclohexanone, respectively. Alkyl aryl ketones and dialkyl ketones are transformed in a regiospecific reaction into 1,4-dicarbonyl compounds. Isoamyl acetate is oxidized to give the 3-hydroxy derivative as sole product. In contrast to the compounds mentioned so far, tetrahydrofuran reacts with nitrobenzene as well as with photoactivated pyridinium salts to afford butyrolactone and octahydro-2,2′-bifuranyl. When acetone is applied as cosolvent, a tetrahydrofuran−acetone derivative is formed as main product.

Photochemical reactions of aromatic nitro compounds have been intensively investigated.[1] Several papers deal with the radical anion formation of aromatic nitro compounds or with hydrogen abstraction reactions which ultimately lead to the reduction of the nitro group. For instance, nitrobenzene is photoreduced by 2-propanol, and the major products under neutral conditions are acetone and phenylhydroxylamine.[2] Ortho-substituted nitrobenzenes can undergo intramolecular hydrogen-transfer reactions, in which the nitro group is reduced to a nitroso function while an oxygen atom is inserted into a CH-bond located in the ortho position.[3] This type of reaction has led to the development of the *o*-nitrobenzyl residue as a protecting group for alcohols, amines, and carboxylic acids. *p*-Methoxy-substituted alkyl benzenes are oxidized at the benzylic CH-bonds by nitrobenzene under irradiation in good yields, whereas ethylbenzene and cyclohexylbenzene did not react under comparable conditions.[4] In a few cases it has been shown that a nitrobenzene moiety attached to a steroid molecule can oxidize the rigid hydrocarbon at a remote position after photochemical excitation, but the yields are low.[5] Irradiation of substituted nitrobenzenes in triethylamine has been reported to afford acetaldehyde, which may
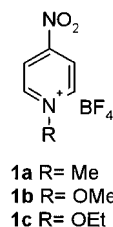

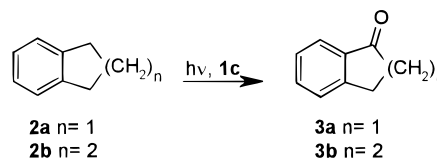**Figure 1.** Nitropyridinium salts **1a**−**c**.

Figure 2. Photooxidation of indan **2a** and tetralin **2b**.

react further with the reduction product of the nitro aromatic compound.[6]

Because electron-transfer processes are essential in photochemical reactions of aromatic nitro compounds, we argued that nitropyridinium salts might be very reactive. Here we report that hydrocarbon chains with different types of substituents can be oxidized by photoactivated nitropyridinium salts.

Results

Initial experiments indicated that activated and unactivated aliphatic hydrocarbons can be oxidized by aromatic nitro compounds under irradiation, but the yields are generally low. When we compared different aromatic and heteroaromatic nitro compounds, it turned out that 4-nitropyridinium salts are far more reactive than aromatic nitro compounds such as nitrobenzene or 1,3-dinitrobenzene. The nitropyridinium salts **1a**−**c** applied in this investigation are easily obtained by alkylation of 4-nitropyridine or 4-nitropyridine *N*-oxide with trimethyl- or triethyloxonium tetrafluoroborate, respectively (Figure 1).

When equimolar amounts of indan **2a** and the nitropyridinium salt **1c** in a solution of acetone are irradiated by a HPK 125 W lamp equipped with a Pyrex filter for 5 h at room temperature, ketone **3a** is produced in a 72% yield. Similary tetralin **2b** reacts to give ketone **3b** in 71% yield (Figure 2) and 2-acetylnaphthalene **5** is obtained from 2-ethylnaphthalene **4** in a 12% yield after 12 h irradiation (Figure 3). In accordance to expectation, a methylene group attached to an aromatic nucleus is activated with respect to this type of photochemical oxidation.

(1) (a) Chow, Y. L. In *The Chemistry of amino, nitroso and nitro compounds and their derivatives* (*The Chemistry of functional groups. Supplement F*); Patai, S., Ed.; Wiley: New York 1982; Vol. 1, pp 181−281. (b) Morrison, H. A. In *The Chemistry of nitro and nitroso groups* (*The Chemistry of functional groups*); Feuer, H., Ed.; Patai, S., Series Ed.; Wiley: New York, 1969; Vol. 1, pp 165−212.
(2) Hurley, R.; Testa, A. C. *J. Am. Chem. Soc.* **1966**, *88*, 4330.
(3) (a) Literature 1a, p 198 and literature cited, therein. (b) Literature 1b, p 185 and literature cited therein.
(4) Libman, J. *J. Chem. Soc., Chem. Commun.* **1977**, 868.
(5) Scholl, P. C.; Van De Mark, M. R. *J. Org. Chem.* **1973**, *38*, 2376.

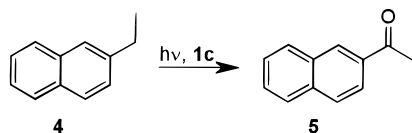(6) Literature 1a, p 190 and literature cited therein.

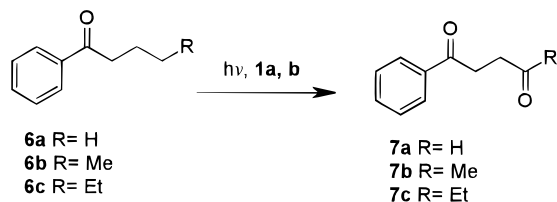**Figure 3.** Photochemical oxidation of 2-ethylnaphthalene **4**.

Figure 4. Oxidation products of ketones **6a−c**.

Table 1. Variation in Yield for Formation of Diketones 7a−c, 9 with Nitro Compounds

entry	substrate	nitro compound	conditions[a]	diketones (% yield[b])
1	**6b**	**1a**	a, 5h	**7b** (39)
2	**6b**	**1b**	a, 5h	**7b** (63)
3	**6c**	**1b**	a, 5h	**7c** (60)
4	**8**	**1b**	a, 5h	**9** (79)
5	**6a**	**1a**	a, 5h	**7a** (7)
6	**6a**	**1a**	b, 5h	**7a** (11)

[a] a: 10 mM ketone, 10 mM nitropyridinium salt, acetone. b: 10 mM ketone, 10 mM nitropyridinium salt, acetonitrile. [b] Yields determined by GC-MS.

Irradiation of equimolar amounts of 1-phenylpentanone **6b** and the salt **1b** in acetone, under the conditions described above, leads to the formation of the diketone **7b** in 63% yield. Besides **7b** only small amounts of a cyclobutanol derivative, resulting from 1,4-biradical photocyclization, and acetophenone can be detected by GC. The same diketone **7b** is also obtained, when the nitropyridinium salt **1a** is applied as oxidizing agent, but the yields are lower (39%). Other examples, which demonstrate the high regioselectivity of this type of photochemical oxidation, are shown in Figure 4 or 5 respectively. 1-Phenylhexanone **6c** and 2-propyltetralone **8** are oxidized to afford the diketones **7c** and **9** in high yields. In contrast, oxidation of 1-phenylbutanone **6a**, when irradiated with **1a** in acetonitrile or acetone, produced the keto aldehyde **7a** in only modest yield (entries 5 and 6, Table 1). Probably the aldehyde group reacts further under irradiation, a process which is still under investigation.

The reaction products were identified by comparison (GC-MS) with commercially available substances or isolated by flash chromatography and identified by spectroscopic data. Quantification was achieved by GC using internal standards.

Compared with the nitropyridinium salts **1a−c**, aromatic nitro compounds are only poor oxidizing agents. For instance: irradiation of equimolar amounts of ketone **6b** and nitrobenzene under the conditions described for the nitropyridinium salts, affords oxidation products in yields below 1%.

Aliphatic ketones with two alkyl side chains are not as reactive as the alkyl aryl ketones discussed so far. Nevertheless, the expected oxidation product can be obtained in moderate yield, when the ketone is applied in high molar ratio with respect to the nitropyridinium salt. For example irradiation of 0.2 mmol **1b** in a mixture
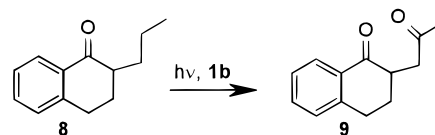

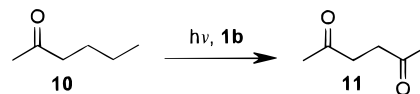**Figure 5.** Photooxidation of ketone **8**.

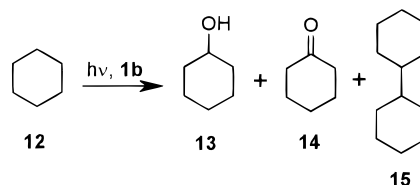**Figure 6.** Photooxidation of the aliphatic ketone **10**.

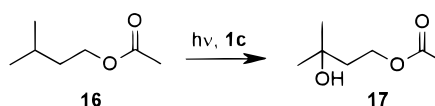**Figure 7.** Photochemical oxidation of cyclohexane **12**.

Figure 8. Photooxidation of ester **16**.

of 5 mL of 2-hexanone and 15 mL of acetonitrile for 5 h affords 0.02 mmol of diketone **11** (Figure 6). Based on the assumption that the nitro compound is reduced to a hydroxylamine moiety, the yield is 8%. Other products detectable by GC can be neglected.

Even unactivated hydrocarbon compounds can be oxidized by photoactivated nitropyridinium salts. Difficulties arise when the molecule contains different CH-groups of comparable reactivity or when the oxidation product may react further. The problem is well-known from the transformation of cyclohexane into cyclohexanone by metal-catalyzed oxidation, a reaction which has been intensively investigated.

Irradiation of a solution of 1 mmol of **1b** in a mixture of 30 mL of cyclohexane and 70 mL of acetone for 5 h leads to the formation of 0.32 mmol of cyclohexanone and 0.82 mmol of cyclohexanol, besides small amounts of bicyclohexyl (Figure 7). Other reaction products of cyclohexane have not been detected by GC-MS analysis.

Similar irradiation of 1 mmol of **1c** in a solvent of isoamyl acetate and acetone provides 1.3 mmol of 3-hydroxyisoamyl acetate. The product was identified as nitrobenzoyl derivative by spectroscopic data. Obviously oxidation of the tertiary carbon atom is the preferred reaction (Figure 8).

In contrast to the compounds discussed so far, photochemical oxidation of tetrahydrofuran cannot only be achieved by action of activated nitropyridinium salts, but with less reactive nitroaromatic compounds as well. Irradiation of 0.2 mol of nitrobenzene in a solution of 5 mL of tetrahydrofuran and 15 mL of acetonitrile leads to the formation of butyrolactone (0.07 mol, 34% yield) and octahydro-2,2′-bifuranyl (0.2 mol, 48% yield, mixture of stereoisomers) as main products (Figure 9). Other compounds detectable by GC can be neglected. On the other hand, irradiation of nitrobenzene in a solvent mixture of tetrahydrofuran and acetone affords the adduct **21** as main product besides lactone **19** and
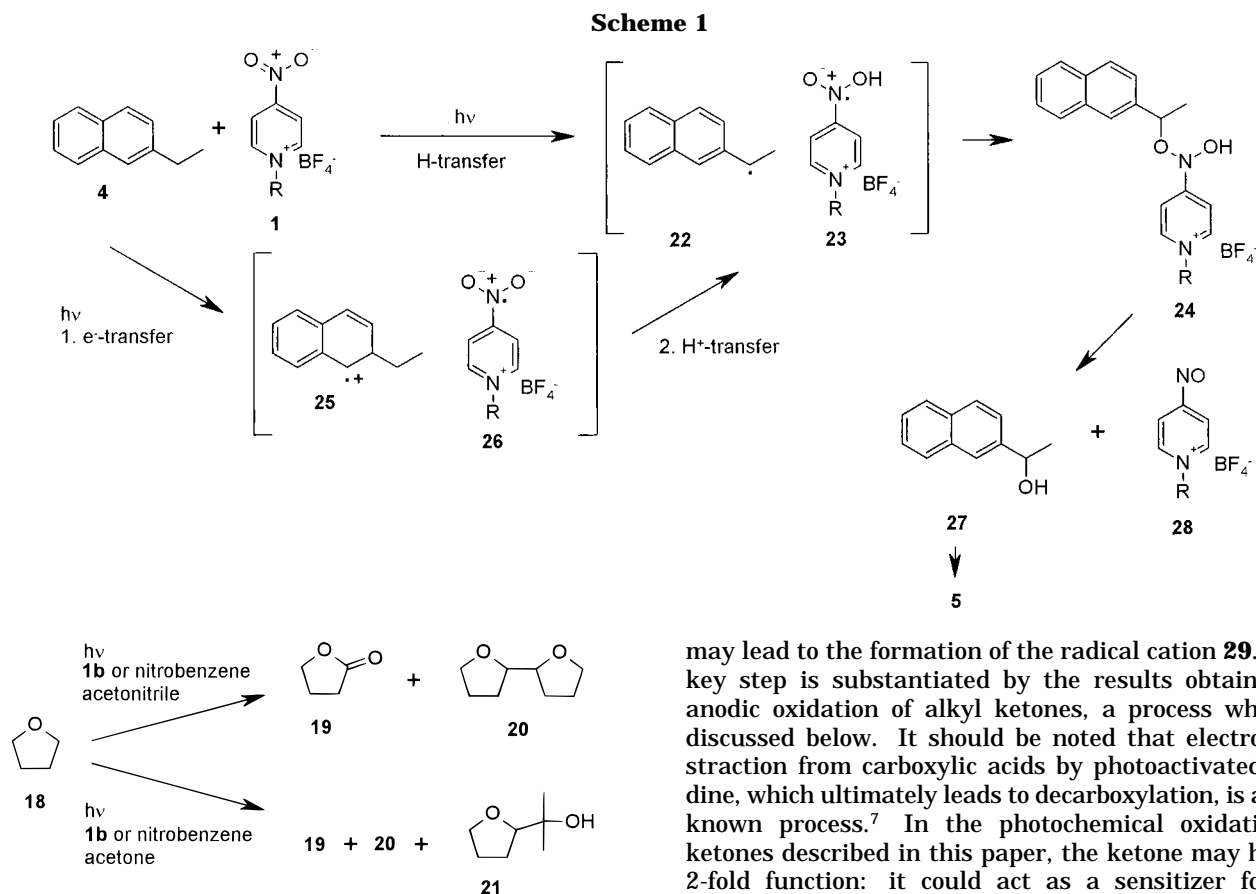
Scheme 1

Figure 9. Oxidation products of THF.

octahydro-2,2′-bifuranyl. The reaction products **19**, **20**, and **21** have been isolated via flash chromatography and identified by comparison of their MS- and NMR-spectral data with literature values.

When the compound to be oxidized was applied in excess, the yields are calculated on the basis that the nitro group is reduced to a hydroxylamine function. Otherwise the yields were referred to the starting materials. Actually the process is more complex, and the reduction products of the nitro compounds have not been separated and analyzed in detail.

Discussion

The results obtained so far should be discussed under mechanistic aspects. Hydrogen atom transfer or successive electron and proton transfer to the photoactivated 4-nitropyridinium salt **(1)** as the first steps of the reaction would account for the formation of the photooxidation products of the aromatic compounds with alkyl side chains. In the formal scheme the reaction mechanism is exemplified by the transformation of 2-ethylnaphthalene into 2-acetylnaphthalene (Scheme 1). Reorganization of the radical pair **[22/23]** may lead to an intermediate of structure **24**, which should degrade to give the nitroso compound **28** and the alcohol **27**. Previously photochemical oxidations of alcohols by nitro or nitroso compounds have been carefully investigated and mechanistically discussed.[1,2]

A mechanism which would explain the regiospecific oxidation of alkyl aryl ketones is depicted in Scheme 2. In the first step an electron transfer from the ground-state ketone to the photoactivated nitropyridinium salt may lead to the formation of the radical cation **29**. This key step is substantiated by the results obtained by anodic oxidation of alkyl ketones, a process which is discussed below. It should be noted that electron abstraction from carboxylic acids by photoactivated acridine, which ultimately leads to decarboxylation, is a well-known process.[7] In the photochemical oxidation of ketones described in this paper, the ketone may have a 2-fold function: it could act as a sensitizer for the activation of the nitro compound, but on the other hand the ground-state carbonyl compound should react with the activated nitropyridinium salt. The further reaction of the radical cation **29** may proceed as follows: intramolecular attack on a remote hydrogen−carbon bond by the oxygen radical would afford the carbon radical **30**, which may transfer a proton to the pyridinium radical **26**. Oxidation of radical **30** by combination with the nitropyridinium derived radical **23** and subsequent NO-bond cleavage should proceed as described above for the 2-ethylnaphthalene radical **22**.

The regioselective photochemical oxidation of alkyl aryl ketones bears similarities to a long known electrochemical process. It has been demonstrated that anodic oxidation of alkyl ketones can lead to a substitution at a remote position.[8] This type of reaction is exemplified by the electrochemical oxidation of 2-hexanone in acetonitrile with lithium perchlorate as electrolyte, which resulted in the formation of 5-acetamido-2-hexanone in 40% yield (Scheme 3). Analogous reactions of other alkyl ketones have been described, but the yields are only modest (10−40%). The first steps of the reaction pathway (**10** ⟶ **30**) are analogous to the photochemical oxidation discussed above.

The regiospecific photochemical oxidation of alkyl aryl ketones can be explained by a different reaction mechanism as well. It has been rigorously established that irradiation of ketones with alkyl side chains can produce biradicals of type **35**, which can typically undergo 1,4-cyclization to cyclobutanol derivatives or fragmentation according to the Norrish Reaction as depicted in Scheme
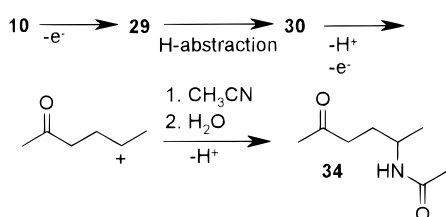
(7) Okada, K.; Okubo, K.; Oda, M. *Tetrahedron Lett.* **1992**, *33*, 83−84.

(8) Becker, J. Y.; Byrd, L. R.; Miller, L. L.; So, Y.-H. *J. Am. Chem. Soc.* **1975**, *97*, 853.
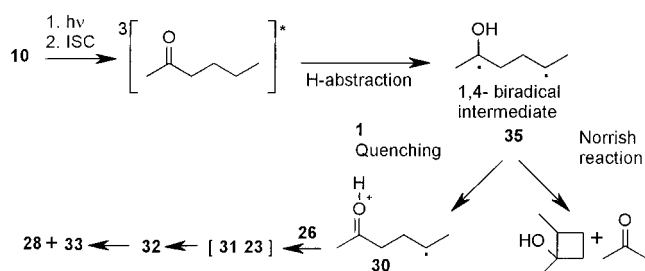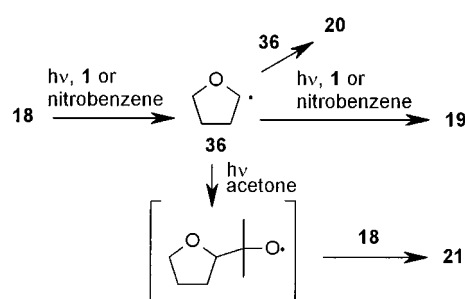
Scheme 2
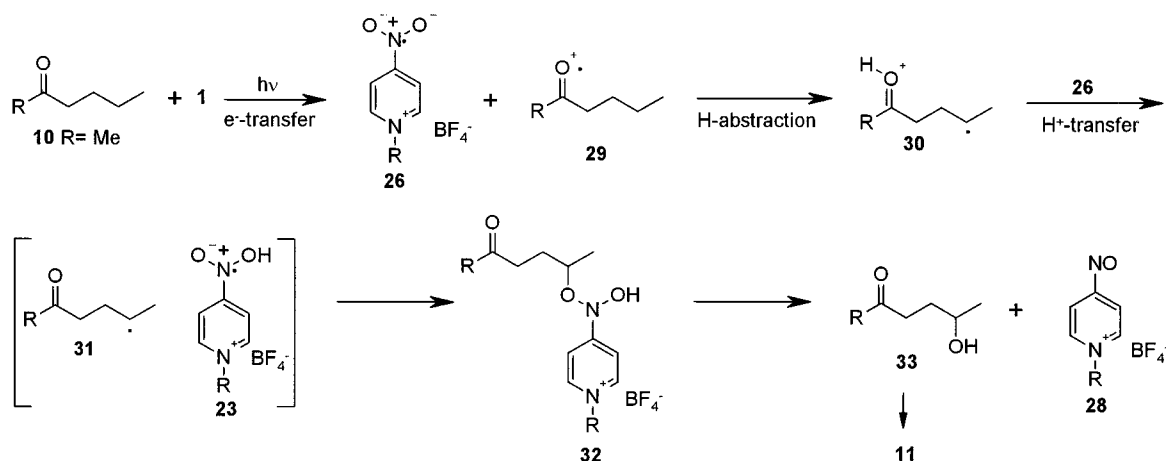
Scheme 3

Scheme 4

Scheme 5

4. During the photochemical reaction of ketones with nitropyridinium salts, cyclobutanols and Norrish products are also formed, but only in a very low amount compared to the oxidation products. The presence of the nitropyridinium salt interferes with the normal behavior of the biradicals and results in the formation of oxidation products by quenching the biradical intermediate. This electron transfer from **35** to the unactivated nitropyridinium salt would lead to the same intermediate **30** as proposed in the first reaction scheme. Proton transfer of the oxonium cation to the nitro radical would afford a species of type [**31/23**], and further oxygenation of the carbon radical **31** should proceed as discussed above.

Even the unactivated hydrocarbon cyclohexane reacts with the nitropyridinium salt **1b** under irradiation to give cyclohexanol and cyclohexanone. The cyclohexyl radical must be considered as an intermediate which should react further to provide cyclohexanol and cyclohexanone. Remarkably bicyclohexyl is produced as byproduct in low amount, which has been detected by GC-MS (not quantified). The comparatively high yield of oxidation products with respect to the pyridinium salts suggests that not only the nitro compound but also the nitrosopyridinium salt is an oxidizing agent under the conditions employed.

The easy photochemical oxidation of a tertiary CH-group is demonstrated by the transformation of **16** to the keto alcohol **17** (Figure 8). It could be argued that the

ester carbonyl group could be involved as has been demonstrated for the ketones **6a–c**, **8**, and **10**. In a series of preliminary investigations, solutions of **1** in aliphatic esters such as pentyl acetate and methyl cyclohexanecarboxylate with the cosolvent acetone or acetonitrile have been irradiated under standard conditions. Analysis of the resulting reaction mixtures by GC-MS showed that the alkyl chains are oxidized preferably at the 3-position, but compared with the ketones **6a–c**, **8**, and **10** the regiospecifity is less pronounced. This type of reaction is still under investigation.

Compared to the compounds discussed so far, electron abstraction from aliphatic ethers is more easily achieved. Irradiation of nitrobenzene in a solution of tetrahydrofuran has been investigated under mechanistic aspects, and the formation of a nitrobenzene radical anion and a species resulting from hydrogen abstraction have been discussed on the basis of esr spectral data.[9] We investigated the formation of the oxidation products of tetrahydrofuran under a variety of conditions (Scheme 5). Lactone **19** and octahydro-2,2′-bifuranyl **20** (mixture of stereoisomers) are obtained as main products, when the pyridinium salt **1b** is irradiated in a solution of tetrahydrofuran and acetonitrile. The electron-donating property of the cyclic ether is demonstrated by the fact that **20** and the lactone **19** are obtained as well by action of photoactivated nitrobenzene as oxidizing agent. On the other hand, in the presence of acetone the C,C-coupling product **21** is obtained in high yield. This compound may arise through addition of the tetrahydrofuranyl-radical to the ketone, followed by a radical chain process. **21** has been synthesized previously by intramolecular cy-

(9) Janzen, E. G.; Gerlock, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 3108.

clization of 4,5-epoxy-5-methylhexan-1-ol.[10] Octahydro-2,2′-bifuranyl was identified as a reaction product of tetrahydrofuran and *tert*-butyl hydroperoxide.[11]

Summarized, photoactivated 4-nitropyridinium salts are effective reagents for the oxidation of hydrocarbon chains.

Experimental Section

Materials and Methods. The following materials were obtained from commercial sources and used as received: acetophenone, butyrolactone, cyclohexane, cyclohexanedione, cyclohexanol, cyclohexanone, ethylnaphthalene, 2-hexanone, 2,5-hexanedione, indan, indanone, isoamyl acetate, 2-methyl-naphthyl ketone, 4-nitropyridine *N*-oxide, octahydro-2,2′-bi-furanyl, 1-phenylbutanone, 1-phenylpentanone, tetralin, te-tralone, triethyloxonium tetrafluoroborate, trimethyloxonium tetrafluoroborate. THF and acetonitrile were purchased and distilled from sodium/benzophenone ketyl or CaH₂, respectively, before use. Other solvents were used without further purification. 4-Nitropyridine,[12] 1-phenylhexanone,[13] and 2-pro-pyltetralone[14] were prepared by literature methods. Photolysis was carried out with a HPK 125 W lamp from Philips. Preparative column chromatography was performed with a 32−63 mesh silica gel using a mixture of ethyl acetate and petroleum ether (1:4) as solvent system. Mass spectra were recorded on a HP 5971 A mass selective detector interfaced with a HP 5890 series II gas chromatograph equipped with a 25 m × 0.25 mm fused silica capillary column. ¹H NMR spectra were obtained in CDCl₃ or D₂O at a 400 MHz spectrometer. Analytical TLC was carried out on aluminum-backed silica plates with detection by UV-light unless other-wise noted.

General Procedure for the Preparation of Nitropyri-dinium Salts 1a−c. A mixture of the corresponding pyridine derivative (0.01 mol) and trimethyl- or triethyloxonium tet-rafluoroborate, respectively (0.01 mol), in 80 mL dichloro-methane was stirred at room temperature for 4 h. The solvent was evaporated in vacuo and the product recrystallized from MeOH and ethyl acetate (4:1).

1-Methyl-4-nitropyridinium tetrafluoroborate (1 a): yield 1.59 g (7.0 mmol, 70%); obtained as pale yellow needles; mp 130 °C; ¹H NMR (D₂O, ppm) 4.56 (s, 3H), 8.73−8.80 (m, 2H), 9.25−9.27 (m, 2H). Anal. Calcd for $C_6H_7N_2O_2BF_4$: C, 31.90%; H, 3.10%; N, 12.40%. Found: C, 31.97%; H, 3.11%; N, 12.19%.

1-Methoxy-4-nitropyridinium tetrafluoroborate (1 b): yield 1.24 g (5.1 mmol, 45%); obtained as pale yellow needles; mp 112 °C; ¹H NMR (D₂O, ppm) 4.47 (s, 3H), 8.36−9.42 (m, 2H), 9.55−9.63 (m, 2H). Anal. Calcd for $C_7H_{10}N_2O_2BF_4$: C, 29.79%; H, 2.92%; N, 11.58%. Found: C, 29.66%; H, 2.96%; N, 11.68%.

1-Ethoxy-4-nitropyridinium tetrafluoroborate (1 c): yield 1.28 g (5.0 mmol, 46%); obtained as pale yellow needles; mp 78 °C; ¹H NMR (D₂O, ppm) 1.47−1.54 (t, 3H) 4.49 (q, 2H), 8.89−8.96 (m, 2H), 9.56−9.64 (m, 2H). Anal. Calcd for $C_8H_{12}N_2O_2BF_4$: C, 32.85%; H, 3.54%; N, 10.94%. Found: C, 32.90%; H, 3.63%; N, 10.67%.

General Procedure for the Photochemical Oxidation. All photochemical reactions were run in a reactor equipped with a high pressure 125 W Hg lamp. The compounds were dissolved as indicated and placed in jacketed Pyrex vessels, equipped with a stirbar and a septum. The resulting solutions were cooled by a circulating water bath and degassed by purging with N₂ for 15 min. The reaction mixtures were irradiated for the indicated time while stirring under N₂. After

the irradiation, the crude reaction mixture was concentrated in vacuo. Unless otherwise noted, all products were identified directly by comparing their retention times and mass or NMR spectra with those of the pure authentic samples used as reference compounds or those given in the literature. Quan-tification was performed by gas chromatography using internal standards as indicated.

1-Phenylpentanone (0.16 g, 1 mmol), 1-phenylhexanone (0.25 g, 1 mmol), or 2-propyltetralone (0.19 g, 1 mmol), respectively, were irradiated as a 10 mM solution in acetone with **1b** (0.25 g, 1 mmol). After 5 h, the solvent was evaporated, and the crude reaction mixtures were purified via flash chromatography to afford **7b** (110 mg, 0.63 mmol, 63%), **7c** (113 mg, 0.59 mmol, 60%), or **9** (160 mg, 0.79 mmol, 79%), respectively. The isolated products were identified by com-parison of their spectroscopic data with literature values.[15,16] The yields were determined using cyclohexanedione as internal standard, and only in the case of 2-propyltetralone was 1-phenylpentanone added. All yields were based on the corresponding starting materials.

1-Phenylbutanone (0.15 g, 1 mmol) and **1a** (0.23 g, 1 mmol) were dissolved in 100 mL of acetonitrile and irradiated for 5 h. The reaction mixture was worked up and quantified as indicated above affording keto aldehyde **7a** (18 mg, 0.11 mmol, 17%).[17,18]

Indan (0.13 g, 1 mmol) or tetralin (0.12 g, 1 mmol), respectively, was irradiated as a 10 mM solution in acetone with **1 c** (0.26 g, 1 mmol). After 5 h, the solvent was removed in vacuo, and the reaction products were identified by coin-jection with authentic samples. Using acetophenone as in-ternal standard, the yields, which were based on the corre-sponding starting materials, are as follows: indanone (95 mg, 0.72 mmol, 72%) and tetralone (104 mg, 0.71 mmol, 71%).

2-Hexanone (5 mL, 40.5 mmol) and **1b** (49.2 mg, 0.2 mmol) were dissolved in 15 mL of acetonitrile and irradiated for 5 h. The solvent was evaporated and the residue analyzed by GC-MS. The chromatogram showed only one product, which was identified as 2,5-hexanedione by coinjection with the authentic sample. The yield of 2,5-hexanedione (1.8 g, 0.02 mmol, 8%) has been achieved using cyclohexanone as internal standard.

2-Ethylnaphthalene (46.8 mg, 0.3 mmol) and **1c** (78 mg, 0.3 mmol) were dissolved in 30 mL of acetonitrile and irradiated for 12 h. The reaction mixture was worked up and quantified as indicated above. The yield of 2-methylnaphthyl ketone (20.4 mg, 0.12 mmol, 12%) was determined using 1-phenylpentanone as internal standard and based on the starting material.

Cyclohexane (30 mL, 0.28 mol) and **1b** (0.25 g, 1 mmol) were irradiated in 70 mL of acetone for 5 h. Acetone was cautiously evaporated and the liquid residue identified by GC-MS-analysis. The spectroscopic data of cyclohexanol, cyclohex-anone, and bicyclohexyl corresponded in all respects with those of the authentic samples. Quantification was achieved by using cycloheptanone as internal standard. The yield of cyclohexanol (31 mg, 0.84 mmol, 32%) was based on 2 mmol of nitro-oxygen of **1b**, whereas the yield of cyclohexanone (82 mg, 0.31 mmol, 41%) is based on 1 mmol of **1b**.

Isoamyl acetate (30 mL, 0.20 mol) was irradiated in 70 mL of acetone with **1c** (0.26 g, 1 mmol). After 5 h, acetone was cautiously removed under reduced pressure and the liquid residue added to a mixture of 1 mmol each of nitrobenzoyl chloride and 4-(dimethylamino)pyridine in 4 mL of dichlo-romethane and stirred 40 min while cooling at 0 °C. The solvent was evaporated and the crude reaction product purified by flash chromatography. The spectroscopic data of **17** and of the nitrobenzoyl derivative of **17** have been compared with

(10) Masaki, Y.; Miura, T.; Mukai, I.; Iwata, I.; Oda, H.; Itoh, A. *Chem. Pharm. Bull.* **1995**, *43*, 686−688.

(11) Kharrat, A.; Gardrat, C.; Maillard, B. *Can. J. Chem.* **1984**, *62*, 2385−2390.

(12) Ochial, E. *J. Org. Chem.* **1953**, *18*, 537, 548, 550.

(13) Simon, I. *Chem. Zentralbl.* **1929**, *100*, I, 2520.

(14) Bachmann, W. E.; Wendler, N. L. *J. Am. Chem. Soc.* **1946**, *68*, 2580.

(15) Severin, T.; König, D. *Chem. Ber.* **1974**, *107*, 1499−1509.

(16) Kellin, A. V.; Kulinkovich, O. *Russ. J. Org. Chem.* **1994**, *30*, 202−206.

(17) Rusell, G. A.; Kulkarni, S. V. *J. Org. Chem.* **1993**, *58*, 2678−2685.

(18) Severin, T.; Adam, R.; Lerche H. *Chem. Ber.* **1975**, *108*, 1756−1767.

the literature data.[19,20] The yield of **17** (196 mg, 1.3 mmol, 67%) was based on 2 mmol of nitro-oxygen of **1 c**, using cyclohexanedione as internal standard.

THF (5 mL, 0.06 mmol) and **1b** (48.4 mg, 0.2 mmol) or nitrobenzene (24.6 mg, 0.2 mmol), respectively, were dissolved in 15 mL of acetonitrile and irradiated for 5 h. The solvent and the excess ether were removed in vacuo, and the liquid residue was analyzed by GC-MS. The spectroscopic data of **19** and **20** corresponded in all respects with those of the authentic samples. Quantification was achieved using cyclohexanedione as internal standard. The yields were determined on the assumption that the nitro group is photoreduced to a hydroxylamine function. Photooxidation with **1b** afforded **19** (16 mg, 0.1 mmol, 28%) and **20** (3.0 mg, 0.03 mmol, 17%). Using nitrobenzene for the irradiation, the yields are as follows: **19** (27 mg, 0.2 mol, 48%) and **20** (5.8 mg, 0.07 mol, 34%).

THF (5 mL, 0.06 mol) and **1b** (48.4 mg, 0.2 mol) or nitrobenzene (24.6 mg, 0.2 mol), respectively, were irradiated in 15 mL of acetone for 5 h. After evaporation of acetone and the excess ether, the residual was treated with 2 N HCl and extracted with dichloromethane. The combined dichloromethane layers were used in subsequent flash chromatography with detection on silica plates using a mixture of vanillin (0.5 g), EtOH (20 mL), and H_2SO_4 (80 mL) and subsequent heating to 120 °C. Beside **19** and **20**, flash chromatography afforded the C,C-coupling product **21**, identified by comparison with literature values.[21] The oxidation products were quantified as indicated above affording **19** (52 mg, 0.4 mmol, 92%), **20** (17.5 mg, 0.2 mmol, 100%), and **21** (24 mg, 0.2 mmol, 26%). Using nitrobenzene for the irradiation, the yields are as follows: **19** (43 mg, 0.3 mmol, 75%), **20** (3.3 mg, 0.04 mmol, 19%), and **21** (4.4 mg, 0.04 mmol, 5%).

(19) Negele, S. Ph.D. thesis, Ludwig-Maximilians-Universität München, Germany, 1996, p 240.

(20) Julia, M.; Perez, C.; Sausinne, L. *J. Chem. Res. M.* **1978**, 3401–3418.

(21) Descotes, G.; Martin J.-C.; Labrit, G. *Bull. Soc. Chim. Fr.* **1969**, 4151–4154.