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[2+2]-Photocycloaddition of 2-Morpholinopropenenitrile to Monosubstituted Benzils

Hamid Reza Memarian[1,*], **Mohammad Dehghani**[1], **Gerald Henkel**[2], and **Dietrich Döpp**[2]

[1] University of Isfahan, Department of Chemistry, Faculty of Sciences, 81746-73441 Isfahan, Iran
[2] Gerhard-Mercator-Universität Duisburg, Institut für Chemie, D-47048 Duisburg, Germany

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Summary. Triplet excited unsymmetrically substituted benzils react with 2-morpholinopropenenitrile to form oxetanes. Whereas the selectivity with respect to the site of addition (benzoyl *vs.* 4-substituted benzoyl) is generally low, the photoadditions observed are all unidirectional ("regioselective") and of high stereoselectivity, as had also been found earlier for benzil itself and for symmetrically 4,4′-disubstituted benzils. The relative configurations of two oxetanes have been unambiguously confirmed by single crystal X-ray structure determinations.

Keywords. Captodative olefins; Oxetanes; *Paternò-Büchi* reaction; Photochemistry.

Introduction

The photocycloaddition of carbonyl compounds to olefins to yield oxetanes has been published for the first time by *Paternò* and *Chieffi* in 1909 [1]. Mechanistic studies have been carried out by *Büchi et al.* [2], and thus this reaction became known as the *Paternò-Büchi* reaction [3–5]. In the course of our studies of reactions with so-called captodative [6] olefins we have encountered highly regio- and stereoselective photocycloadditions of such olefins to benzil [7, 8]. In this study we report the photochemical behaviour of unsymmetrically substituted benzils **1a**–**1e** towards a typical captodative olefin, namely 2-morpholinopropenenitrile (**2**). It should be pointed out that these additions are governed by three modes of selectivity: (i) site selectivity (discrimination between the two non-equivalent carbonyl groups), (ii) directional selectivity of addition ("regioselectivity"), and (iii) stereoselectivity.

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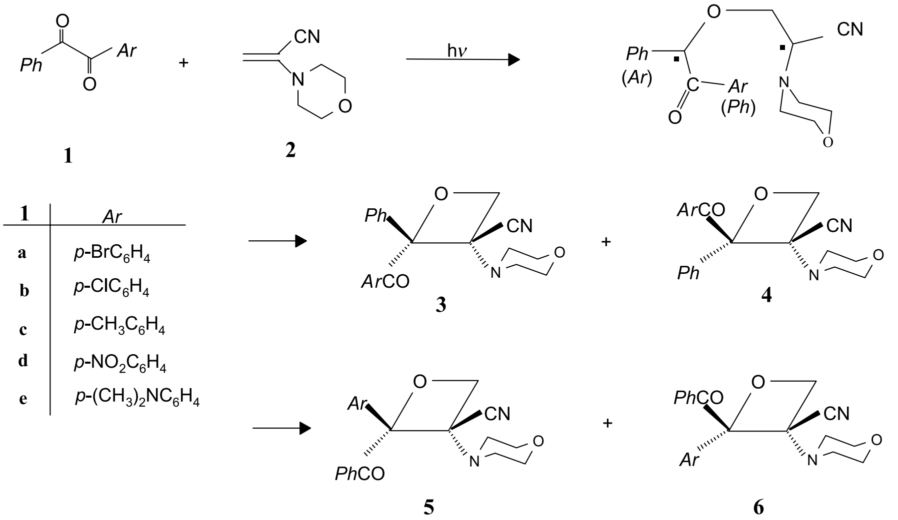
[*] Corresponding author. E-mail: memarian@sci.ui.ac.ir

Results and Discussion

Common solutions of each of **1a**–**1e** and **2** in acetonitrile were irradiated with a high pressure mercury vapour lamp ($\lambda \geq 280\,\text{nm}$) under an argon atmosphere. Formation of photoproducts has been observed only from **1a**–**1d**, whereas in the case of **1e**, only unchanged starting material has been recovered even after 35 hours of irradiation. The *Paternò-Büchi* reaction is generally assumed to be initiated by attack of the electron-deficient carbonyl oxygen atom of the n,π^*-state of the carbonyl compound [5, 9] on one terminus of the alkene. The failure of the photoaddition in the case of **1e** is probably due to a π,π^*-nature of the excited state, which is supported [10] by the bathochromic shift of the long wavelength band by changing the solvent from benzene and acetonitrile to methanol.

Formation of a triplet biradical intermediate has been proposed in the *Paternò-Büchi* reaction between triplet ketones and moderately electron rich alkenes, which can subsequently undergo intersystem crossing and ring closure to form oxetanes [11]. Since the formation of different biradical intermediates is *a priori* possible with unsymmetrically substituted olefins, the major oxetane isomer is usually that which would be expected from formation of the most stable biradical intermediate [2, 4]. The captodative effect [6], the combined action of an electron withdrawing (captor) and an electron releasing (donor) substituent on a radical center, leads to an enhanced stabilization of the latter [12]. Therefore, due to captodative stabilization of one radical center of the proposed biradical intermediate and by considering the involvement of two different carbonyl groups in our study, the formation of two constitutional isomers, each as a pair of diastereomers (**3**, **4** and **5**, **6**), should be expected.

Irradiation of **1a**, **1b**, **1c**, and **1d** in the presence of **2** resulted in the formation of mixtures of isomeric products of type **4** and **6**. In the cases of irradiation of **1a** and **1b** the products have been isolated only as mixtures, whereas in the case of **1d**, the products decomposed on attempted separation on silica gel and therefore could



1 2 3 4 5 6

1	Ar
a	p-BrC$_6$H$_4$
b	p-ClC$_6$H$_4$
c	p-CH$_3$C$_6$H$_4$
d	p-NO$_2$C$_6$H$_4$
e	p-(CH$_3$)$_2$NC$_6$H$_4$

Scheme 1

not be isolated. ^{1}H NMR spectra of the mixture of products from **1a** and **1b** show two partially overlapping AB-quartets for the oxetane CH_2 groups with coupling constants $|^2J| = 6.25$ and 6.23 Hz. The ^{1}H NMR spectrum of the products from **1c** and **2** before recrystallization shows two broad triplets at $\delta = 4.61$ and 4.76 ppm. Recrystyllisation from methanol gave pure **4c** and its ^{1}H NMR spectrum shows a quartet for the oxetane CH_2 group at $\delta_B = 4.62$ and $\delta_A = 4.77$ ppm with a coupling constant of $|^2J| = 6.07$ Hz. Concentration of the mother liquor to dryness and crystallization of the residue from *n*-hexane gave **6c** and its ^{1}H NMR spectrum shows a quartet at $\delta = 4.61$ and 4.75 ppm with a coupling constant $|^2J| = 5.95$ Hz. The IR spectrum of **4c** shows CO group absorption at $\bar{\nu} = 1668\,cm^{-1}$, whereas the corresponding absorption for both CO groups in **1c** appears at $\bar{\nu} = 1668$–$1680\,cm^{-1}$. The ^{13}C NMR spectrum shows a CO resonance at $\delta = 195.25$ ppm, signals for C-2 and C-4 at $\delta = 96.82$ and 72.44 ppm as well as 13 signals for all other carbon atoms (see Experimental). The ^{1}H NMR spectrum of the reaction mixture of **1d** with **2** reveals two AB-quartets centered at $\delta = 4.78$ and 4.79 ppm with $|^2J| = 6.27$ and 6.31 Hz, respectively. The ^{13}C NMR spectra of the mixtures of products derived from **1a** and **1b** with **2** showed two resonances each for CO groups at $\delta = 194.86$, 195.67 and 194.52, 195.61 ppm, and additionally 25 peaks for all other C-atoms of both isomers present. This indicates the formation of two isomeric products in either case.

The *cis*-orientation of the morpholino group and the phenyl ring was confirmed for **4a** and **4c** by a single crystal X-ray structural determination [13] (Fig. 1). Therefore, the second product could be either the C-2-epimer of the C-2 positional isomer (**5** or **6**). A comparison of ^{1}H NMR data with those obtained for other benzil derivatives **1f** and **7a**–**7e** suggests the formation of a product of type **6** as the second product.

4a

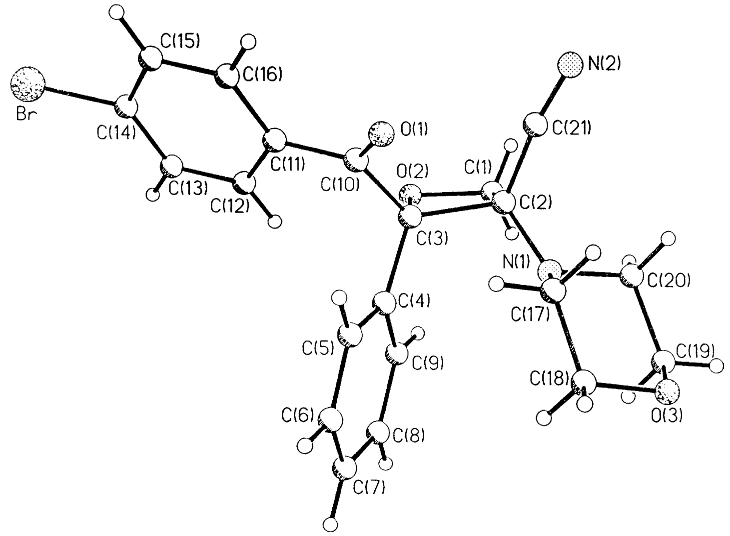


Fig. 1. Structures of **4a** (top) and **4c** (bottom) in the crystal; the crystallographic numbering does not reflect systematic numbering

4c

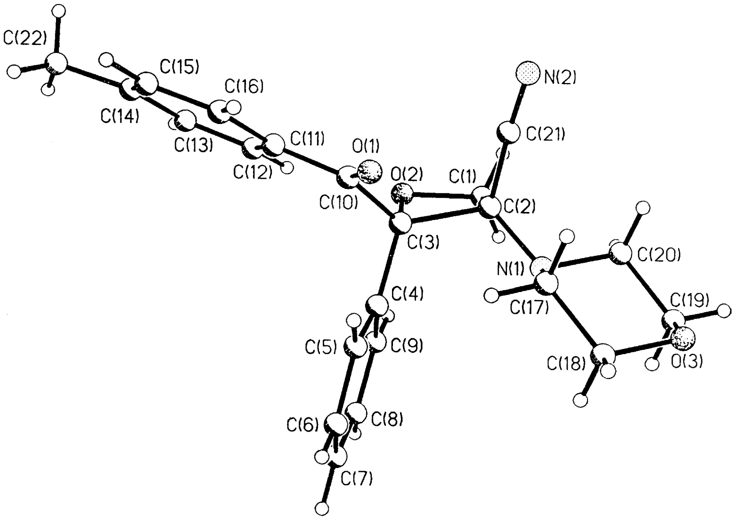


Fig. 1 (*continued*)

The ratio of products **4**:**6** was obtained by comparison of the integral ratios of the AB systems of the oxetane CH$_2$ moieties. As is shown in Table 1, the relative proportions of products **4** and **6** indicate that the substituted benzoyl group reacts only slightly faster in this addition. This phenomenon has been observed also for photochemical reductions of unsymmetrical benzils in 2-propanol solution [14]. These results indicate that the 4-substituted benzoyl group is preferentially reduced in the order 4-CN > 4-Cl > 4-H > 4-*Me* > 4-*Me*O $\sim$ 4-NMe_2 [14]. This means, that an electron withdrawing effect of the substituent increases the n,π^*-character of the lowest energy transition, which is beneficial both for photoreduction and for the *Paternò-Büchi* reaction.

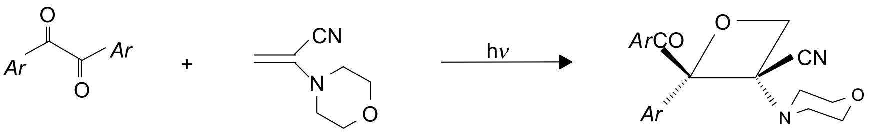
The triplet excited state of **1a**–**1d** is involved in the reaction, and the rate constants for quenching of the triplet excited states of **1a**–**1d** by compound **2** had been estimated to $k_q = 2.98$, 2.78, 0.94, and 13.04 dm^3 mol^{-1} s^{-1} [15].

A few remarks with regard to stereocontrol are appropriate. The triplet states, by addition to C-2 of the alkene **2**, form 2-oxatetramethylene 1,4-biradicals, which have to undergo intersystem crossing (ISC) prior to final ring clousure. ISC in turn depends on the biradical geometry [16], which is outlined in depth in a recent review [17]. According to this concept, a favourable geometry for the biradical B would be such that the bulky aryl group initially points away from the morpholino and cyano moieties and slides into a *cis* orientation to morpholino upon ring closure after ISC avoiding an approach towards the CN group and thus allowing for the two acceptor dipoles to interact favourably [18], giving rise to the observed geometries of all four oxetanes.

The structures of compounds **4a** and **4c** in the crystal shall be commented briefly. The longest C–C bond (1.580 (4) and 1.583 (4) Å) in the oxetane unit is the one sterically most encumbered (C2–C3) and probably the most labile one. Aside of this, there are no signifinant deviations of bond lengths and angles from

Table 1. Photoaddition of 2-morpholinopropenenitrile (**2**) to 1,2- diarylethanediones **1a**–**1f** and **7a**–**7e**; typical spectral data of products

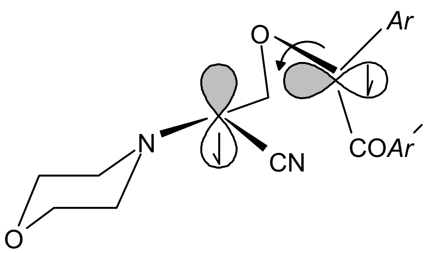
Starting material	Product (parts)	AB(4-CH_2)			δ_{CO}/ppm	Ref.
		δ_A/ppm	δ_B/ppm	$\lvert ^2J_{AB} \rvert$/Hz		
1a	**4a** (44)	4.82	4.67	6.26	194.86	
	6a (56)	4.78	4.67	6.17	195.67	
1b	**4b** (35)	4.82	4.67	6.17	194.52	
	6b (65)	4.78	4.67	6.18	195.61	
1c	**4c**	4.77	4.62	6.07	195.25	
	6c	4.75	4.61	5.95		
1d	**4d** (31)	4.86	4.70	6.27		
	6d (69)	4.84	4.73	6.31		
1f	**4f** (37)	4.80	4.65	6.15		[8]
	6f (63)	4.77	4.63	6.2		[8]
7a	**8a**	4.82	4.66	6.2	195.6	[7]
7b	**8b**	4.77	4.64	6.1	194.0	[8]
7c	**8c**	4.79	4.63	6.1	195.2	[8]
7d	**8d**	4.79	4.63	6.2	194.2	[8]
7e	**8e**	4.85	4.73	6.3	194.6	[8]



7 **2** **8**

7 / 8	**a**	**b**	**c**	**d**	**e**
Ar	C_6H_5	4-$CH_3OC_6H_4$	4-$CH_3C_6H_4$	4-ClC_6H_4	4-$CF_3C_6H_4$

Scheme 2



B

Formula 1

standard values. It is noteworthy that **4c** underwent spontaneous resolution (space group $P2_12_12_1$) upon crystallisation.

Experimental

All melting points were determined with a Stuart Scientific SMP2-apparatus. IR spectra were recorded (KBr discs) on a Shimadzu IR-435 spectrometer. ^{1}H NMR spectra were recorded with the Bruker AW 80 (80 MHz), Bruker WM 300 (300 MHz) and Bruker DRX 500 (500 MHz) instruments, ^{13}C NMR spectra were recorded with a Bruker DRX 500 (125.76 MHz) spectrometer. Mass-spectra were obtained on an AMD 604 instrument; EI-mode: Electron energy and temperature of inlet system given; FD-mode: High voltage applied and emitter filament heating current given. Elemental analyses have been done with a Carlo Erba 1106 CHN-analyzer; their values agree favourably with the calculated values. UV spectra were measured on a Shimadzu UV-160 spectrometer. Starting materials **1a**–**1e** and **2** were prepared according to known procedures [19–24]. Preparative layer chromatography (PLC) was carried out on 20 cm × 20 cm plates, coated with a 1 mm layer of Merck silica gel PF_{254}, prepared by applying the silica gel as a slurry and air drying. Since **2** decomposed on the silica gel, the amount of unconverted **2** has not been determined. All irradiations were carried out in water cooled Duran ($\lambda \geq 280$ nm) cells (1.5 cm thickness) using a 400-W high-pressure Hg-vapor lamp (NARVA). The irradiated samples were purged with Ar throughout the experiment. Details of X-ray determination and the structural data of **4a** and **4c** were deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151977 (for **4a**) and CCDC-151978 (for **4c**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44-1233/336-033; E-mail: deposit@ccdc.cam.ac.uk].

*Irradiation of 4-Bromobenzil (**1a**) in the Presence of 2-Morpholinopropenenitrile (**2**)*

A solution of 231 mg (0.8 mmol) of **1a** and 110 mg (0.8 mmol) of **2** in 16 cm^3 of dry acetonitrile ($c = 0.05\,M$ each) was irradiated under Ar for 2.5 h. The solvent was evaporated and PLC of the residue (petroleum ether:ethyl acetate = 10:3) gave zone 1 ($R_f = 0.67$, 101 mg of **1a**), zone 2 ($R_f = 0.5$, **2**), and zone 3 ($R_f = 0.21$, 158 mg, consisting of a mixture of **4a** and **6a**, yield 46% based on **1a** used and 82% based on **1a** consumed), which was crystallized from methanol, mp 148–154°C.

(2R,3S*)-2-(4-Bromobenzoyl)-3-morpholino-2-phenyloxetane-3-carbonitrile* (**4a**, $C_{21}H_{19}BrN_2O_3$) *and (2R*,3S*)-2-Benzoyl-2-(4-bromophenyl)-3-morpholinooxetane-3-carbonitrile* (**6a**, $C_{21}H_{19}BrN_2O_3$)

IR (KBr): $\bar{\nu} = 2200$ (CN), 1672 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.36$–2.41 [m, 2H, $N(CH_{ax})_2$], 2.50–2.52 [m, 2H, $N(CH_{eq})_2$], 3.33 [br d, 2H, $O(CH_{ax})_2$], 3.43–3.51 [m, 2H, $O(CH_{eq})_2$], two AB-systems with an integral ratio of 56:44, namely $\delta_A = 4.78$, $\delta_B = 4.67$, $|^2J_{AB}| = 6.17$ Hz (CH_2, **6a**) and $\delta_A = 4.82$, $\delta_B = 4.67$, $|^2J_{AB}| = 6.26$ Hz (CH_2, **4a**), 7.35–7.86 (9H, several m, aromatic H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 47.94$, 47.99 [$N(CH_2)_2$], 66.17 [$O(CH_2)_2$], 67.46 and 67.48 (both C-3), 72.54 and 72.69 (both C-4), 96.65 and 96.8 (both C-2), 116.24 and 116.39 (both CN), 123.99, 126.60, 128.42, 128.55, 128.82, 129.43, 129.71, 130.32, 131.84, 131.95, 131.97, 132.64, 133.02, 133.07, 134.23 (aromatic carbons), 194.86 (CO, **4a**), 195.67 (CO, **6a**) ppm; EI-MS (145°C): m/z (%) = 401 [M^+–HCN] (0.2), 290 (1.3) and 288 [representing **1a**$^+$] (1.4), 258 (1.2), 243 [M^+-bromobenzoyl] (0.4), 209 [**1a**$^+$–Br] (1.3), 185 (21) and 183 [$BrC_6H_4CO^+$] (21), 157 (13) and 155 [$BrC_6H_4{}^+$] (13), 138 [representing **2**$^+$] (52), 105 [$PhCO^+$] (100), 77 [Ph^+] (38); FD-MS (0.01 V): m/z (%) = 427.8 [M^+] (8.2), 288.2 [representing **1a**$^+$] (6.5), 138.2 [representing **2**$^+$] (100), 58.5 (35.78).

*Irradiation of 4-Chlorobenzil (**1b**) in the Presence of **2***

A solution of 165 mg (0.67 mmol) of **1b** and 138 mg (1 mmol) of **2** in 16 cm^3 of dry acetonitrile was irradiated under Ar for 80 min. The solvent was evaporated and PLC of the residue (petroleum ether:ethyl acetate = 10:3) gave zone 1 ($R_f = 0.78$, 61 mg of **1b**), zone 2 ($R_f = 0.5$, **2**), and zone 3 ($R_f = 0.31$, 122 mg, a mixture of **4b** and **6b**, yield 48% based on **1b** used and 76% based on **1b** consumed), which was recrystallized from methanol, mp141–146°C.

(2R,3S*)-2-(4-Chlorobenzoyl)-3-morpholino-2-phenyloxetane-3-carbonitrile* (**4b**, $C_{21}H_{19}ClN_2O_3$) *and (2R*,3S*)-2-Benzoyl-2-(4-chlorophenyl)-3-morpholinooxetane-3-carbonitrile* (**6b**, $C_{21}H_{19}ClN_2O_3$)

IR (KBr): $\bar{\nu} = 2200$ (CN), 1668 (CO) cm^{-1}; ^{1}H NMR (CDCl$_3$): $\delta = 2.36$–2.41 [m, 2H, N(CH$_{ax}$)$_2$], 2.50–2.54 [m, 2H, N(CH$_{eq}$)$_2$], 3.33 [br, 2H, O(CH$_{ax}$)$_2$], 3.44–3.52 [m, 2H, O(CH$_{eq}$)$_2$], two AB-systems with an integral ratio of 65:35, namely $\delta_A = 4.78$, $\delta_B = 4.67$, $|^2J_{AB}| = 6.18$ Hz (CH$_2$, **6b**) and $\delta_A = 4.82$, $\delta_B = 4.67$, $|^2J_{AB}| = 6.17$ Hz (CH$_2$, **4b**), 7.32–7.51 (several m, 9H, aromatic hydrogens) ppm; ^{13}C NMR (CDCl$_3$): $\delta = 47.86$ [N(CH$_2$)$_2$], 66.06 [O(CH$_2$)$_2$], 67.34 and 67.41 (both C-3), 72.42 and 72.56 (both C-4), 96.47 and 96.71 (both C-2), 116.1 and 116.26 (both CN), 126.49, 128.03, 128.42, 128.69, 128.74, 128.89, 129.58, 130.21, 131.42, 131.68, 131.97, 132.98, 134.09, 135.63, 140.45 (aromatic carbons), 194.52 (CO, **4b**), 195.61 (CO, **6b**) ppm; EI-MS (145°C): m/z (%) = 355 [M$^+$–HCN] (0.28), 347 [M$^+$- Cl] (0.1), 246 (0.7) and 244 [**1b**$^+$] (2), 209 [**1b**$^+$–Cl] (0.8), 141 (11) and 139 [chlorobenzoyl$^+$] (38), 138 [**2**$^+$] (68), 113 (8) and 111 [chlorophenyl$^+$] (23), 105 [PhCO$^+$] (100), 77 [Ph$^+$] (42), 51 [**2**$^+$–morpholine] (16); FD-MS (0.01 V): m/z (%) = 384 [M$^+$] (3.12), 381.95 [M$^+$] (0.1), 324.2 (2.23), 277 [M$^+$–PhCO] (4), 246 (3) and 244 [**1b**$^+$] (6), 138 [**2**$^+$] (100).

*Irradiation of 4-Methylbenzil (**1c**) in the Presence of **2***

A solution of 202 mg (0.9 mmol) of **1c** and 124 mg (0.9 mmol) of **2** in 18 cm^3 of dry acetonitrile ($c = 0.05\,M$ each) was irradiated under Ar for 2 h. The solvent was evaporated and PLC of the residue (cyclohexane:ethyl acetate = 4:1) gave zone 1 ($R_f = 0.77$, 67 mg of **1c**), zone 2 ($R_f = 0.5$, **2**), and zone 3 ($R_f = 0.21$, 141 mg, **4c** and **6c** (43% based on **1c** used, 65% based on **1c** consumed). **4c** was isolated by crystallization from methanol, mp 146–148°C. On evaporation of the mother liquor and crystallization of the residue from *n*-hexane a small amount of **6c** has been obtained, mp 126–128°C.

(2R,3S*)-2-(4-Methylbenzoyl)-3-morpholino-2-phenyloxetane-3-carbonitrile* (**4c**, $C_{22}H_{22}N_2O_3$)

IR (KBr): $\bar{\nu} = 2208$ (CN), 1668 (CO) cm^{-1}; ^{1}H NMR (CDCl$_3$): $\delta = 2.31$ (s, 3H, CH$_3$), 2.33–2.35 [m, 2H, N(CH$_{ax}$)$_2$], 2.47–2.50 [m, 2H, N(CH$_{eq}$)$_2$], 3.25 [br, 2H, O(CH$_{ax}$)$_2$], 3.40–3.45 [m, 2H, O(CH$_{eq}$)$_2$], AB-system (2H, $\delta_A = 4.77$, $\delta_B = 4.62$, $|^2J_{AB}| = 6.07$ Hz, CH$_2$), 7.11–7.13 (m, 2H, *m*-H of methylbenzoyl group), 7.35–7.40 (m, 3H, *p*- and *m*-H of phenyl group), 7.51–7.53 (m, 2H, *o*-H of phenyl group), 7.72–7.74 (m, 2H, *o*-H of methylbenzoyl group) ppm; ^{13}C NMR (CDCl$_3$): $\delta = 21.78$ (CH$_3$), 47.83 [N(CH$_2$)$_2$], 66.11 [O(CH$_2$)$_2$], 47.36 (C-3), 72.44 (C-4), 96.82 (C-2), 116.44 (CN), 126.55, 128.55, 129.06, 129.34, 130.38 (aromatic CH), 130.63 (*C*-CH$_3$), 133.44 (C1 of phenyl at oxetane), 144.96 (C1 of aryl at CO), 195.25 (CO) ppm; EI-MS (140°C): m/z (%) = 347 [M$^+$–CH$_3$] (0.4), 335 [M$^+$–HCN] (0.6), 332 [M$^+$–CH$_2$O] (0.5), 257 [M$^+$–PhCO] (0.7), 224 [**1c**$^+$] (3), 138 [**2**$^+$] (28), 119 [methylbenzoyl$^+$] (100), 105 [benzoyl$^+$] (28), 91 [methylphenyl$^+$] (45); FD-MS (0.01 V): m/z (%) = 362 [M$^+$] (12), 224 [**1c**$^+$] (14), 138 [**2**$^+$] (100), 119 [methylbenzoyl$^+$] (12); UV (CH$_3$CN): λ_{max} (lg ε) = 263 (4.23) nm.

Table 2. Compounds **4a** and **4c**; crystal data and structure refinement

Chemical formula	**4a** $C_{21}H_{19}BrN_2O_3$	**4c** $C_{22}H_{22}N_2O_3$
formula weight	427.29	362.42
temperature	150 K	150 K
wavelength	0.71073 Å	0.71073
crystal system, space group	monoclinic, $P2_1/n$	Orthorhombic, $P2_12_12_1$
unit cell dimensions	$a = 7.632$ (2) Å $b = 11.742$ (4) Å $c = 20.925$ (6) Å $\beta = 93.05$ (2)°	$a = 9.083$ (1) Å $b = 11.326$ (2) Å $c = 18.085$ (3) Å
volume	1872.5 (10) Å^3	1860.5 (5) Å^3
Z, calculated density	4, 1.516 Mg/m^3	4, 1.294 Mg/m^3
absorption coefficient	2.219 mm^{-1}	0.087 mm^{-1}
F (000)	872	768
crystal size	0.69 × 0.28 × 0.19 mm	0.71 × 0.23 × 0.18 mm
theta range	2.61° to 25.99°	2.12° to 26.99°
limiting indices	$-9 \leq h \geq 0$, $0 \leq k \geq 13$, $-24 \leq l \geq 24$	$-11 \leq h \geq 0$, $0 \leq k \geq 14$, $0 \leq l \geq 23$
reflections collected/unique	3534/3274 [R(int) = 0.0201]	2327/2327 [R(int) = 0.0000]
min. and max. transmission	0.628 and 0.880	
absorption correction		Not applied
refinement method	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)
data/restraints/parameter	3274/0/246	2327/0/246
goodness-of-fit on F^2	1.058	1.061
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0345$, $wR2 = 0.0733$	$R1 = 0.0480$, $wR2 = 0.1144$
R indices (all data)	$R1 = 0.0532$, $wR2 = 0.0799$	$R1 = 0.0629$, $wR2 = 0.1237$
extinction coefficient	0.0034 (5)	0.012 (2)
largest diff. peak and hole	0.329 and −0.282 eA^{-3}	0.302 and −0.290 eA^{-3}

(2R,3S*)-2-Benzoyl-2-(4-methylphenyl)-3-morpholinooxetane-3-carbonitrile*
(**6c**, $C_{22}H_{22}N_2O_3$)

^{1}H NMR (CDCl$_3$): $\delta = 2.31$–2.34 [br, 5H, CH$_3$ and N(CH$_{ax}$)$_2$], 2.47–2.50 [m, 2H, N(CH$_{eq}$)$_2$], 3.27 [br, 2H, O(CH$_{ax}$)$_2$], 3.40–3.46 [m, 2H, O(CH$_{eq}$)$_2$], AB-system (2H, $\delta_A = 4.75$, $\delta_B = 4.61$, $|^2J_{AB}| = 5.95$ Hz, CH$_2$), 7.1–7.1 (several m, 9H, aromatic hydrogens) ppm.

Acknowledgements

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References

[1] Paterno E, Chieffi G (1909) Gazz Chim Ital **39**: 341
[2] Büchi G, Inman CG, Lipinsky ES (1954) J Am Chem Soc **76**: 4327
[3] Muller LL, Hamer J (1976) In: 1,2-Cycloaddition Reactions. Interscience, New York, p 111
[4] Arnold DR (1986) Adv Photochem **6**: 301
[5] Arnold DR, Hinman RL, Glick AH (1964) Tetrahedron Lett 1425
[6] Viehe HG, Janousek Z, Merenyi R, Stella L (1985) Acc Chem Res **18**: 148 and earlier papers
[7] Döpp D, Memarian HR, Fischer MA, van Eijk AMJ, Varma CAGO (1992) Chem Ber **125**: 983. The structural assignment given there has later been revised, see Ref. [8]
[8] Döpp D, Fischer MA (1995) Recl Trav Chim Pays-Bas **114**: 498
[9] Yang NC, Nussim M, Jørgenson MJ, Murov S (1964) Tetrahedron Lett 3657
[10] Becker HGO (1983) In: Einführung in die Photochemie. Thieme, Stuttgart, S 51
[11] Yang NC (1964) Pure Appl Chem **9**: 591
[12] Crans D, Clark T, Schleyer PR (1980) Tetrahedron Lett **21**: 3681
[13] Sheldrick GM, SHELXS-97 (1997) Program for Crystal Structure Solution and SHELXL-97 Program for Crystal Structure Refinement, University of Göttingen, Germany, were used
[14] Ogata Y, Takagi K, Fujii Y (1972) J Org Chem **37**: 4026
[15] We thank Dr. *H. Görner*, Max-Planck-Institut für Strahlenchemie, Mülheim a. d. Ruhr, for these measurements
[16] Salem L, Rowland C (1972) Angew Chem **84**: 86; (1972) Angew Chem Int Ed Engl **11**: 92
[17] Griesbeck AG, Fiege M (2000) In: Ramamurthy V, Schanze KS (eds) Stereoselectivity of Photocycloadditions and Photocyclization, Physical and Materials Photochemistry (Molecular and Supramolecular Photochemistry, vol 6). Marcel Dekker, New York, p 33
[18] Ref. [17] p 51, 52
[19] Arnold RT, Fuson RC (1963) J Am Chem Soc **58**: 1295
[20] van Es T, Backeberg OG (1963) J Chem Soc 1371
[21] Clark MT, Hendley EC, Neville OK (1955) J Am Chem Soc **77**: 3280
[22] Womack EB, Campbell N, Dodds GB (1938) J Chem Soc 1402
[23] Francis AG, Keane CA (1911) J Chem Soc 344
[24] Temin SC (1957) J Org Chem **22**: 1714