PHOTOCHEMICAL REACTIONS OF SUBSTITUTED 2(3*H*)-OXAZOLONES WITH CARBONYL COMPOUNDS

Stanislav SEKRETÁR[a], Jan KOPECKÝ[b] and Augustín MARTVOŇ[c]

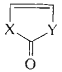
[a] *Department of Organic Chemistry,*
Slovak Institute of Chemical Technology, 880 37 Bratislava,
[b] *Institute of Hygiene and Epidemology, 100 41 Prague and*
[c] *Research Institute for Drugs, 900 01 Modra*

Received August 12th, 1981

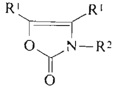
Photocycloaddition of carbonyl compounds of various triplet energy to 3-acetyl-2(3*H*)-oxazolone (*V*) and 3-acetyl-4,5-dimethyl-2(3*H*)-oxazolone (*VI*) afforded oxetanes *XIII*–*XX*. Other investigated 2(3*H*)-oxazolones *VII*–*IX* gave no oxetanes. The photoreactivity of 2(3*H*)-oxazolones and the regioselectivity of the photocycloaddition were correlated with the HMO reactivity indices.

Acylation of nitrogen heterocyclic systems at the nitrogen atom enhances their reactivity in [2+2]photocycloaddition reactions as observed with indole[1,2], pyrrole[3,4] and imidazole[5,6]. In compounds *I*–*V* there is, moreover, an effect of the hetero atom. Whereas 1,3-dioxol-2-one (*I*) is a good partner in [2+2]photocycloadditions with carbonyl compounds[7,8], 2(1,3*H*)-imidazolone (*II*) is practically unreactive in analogous reactions; a comparable reactivity is shown only by its 1,3-diacetyl derivative[9,10] *III*. It was found that in acetone-sensibilized photocycloadditions with olefins, 2(3*H*)-oxazolone (*IV*) is less reactive than its 3-acetyl derivative[11] *V*. In this study we investigate photochemical reactions of substituted 2(3*H*)-oxazolones *V*–*IX* with carbonyl compounds of various triplet energy. The results are given in Table I. The photodimerization of compounds *V* and *VI* is sensibilized by acetone. Compound *V* afforded a mixture of dimers *X* and the homopolymer *XI* whereas *VI* gave only the dimer *XII*. Other carbonyl compounds (Table I) reacted with compounds *V* and *VI* to give mainly the oxetanes *XIII*–*XX*. The borderline between sensibilization and addition in the case of *V* and *VI* bears an approximate information about the triplet energy of these compounds[14,15]. The triplet sensibilization is diffusion-controlled and the energy transfer between the triplet states requires the difference E_T donor − E_T acceptor to be at least 12·5 kJ mol^{-1}. It follows therefore that E_T values for compounds *V* and *VI* are about 295 mol^{-1} and 315 kJ mol^{-1}, respectively.

No reactions of the oxazolones *VII*–*IX* with carbonyl compounds were observed. Determination of the structure of the dimers *X* and *XII* from the spectra (see Experimental) is not unequivocal although analogous data for the dimers of 1,3-dioxol-2-one[16] and 1,3-diacetyl-2(1,3*H*)-imidazolone[9] are available. The structure of oxetanes *XIII*–*XX* was determined mainly on the basis of their ^{1}H NMR spectra. Reaction of benzaldehyde with compound *V* afforded two isomers *XIII* and *XIV*. According to the ^{1}H NMR spectrum, all the oxetane ring protons in compound *XIII* (δ_{H_1} = 6·31 ppm, δ_{H_5} = 4·87 ppm, δ_{H_6} = 5·66 ppm) are more shielded than



I, X = Y = O
II, X = Y = NH
III, X = Y = $NCOCH_3$
IV, X = O, Y = NH



V, R^1 = H, R^2 = CH_3CO
VI, R^1 = CH_3, R^2 = CH_3CO
VII, R^1 = C_6H_5, R^2 = CH_3CO
VIII, R^1 = R^2 = C_6H_5
IX, R^1 = H, R^2 = C_6H_5

TABLE I

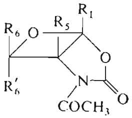
Comparison of reactivity of 2(3*H*)-oxazolone *V*–*IX* and products of the photoreactions

Carbonyl compound E_{T}[a] (kJ mol^{-1})	*V*	*VI*	*VII*	*VIII*	*IX*
Acetone 335	dimers (35)% polymers (55%)	dimers (31%)	0[b]	—	0
Acetophenone 309/312	dimers (8%)	oxetane (36)%	0	—	—
Xanthone 297/311	0	oxetane (41%)	—	—	0
Benzaldehyde 300/303	oxetanes (13%)	oxetane (46%)	—	—	—
4-Methoxybenzaldehyde 297/301	copolymers	oxetane (71%)	—	—	—
Benzophenone 287/291	oxetane (90%)	oxetane (53%)	0	0	0
Diacetyl 230/236	0	—[c]	—	—	—
Benzil 222/225	copolymers	copolymer	0	—	—

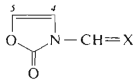
---

[a] Taken from ref.[12,13]; [b] no cycloaddition reaction; [c] the experiment was not performed.

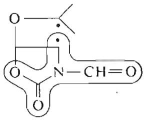
in the compound *XIV* ($\delta_{H_1} = 6{\cdot}62$ ppm, $\delta_{H_5} = 5{\cdot}03$ ppm, $\delta_{H_6} = 5{\cdot}76$ ppm). On the other hand, the acetyl and phenyl groups ($\delta_{CH_3} = 2{\cdot}61$ ppm, $\delta_{C_6H_5} = 7{\cdot}43$ ppm) are less shielded in *XIII* than in *XIV* ($\delta_{CH_3} = 2{\cdot}59$ ppm, $\delta_{C_6H_5} = 7{\cdot}43$ ppm). Structure of the oxetanes *XIII*–*XX* was derived from the structure of the compound *XV*. As seen from the chemical shift of acetyl protons, this group is more shielded in *XV* (δ 2·10 ppm) than in the oxetanes *XIII* and *XIV*; this can be caused by the presence of two neighbouring phenyl groups. On the other hand, in the alternative regioisomer there would be probably no shielding effect of the phenyl rings. For example, the ^{1}H NMR spectrum of the adduct of 1,3-diacetyl-2(1,3*H*)-imidazolone with benzophenone exhibits the shift of acetyl protons $\delta = 2{\cdot}15$ and $2{\cdot}58$ ppm (ref.[9]). An even more marked is the shielding effect of the xanthene moiety in the oxetane *XVI* (chemical shift of acetyl protons $\delta = 1{\cdot}94$ ppm). It has already been known previously, that quantum chemical reactivity indices can be correlated with the photochemical reactivity[17–19]. In our case we correlated the HMO reactivity indices of the model compound *XXI* with the photochemical reactivity of 2(3*H*)-oxazolones *V*–*IX*. By changing the coulomb integral α_X we simulated the effect of substituent on the HMO reactivity indices (Table II). An electron-accepting substituent increases the $p_{4,5}$ and $\Delta p_{4,5}$ values and thus also the reactivity *e.g.* in a photodimerisation. The F_5 value is in all cases higher than the value of F_4 and on the basis of the known mechanism of photocycloaddition of carbonyl compounds to olefins[20,21] we assume that carbonyl group in the excited triplet state attacks the compound *XXI* preferentially in the position 5. Of the two possible diradical intermediates *XXII* and *XXIII*, the former has a higher localization energy of the corresponding fragment and is therefore more stable. The experimentally found regioselectivity corresponds to the pathway *via* the diradical *XXII*.



XIII, $R^1 = R^5 = R^6 = H$, $R^{6'} = C_6H_5$
XIV, $R^1 = R^5 = R^6 = H$, $R^{6'} = C_6H_5$
XV, $R^1 = R^5 = H$, $R^6 = R^{6'} = C_6H_5$
XVI, $R^1 = R^5 = CH_3$, R^6—$R^{6'}$ = 9-xantylidene
XVII, $R^1 = R^5 = R^6 = CH_3$, $R^{6'}$-C_6H_5
XVIII, $R^1 = R^5 = CH_3$, $R^{6'} = H$, $R^6 = CH_3OC_6H_4$
XIX, $R^1 = R^5 = CH_3$, $R^6 = C_6H_5$, $R^{6'} = H$
XX, $R^1 = R^5 = CH_3$, $R^6 = R^{6'} = C_6H_5$

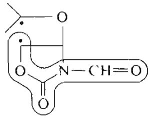


XXI



XXII

$E = 15{\cdot}623\beta$



XXIII

$E = 15{\cdot}565\beta$

EXPERIMENTAL

The starting 2(3*H*)-oxazolones *V* (ref.[22]), *VI* (ref.[23]), *VII* (ref.[24]), *VIII* (ref.[24]) and *IX* (ref.[25]) were prepared according to the literature. Photochemical preparations were carried out in a 150 ml reactor[26]. Solidex ($\lambda > 260$ nm), Jena Glass ($\lambda > 300$ nm) or GWC ($\lambda > 330$ nm) filters were used. Prior to the reaction, nitrogen was passed through the reaction mixture (15 min) which was then irradiated by a medium-pressure mercury lamp (Tesla RVK 125) at the cooling water temperature. The reaction was followed by thin-layer chromatography on Silufol UF_{254}. Melting points were determined on a Kofler block and are uncorrected. The IR spectra were determined on a UR-20 (Zeiss, Jena) spectrophotometer, UV spectra (values of ε in $m^2 \, mol^{-1}$) on a UV-VIS Specord instrument and ^1H NMR spectra (δ, ppm internal standard tetramethylsilane) on a Tesla BS C (80 MHz) spectrometer. Mass spectra were taken on an MS 902 S (AEI Manchester) instrument (ionization energy 70 eV, emission 100 μA, ionization chamber temperature 50 to 210°C, depending on volatility of the sample).

Photodimerization of 3-Acetyl-2(3*H*)-oxazolone (*V*)

A solution of compound *V* (1·27 g; 0·01 mol) in acetone (100 ml) was irradiated through a Solidex filter for 43 h. Evaporation of the solvent and washing with diethyl ether (20 ml; removal of the starting compound) afforded 1·27 g of a mixture of dimers and polymers which on crystallization

TABLE II

HMO Indices of *XXI* for various α_X

α_X [a]	$p_{4,5}$ [b]	$\Delta p_{4,5}$ [c]	F_4 [d]	F_5 [d]
−0·5	0·904	0·103	0·497	0·538
0·0	0·908	0·228	0·500	0·535
0·5	0·911	0·317	0·503	0·533
1·0	0·913	0·349	0·505	0·532
1·5	0·914	0·359	0·507	0·531
2·0	0·914	0·363	0·507	0·531

[a] Coulomb integral; [b] $C_{(4)}$—$C_{(5)}$ bond order in the ground state; [c] difference between the $C_{(4)}$—$C_{(5)}$ bond order in the ground and first excited states; [d] free valence index,

from acetonitrile yielded 0·35 g (27%) of the dimer *X*, m.p. 290—292°C (sealed capillary, sublimation at 210°C and 13 Pa). Further material, (0·2 g; 8%) was obtained by evaporation of mother liquors and crystallization from ethyl acetate; m.p. 278—280°C (sealed capillary, sublimation at 210°C and 13 Pa). The mother liquors were taken down, dissolved in acetone and precipitated with chloroform, affording thus 0·7 g (55%) of the polymer *XI*, m.p. ~300°C (decomposition); stated[27] m.p. >300°C. For *X*: IR spectrum (KBr), cm^{-1}: 1 790, 1 710, 1 640, 1 375, 1 305, 1 275; ^{1}H NMR spectrum: (hexadeuteriodimethyl sulfoxide): 2·43 (s, 6 H, CH_3); 4·81 (d, 2 H, CH, $J = 7$ Hz); 5·03 (d, 2 H, CH, $J = 7$ Hz); mass spectrum, m/z (rel. intensity, %): 170 (11), 128 (32), 127 (13), 86 (33), 85 (20), 43 (100), 28(10). For $C_{10}H_{10}N_2O_6$ (254·2) calculated: 47·25% C, 3·97% H, 11·02% N; found: 47·13% C, 3·95% H, 10·58% N.

Photodimerization of 3-Acetyl-4,5-dimethyl-2(3*H*)-oxazolone (*VI*)

A solution of compound *VI* (1·55 g; 0·01 mol) in acetone (100 ml) was irradiated (Solidex filter) for 64 h. Evaporation of solvent, followed by column chromatography on silica gel (chloroform--acetone 7 : 3), afforded 0·5 g (31%) of the dimer *XII*, m.p. 204—205°C (ethanol, sublimation at 190°C and 13 Pa). IR spectrum (chloroform), cm^{-1}: 1 785, 1 725, 1 305, 1 115; ^{1}H NMR spectrum (deuteriochloroform): 1·44 (s, 3 H), 1·50 (s, 3 H), 1·57 (s, 3 H), 1·60 (s, 3 H), 2·51 (s, 3 H), 2·55 (s, 3 H); mass spectrum, m/z (rel. intensity): 156 (17), 155 (22), 114 (44), 113 (100), 43 (46), 42 (17), 28 (11). For $C_{14}H_{18}N_2O_6$ (310·3) calculated: 54·19% C, 5·85% H, 9·03% N; found: 54·04% C, 5·76% H, 8·86% N.

exo- and *endo*-6-Phenyl-4-acetyl-2,7-dioxa-4-azabicyclo[3,2,0]heptan-3-one (*XIII* and *XIV*)

A mixture of compound *V* (1·27 g; 0·01 mol), benzaldehyde (1·06 g; 0·01 mol) and benzene (100 ml) was irradiated through a Jena Glass filter for 50 h. After evaporation of the solvent, polymeric material was precipitated by addition of ether (20 ml) and the residue was chromatographed in benzene on a column of silica gel, affording 0·2 g (9%) of *XIII*, m.p. 133—133·5°C (ethanol). IR spectrum (chloroform), cm^{-1}: 1 805, 1 715, 1 375, 1 305, 1 140, 1 065; UV spectrum (methanol) λ_{max} 208 nm (log ε 3·08), 218 (2·88), 263 (1·3); ^{1}H NMR spectrum (deuteriochloroform): 2·61 (s, 3 H, CH_3), 4·87 (dd, 1 H, H_5), 5·66 (dd, 1 H, H_6), 7·31 (dd, 1 H, H_1), 7·43 (m, 5 H, C_6H_5), $J_{1,5} = 4·4$ Hz, $J_{5,6} = 3·1$ Hz, $J_{1,6} = 0·8$ Hz. Mass spectrum, m/z (rel. intensity): 189 (5), 160 (4), 150 (6), 147 (9), 127 (13), 119 (9), 108 (4), 107 (41), 105 (7), 91 (9), 79 (7), 77 (10), 51 (6), 44 (21), 43 (100), 28 (24). For $C_{12}H_{11}NO_4$ (233·2) calculated: 61·80% C, 4·76% H, 7·01% N; found 61·86% C, 4·80% H, 5·86% N. Further elution gave 0·1 g (4%) of *XIV*, m.p. 147°C (ethanol). IR spectrum (chloroform), cm^{-1}: 1 805, 1 725, 1 375, 1 305, 1 145, 1 085. UV spectrum (methanol) λ_{max} 210 nm (log ε 2·96), 218 (2·88), 262 (1·3). ^{1}H NMR spectrum (deuteriochloroform): 2·59 (s, 3 H, CH_3), 5·03 (dd, 1 H, H_5), 5·76 (d, 1 H, H_6), 6·62 (d, 1 H, H_1), 7·42 (s, 5 H, C_6H_5), $J_{1,5} = 5$ Hz, $J_{5,6} = 3$ Hz. Mass spectrum, m/z (rel. intensity): 183 (2), 150 (4), 127 (12), 108 (3), 107 (33), 105 (12), 91 (6), 85 (19), 79 (8), 77 (13), 51 (10), 44 (19), 43 (100), 41 (10), 28 (19). For $C_{12}H_{11}NO_4$ (233·2) calculated: 61·80% C, 4·76% H, 6·01% N; found: 62·20% C, 4·86% H, 6·17% N.

In addition, the starting compound (0·4 g; first fractions), as well as the polymeric material (1 g; last fraction), were obtained.

6,6-Diphenyl-4-acetyl-2,7-dioxa-4-azabicyclo[3,2,0]heptan-3-one (*XV*)

A mixture of compound *V* (1·27 g; 0·01 mol), benzophenone (1·82 g; 0·01 mol) and benzene (100 ml) was irradiated through a GWC filter for 15 h. Evaporation of the solvent, followed by column chromatography on silica gel (eluant benzene), afforded 2·8 g (90%) of the product *XV*, m.p. 138—138·5°C (cyclohexane), and 0·1 g of triphenylmethanol. IR spectrum (chloroform), cm^{-1}: 1 808, 1 715, 1 608, 1 375, 1 305, 1 145, 1 005; UV spectrum (methanol): λ_{max} 210 nm (log ε 3·34), 220 (3·14); ^1H NMR spectrum (deuteriochloroform): 2·10 (s, 3 H, CH_3), 5·66 (d, 1 H, H_5), 6·21 (d, 1 H, H_1), 7·10—7·75 (m, 10 H, 2 × C_6H_5), $J_{1,5}$ = 5·5 Hz; mass spectrum, *m/z* (rel. intensity): 265 (2), 238 (2), 237 (9), 226 (6), 225 (28), 206 (2), 196 (3), 195 (17), 194 (9), 184 (2), 183 (100), 182 (8), 167 (4), 165 (10), 106 (5), 105 (53), 85 (9), 77 (22), 51 (7), 44 (20), 43 (53), 28 (20). For $C_{18}H_{15}NO_4$ (309·3) calculated: 69·89% C, 4·89% H, 4·53% N; found: 70·07% C, 4·81% H, 4·72% N.

4-Acetyl-1,5-dimethyl-3-oxo-2,7-dioxa-4-azabicyclo[3,2,0]heptane < 6-spiro-9 > xanthene (*XVI*)

A mixture of compound *VI* (0·77 g; 5 mmol), xanthone (0·98 g; 5 mmol) and benzene (100 ml) was irradiated through a GWC filter for 65 h. Evaporation and column chromatography on silica gel in chloroform afforded 0·7 g (41%) of the product *XVI*, m.p. 186—188°C (cyclohexane). IR spectrum (chloroform), cm^{-1}: 1 790, 1 715, 1 605, 1 455, 1 390, 1 370, 1 306. UV spectrum (methanol): λ_{max} 208 nm (log ε 3·57), 215 (3·56), 243 (3·0), 290 (2·66); ^1H NMR spectrum (deuteriochloroform): 1·25 (s, 3 H, CH_3 at $C_{(5)}$), 1·92 (s, 3 H, CH_3 at $C_{(1)}$), 1·94 (s, 3 H, CH_3), 7·10—7·45 (m, 6 H, arom.), 7·63—7·87 (m, 2 H, arom).; mass spectrum *m/z* (rel. intensity): 307 (2), 265 (2), 264 (3), 239 (11), 200 (18), 199 (100), 198 (13), 181 (13), 168 (6), 155 (9), 139 (6), 113 (45), 111 (26), 84 (5), 77 (3), 70 (3), 69 (16), 56 (6), 44 (15), 43 (32), 42 (16), 28 (18). For $C_{20}H_{17}NO_5$ (351·3) calculated: 68·37% C, 4·88% H, 3·99% N; found: 68·70% C, 5·05% H, 3·91% N.

4-Acetyl-6-phenyl-1,5,6-trimethyl-2,7-dioxa-4-azabicyclo[3,2,0]heptan-3-one (*XVII*)

A mixture of compound *VI* (0·77 g; 5 mmol), acetophenone (0·60 g; 5 mmol) and benzene (100 ml) was irradiated through a GWC filter for 70 h. Evaporation and crystallization gave 0·5 g (36%) of *XVII*, m.p. 110—111°C (diethyl ether–hexane). IR spectrum (chloroform), cm^{-1}: 1 788, 1 710, 1 603, 1 390, 1 376, 1 306; UV spectrum (methanol): λ_{max} 210 nm (log ε 3·09), 215 (2·98); ^1H NMR spectrum (deuteriochloroform): 1·24 (s, 3 H, CH_3 at $C_{(5)}$), 1·58 (s, 3 H, CH_3 at $C_{(6)}$), 1·60 (s, 3 H, CH_3 at $C_{(1)}$), 2·64 (s, 1 H, CH_3), 7·40 (s, 5 H, C_6H_5); mass spectrum, *m/z* (rel. intensity): 189 (0·7), 173 (2), 155 (26), 121 (14), 114 (8), 113 (100), 105 (10), 77 (10), 44 (17), 43 (51), 41 (17), 28 (29). For $C_{15}H_{17}NO_4$ (275·3) calculated: 65·44% C, 6·22% H, 5·09% N; found: 65·21% C, 6·13% H, 4·97% N.

4-Acetyl-6-(4-methoxyphenyl)-1,5-dimethyl-2,7-dioxa-4-azabicyclo[3,2,0]heptan-3-one (*XVIII*)

A mixture of compound *VI* (0·77 g; 5 mmol), 4-methoxybenzaldehyde (0·7 g; 5 mmol) and benzene (100 ml) was irradiated through a Jena Glass filter for 82 h. Evaporation of solvent and two crystallizations afforded 1·1 g (76%) of compound *XVIII*, m.p. 135—136°C (cyclohexane–ethanol 5 : 1). IR spectrum (chloroform), cm^{-1}: 2 840, 1 792, 1 720, 1 615, 1 300, 1 140; UV spectrum (methanol): λ_{max} 205 nm (log ε 3·00), 230 (3·20), 276 (2·20), 284 (2·15); ^1H NMR spectrum (deuteriochloroform): 1·18 (s, 3 H, CH_3 at $C_{(5)}$), 1·68 (s, 3 H, CH_3 at $C_{(1)}$), 2·60 (s, 3 H, CH_3), 3·81 (s, 3 H, CH_3O), 5·63 (s, 1 H, H_6), 6·82—7·00 (m, 2 H, arom.), 7·23—7·43 (m, 2 H, arom.); mass spectrum, *m/z* (rel. intensity): 291 (2), 204 (6), 179 (15), 163 (5), 155 (18), 138 (5), 137 (50), 136 (5), 135 (13), 114 (8), 113 (100), 111 (8), 105 (3), 77 (7), 60 (4), 57 (7), 44 (9), 43 (40), 42 (15), 41 (8), 39 (4), 28 (13). For $C_{15}H_{17}NO_5$ (291·3) calculated: 61·85% C, 5·88% H, 4·81% N; found: 61·75% C, 5·68% H, 5·51% N.

4-Acetyl-6-phenyl-1,5-dimethyl-2,7-dioxa-4-azabicyclo[3,2,0]heptan-2-one (*XIX*)

A mixture of compound *VI* (0·77 g; 5 mmol), benzaldehyde (0·53 g; 5 mmol) and benzene (100 ml) was irradiated through a GWC filter for 38 h. Evaporation of solvent followed by column chromatography on silica gel in benzene, afforded 0·6 g (46%) of *XIX*, m.p. 124—124·5°C (cyclohexane). IR spectrum (chloroform), cm^{-1}: 1 795, 1 710, 1 390, 1 380, 1 308, 1 140, 1 066; UV spectrum (methanol): λ_{max} 210 nm (log ε 3·13), 215 (3·03); ^{1}H NMR spectrum (deuteriochloroform): 1·11 (s, 3 H, CH_3 at $C_{(5)}$), 1·63 (s, 3 H, CH_3 at $C_{(1)}$), 2·55 (s, 3 H, CH_3), 5·67 (s, 1 H, H_6), 7·36 (s, 5 H, phenyl); mass spectrum, *m/z* (rel. intensity): 174 (1), 155 (23), 114 (9), 113 (100), 107 (7), 106 (2), 105 (6), 77 (6), 44 (5), 43 (40), 42 (15), 28 (13). For $C_{14}H_{15}NO_4$ (261·3) calculated: 64·36% C, 5·78% H, 5·36% N; found: 65·21% C, 5·86% H, 5·33% N.

4-Acetyl-6,6-diphenyl-1,5-dimethyl-2,7-dioxa-4-azabicyclo[3,2,0]heptan-3-one (*XX*)

A mixture of compound *VI* (0·77 g; 5 mmol), benzophenone (0·91 g; 5 mmol) and benzene (100 ml) was irradiated through a GWC filter for 50 h. Evaporation of solvent and chromatography on silica gel in benzene gave 0·9 g (53%) of *XX*, m.p. 97—98°C (cyclohexane). IR spectrum (chloroform), cm^{-1}: 1 795, 1 710, 1 610, 1 500, 1 455, 1 390, 1 380, 1 306, 1 175, 1 670; UV spectrum (methanol): λ_{max} 208 nm (log ε 3·35), 220 (3·15), 260 (1·60). ^{1}H NMR spectrum (deuteriochloroform): 1·61 (s, 3 H, CH_3 at $C_{(5)}$), 1·68 (s, 3 H, CH_3 at $C_{(1)}$), 2·05 (s, 3 H, CH_3), 7·12 to 7·75 (m, 10 H, $2 \times C_6H_5$); mass spectrum, *m/z* (rel. intensity): 183 (52), 165 (10), 155 (28), 149 (17), 113 (100), 105 (52), 77 (38), 55 (10), 51 (11), 44 (14), 43 (83), 42 (38), 41 (17), 28 (45). For $C_{20}H_{19}NO_4$ (337·3) calculated: 71·20% C, 5·68% H, 4·15% N; found: 71·27% C, 5·77% H, 4·29% N.

This study was partially conducted by one of the author (J. K.) at Max Planck Institute für Kohlenforschung, Abteilung Strahlenchemie, Mülheim/Ruhr, BRD. We are grateful to the Max Planck Society for fellowship.

REFERENCES

1. Jullian D. R., Tringham G. D.: Chem. Commun. *1973*, 13.
2. Jullian D. R., Foster R.: Chem. Commun. *1973*, 311.
3. Rivas C., Bolivar R. A.: J. Heterocycl. Chem. *13*, 1037 (1976)
4. Jones G. II., Gilow H. H., Low J.: J. Org. Chem. *44*, 2949 (1979).
5. Nakano T., Rivas C., Perez C., Larrauri J. M.: J. Heterocycl. Chem. *13*, 173 (1976).
6. Nakano T., Rodriguez W., Deroche S. Z., Larrauri J. M., Rivas C., Perez C.: J. Heterocycl. Chem. *17*, 1777 (1980).
7. Farid S., Hess D., Krach C. H.: Chem. Ber. *100*, 3266 (1967).
8. Araki Y., Nagasawa J., Ishido Y.: J. Chem. Soc., Perkin Trans. *1*, 1981, 12.
9. Steffan G., Schenck G. O.: Chem. Ber. *100*, 3961 (1967).
10. Scholz K. H., Hinz J., Heine H. G., Hartmann W.: Justus Liebigs Ann. Chem. *1981*, 248.
11. Scholtz K. H., Heine H. G., Hartmann W.: Tetrahedron Lett. *1978*, 1467.
12. Collective: *Vvedenie v Fotochimiju Organičeskich Sojedinenii* (translation from German). Khimija, Moscow 1976.
13. Murov S. L.: *Handbook of Photochemistry*. Dekker, New York 1973.
14. Lamola A. A., Herkstroeter W. G., Dalton J. C., Hammond G. S.: J. Chem. Phys. *42*, 1715 (1965).
15. Sandros K., Bäckström H. L. J.: Acta Chem. Scand. *16*, 958 (1962).

16. Hartmann W., Steinmetz R.: Chem. Ber. *100*, 217 (1967).
17. Danilov V. I.: Photochem. Photobiol. *6*, 233 (1967).
18. Mantione M. J., Pullman B.: Biochim. Biophys. Acta *91*, 387 (1964).
19. Nagata C., Imamura A., Tageshira Y., Kodama M., Fukuda N.: J. Theor. Biol. *9*, 357 (1965).
20. Streitwieser A.: *Teória Molekulových Orbitov v Organickej Chémii* (translation from English). Published by Slovak Academy of Sciences, Bratislava 1968.
21. Turro N. J.: *Modern Molecular Photochemistry*. Benjamin, Menlo Park, California 1978.
22. Scholz K. H., Heine H. G., Hartmann W.: Justus Liebigs Ann. Chem. *1976*, 1319.
23. De Stevens G.: J. Org. Chem. *23*, 1572 (1958).
24. Gompper R.: Chem. Ber. *89*, 1748 (1956).
25. Kopecký J., Šmejkal J.: Unpublished results.
26. Liška F., Dědek V., Kopecký J., Mostecký J., Dočkal A.: Chem. Listy *72*, 637 (1978).
27. Abe Y., Kunieda T.: Tetrahedron Lett. *1979*, 5007.

Translated by M. Tichý.