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# EFFICIENT PHOTOCHEMICAL OXETANE FORMATION FROM 1-METHYL-2,4,5-TRIPHENYLIMIDAZOLE AND BENZOPHENONES

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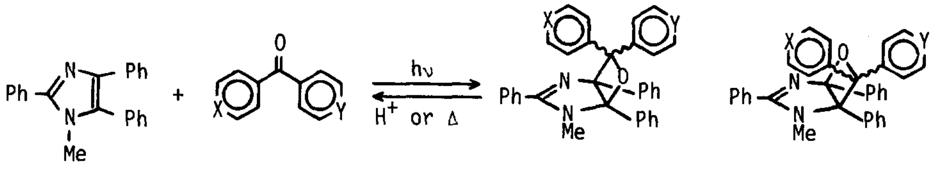
Summary: In contrast to simple imidazoles, 1-methyl-2,4,5-triphenylimidazole (**1**) produced stable oxetane photoadducts **3b** - **e** with good efficiency upon irradiation in the presence of benzophenone derivatives **2b** - **e** in acetonitrile solution. Irradiation in the solid-phase was also studied. The oxetanes **3b** - **e** readily underwent cycloreversion by acid catalysis or by heating.

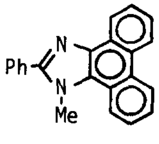
Several years ago we found that 1-methyl-2,4,5-triphenylimidazole (**1**), in contrast to simple imidazoles, owned unique photochemical reactivity toward 2-cyanopyridine.[1] In this paper we will report efficient photocycloaddition of **1** and benzophenone derivatives **2b** - **e** affording oxetanes **3b** - **e**. This reactivity displayed by **1** also appears unique, since it is known that production of (stable) oxetanes through photocycloaddition of nitrogen-containing heteroaromatics such as imidazoles,[2,3a] pyrroles[3,4] and indoles[4] to carbonyl compounds is achievable only when there is an N-acyl ring-substituent on the heterocycles.

As summarized in Table I, irradiation of mixtures of imidazole **1** and excess carbonyl compounds (PhCOMe, PhCHO and benzophenone derivatives **2a** - **e**) in acetonitrile with Pyrex-filtered light (> 290 nm) led to formation of oxetane photoadducts **3b** - **e** and/or a phenanthrene derivative **4** as the sole product(s).[5] Mass balances were excellent (~100 %) in all cases. The same reaction occurred also in benzene but was slower in rate than in acetonitrile (cf.

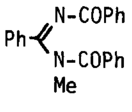


**1** **2** **3** **3'**

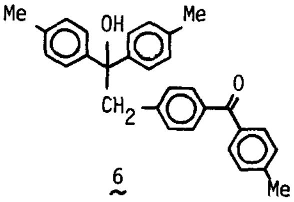
**2** and **3** (**3'**)
**a**; X = Y = MeOC
**b**; X = Y = MeC
**c**; X = MeC, Y = HC
**d**; X = Y = HC
**e**; X = HC, Y = N



**4**



**5**



**6**

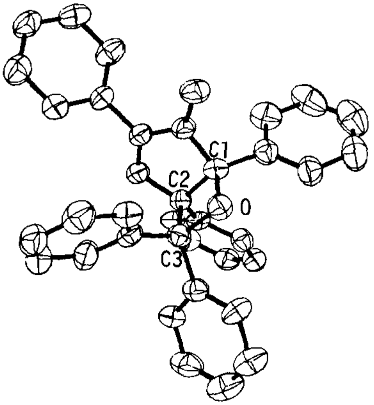
runs 6 and 8). As these oxetanes were sensitive to silica gel at room temperature, their isolation by column chromatography on silica gel was performed at low temperatures (ca. -20 °C) using ethyl acetate - hexane (1:4 v/v) as eluent. Photolyses of unsubstituted imidazole, 1-methylimidazole, 1-methyl-2,5-diphenylimidazole and 2,4,5-triphenylimidazole in the presence of benzophenone (**2d**) under similar conditions produced no significant products.

The structure of oxetane **3d** was established by X-ray crystallography (Figure 1).[6] The assignment of the same structure **3** to other oxetanes are based on their NMR, IR, mass and UV spectra that are analogous to those of **3d**. However, the possibility of the alternative structure **3'** cannot rigorously be excluded for the latter oxetanes.

Table I shows that phenanthrene **4** is obtained in moderate yields in those cases where the triplet energies of the phenyl ketones are higher than 71 kcal/mol (runs 1 - 3) or a substantial fraction of the incident light was absorbed by **1** (run 7, where the molar ratio of ketone to **1** is relatively low). The absorption spectrum of imidazole **1** exhibits a maximum at 284 nm ($\varepsilon$ = 20900) with the absorption edge around 355 nm ($\varepsilon$ at 350 nm ∿ 10). Therefore, **4** must have been produced through either direct excitation of **1**,[1] triplet energy transfer from excited phenyl ketones to **1** or both.

The quantum yield of product formation from photolysis of a degassed acetonitrile solution of **1** (20 mM) and **2d** (200 mM) using 366-nm light[7] was determined to be 0.30 for oxetane **3d** and 0.009 for **4**. Phosphorescence of **2d** was found to be easily quenched by **1** with $k_q\tau = 1.6 \times 10^5\ M^{-1}$ in degassed acetonitrile at room temperature.[11]

There is inherent interest in thermoreversible photoreactions, which may serve as model systems for photochromic information storage [8] and solar energy storage.[9] From this viewpoint, oxetane cycloreversion and solid-state irradiation of **1** and **2** were studied. Treatment of **3b** - **e** in benzene with either silica gel slurry in benzene or a few drops of concentrated sulfuric acid at room temperature for a few hours gave quantitatively **1** and the corresponding ketones **2b** - **e**, respectively. Heating a solution of **3d** in tert-butylbenzene at 120 °C for 2.5 h also led to complete disappearance of **3d** giving **1** and **2d** in a quantitative yield. The solid-state DSC diagram of **3d** showed that 16.24 ± 0.05 kcal/mol of energy was released upon thermal decomposition of **3d**.



bond distances (Å)
C1-C2 = 1.580(7), C2-C3 = 1.598(7),
C1-O = 1.431(6), C3-O = 1.465(6)
bond angles (deg)
C1-C2-C3 = 82.81(33), C2-C3-O = 90.41(33),
C3-O-C1 = 93.06(33), C2-C1-O = 92.40(34)
crystal data: orthorhombic, space group
$P2_12_12_1$, a = 17.48, b = 10.99, c = 13.87
Å, final R = 0.054

Figure 1. X-ray structure of oxetane **3d**.

Table I. Photoreaction of 1-Methyl-2,4,5-triphenylimidazole (1) with Phenyl Ketones in Solution.[a]

| run | 1, mM | phenyl ketone ($E_T$, kcal/mol) | molar ratio, ketone/1 | irradn time, h | yield, %[b] | | |
|---|---|---|---|---|---|---|---|
| | | | | | oxetane[c] 3 | phenanthrene 4 | recovered 1 |
| 1 | 24 | PhCOMe (74.1) | 8.7 | 8.5 | 0 | 16 | 84 |
| 2 | 8 | PhCHO (71.7) | 11.9 | 7 | 0 | 18 | 82 |
| 3 | 17 | 2a (71.1) | 5.7 | 6 | 0 | 54 | 46 |
| 4 | 17 | 2b (69.3) | 5.7 | 3 | 53 (3b) | 9 | 38 |
| 5 | 17 | 2c (69.2) | 5.7 | 0.8 | 59 (3c)[d] | 6 | 35 |
| 6 | 24 | 2d (69.2) | 5.7 | 1.5 | 64 (3d) | 3 | 33 |
| 7 | 24 | 2d | 1.7 | 3 | 38 (3d) | 13 | 49 |
| 8[e] | 24 | 2d | 5.7 | 1.5 | 22 (3d) | 1 | 77 |
| 9 | 17 | 2e (67.2) | 2.8 | 3 | 85 (3e)[f] | 0 | 15 |

[a] An acetonitrile solution unless otherwise specified. Irradiations were carried out with a 400-W high pressure mercury lamp through Pyrex. During the irradiation, nitrogen gas was passed through the solution which was cooled externally with ice-water. [b] Estimated from NMR analyses. [c] Data for melting points and NMR spectra: 3b, 160 - 161.5 °C, $\delta(CDCl_3)$ 2.58 ($N-CH_3$), 2.29 ($C-CH_3$), 2.14 ($C-CH_3$); 3c (a 7:3 mixture of two stereoisomers), 159 - 161 °C, $\delta(CDCl_3)$ 2.60 ($N-CH_3$), 2.30 and 2.15 (7:3, $C-CH_3$); 3d, 169 - 170 °C, $\delta(CDCl_3)$ 2.60 ($N-CH_3$); 3e, 129 - 132 °C, $\delta$(acetone-$d_6$) 2.63 ($N-CH_3$); 3e, 153 - 155 °C, $\delta(CDCl_3)$ 2.59 ($N-CH_3$). These two stereoisomers of 3e are listed in order of retention times. [d] A mixture of two stereoisomers with a molar ratio 7:3 (from NMR). Separation of these isomers was unsuccessful. [e] In benzene. [f] A 1:1 mixture of two stereoisomers (from NMR). These were separated by low-temperature column chromatography.

A mixture of crystals of 1 and respective benzophenone derivatives 2a - e (1, 62 mg (0.2 mmol) and 2a - e, 1.2 mmol) in a mortar was ground to a fine powder with a pestle. The powder was put between two Pyrex plates and irradiated under a nitrogen atmosphere at 0 °C.[10] As shown in Table II, oxetane formation proceeded only in the case of 2d (runs 4 and 5). Production of an oxidation product 5 can probably be attributed to residual oxygen in the nitrogen tank employed. In one case (run 2), a benzhydrol derivative 6 was obtained. Further study is in progress in order to understand these results, especially the anomalous behavior (solid-state oxetane formation) of 2d.

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Table II. Photoreaction of 1-Methyl-2,4,5-triphenylimidazole (**1**) with Phenyl Ketones **2** in the Solid State.[a]

| run | phenyl ketone (mp, °C)[b] | irradn time, h | yield, %[c] | | |
|---|---|---|---|---|---|
| | | | oxetane **3** | recovered **1** | others[d] |
| 1 | **2a** (141-143) | 10 | 0 | 85 | 15 (**5**) |
| 2 | **2b** (95) | 10 | 0 | 99 | 1 (**5**), 15 (**6**) |
| 3 | **2c** (59-60) | 10 | 0 | 92 | 8 (**5**) |
| 4 | **2d** (48) | 4 | 47 (**3d**) | 53 | none |
| 5[e] | **2d** | 15 | 22 (**3d**) | 78 | none |
| 6 | **2e** (69-71) | 10 | 0 | 94 | 6 (**5**) |

[a] *Irradiations were carried out with a 400-W high pressure mercury lamp through Pyrex under a nitrogen atmosphere at 0 °C (or at -20 °C in run 5).* [b] The mp of **1** is 148-149 °C. [c] Estimated from NMR analyses. [d] Melting points: **5**, semisolid which resisted to crystallization; **6**, 52 - 55 °C. [e] At -20 °C.

## References and Notes

(1) Ito, Y.; Matsuura, T. *J. Org. Chem.* 1979, 44, 41. (The values for the quantum yields reported there are erroneous because of the improper choice of a filter solution for ferrioxalate actinometry. The true values should be much higher than reported.)

(2) (a) Matsuura, T.; Banba, A.; Ogura, K. *Tetrahedron* 1971, 27, 1211. (b) Nakano, T.; Rodríguez, W.; Z. de Roche, S.; Larrauri, J. M.; Rivas, C.; Pérez, C. *J. Heterocyclic Chem.* 1980, 17, 1777.

(3) (a) Jones, G., II; Gilow, H. M.; Low, J. *J. Org. Chem.* 1979, 44, 2949. (b) Rivas, C.; Vêlez, M.; Cucarella, M.; Bolívar, R. A.; Flores, S. E. *Acta. Cient. Venez.* 1971, 22, 145. (c) Rivas, C.; Bolívar, R. A. *J. Heterocyclic Chem.* 1976, 13, 1037.

(4) Julian, D. R.; Tringham, G. D. *J. Chem. Soc., Chem. Commun.* 1973, 13.

(5) The new compounds **3b** - **e**, **5** and **6** gave satisfactory spectral ($^1$H NMR, $^{13}$C NMR, IR, UV and mass spectra) and analytical data.

(6) Details of the X-ray structure will be reported elsewhere.

(7) The 366-nm line was isolated with filter solutions: $BiCl_3$ (1 g in 150 mL of 10 % HCl) and $CoSO_4$ (240 g/L). These conditions ensure that most of the incident light is absorbed by **2d**. Product analyses were done by using reverse-phase HPLC over Zorbax ODS with acetonitrile/water 90:10 as the mobile phase.

(8) Delzenne, G. A. *Adv. Photochem.* 1979, 11, 1.

(9) Jones, G., II, Chiang, S.-H.; Xuan, P. T. *J. Photochem.* 1979, 10, 1.

(10) A resolidified sample of the molten mixture of **1** and **2**, being irradiated under the same conditions, gave a similar result.

(11) Assuming that the triplet lifetime of **2d** is ca. 10 μs, one calculates $k_q \sim 1 \times 10^{10}$ $M^{-1}s^{-1}$.

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