PREPARATION AND SPECTROSCOPIC PROPERTIES OF SPIROCYCLIC 1-METHYL-2,4,4,6-TETRAARYL-1,4-DIHYDROPYRIDINES

Stanislav BOHM[a], Michal HOCEK[a], Jan NEMECEK[b], Vladimir HAVLICEK[b]
and Josef KUTHAN[a]

[a] *Department of Organic Chemistry,*
Prague Institute of Chemical Technology, 166 28 Prague 6, The Czech Republic
[b] *Institute of Microbiology,*
Academy of Sciences of the Czech Republic, 142 20 Prague 4, The Czech Republic

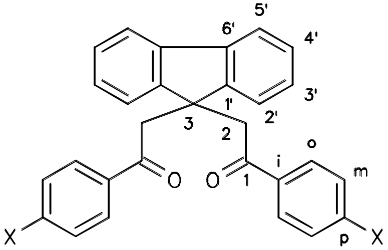
Received June 10, 1993
Accepted September 3, 1993

1,5-Diones *Ib* – *Ie* were converted to spirocyclic 1,4-dihydropyridines *IIb* – *IIe* by treatment with methanolic methylamine. The starting diketones *Ib* – *Ie* were obtained from corresponding acetophenones 4-X-C_6H_4COMe and fluorenone with sodium amide except of *If* where only ketone *III* and 1,4-dione *IV* were isolated. Molecular spectra (UV-VIS, NMR, IR and MS) of compounds *Ib* – *Ie*, *IIa* – *IIe*, *III*, and *IV* were assigned and interpreted.

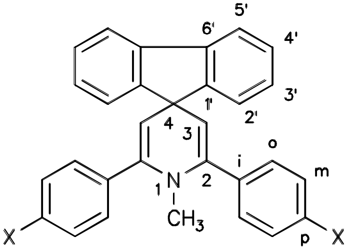
2,4,4,6-Tetraaryl-1,4-dihydropyridines are of interest because of their UV and sunlight induced photocoloration[1 – 5]. This phenomenon seems to be significantly affected by an additional *ortho-ortho*-linking of the 4,4-aryl groups. Thus, bathochromic shifts of about 50 nm from the long-wave photochromic band of spirocyclic 4,4-(biphenyl-2,2′-diyl)-2,6-diphenyl-1, 4-dihydropyridine with respect to that of non-linked 2,4,4,6-tetraphenyl-1,4-dihydropyridine and between the bands of corresponding 1-methyl derivatives were observed[4,6]. To generalize this “bridge-effect” we have attempted at a preparation of X-substituted spirocyclic 1,4-dihydropyridines *IIb* – *IIf*. In addition, molecular spectra of intermediates *Ib* – *Ie* as well as the heterocycles *IIa* – *IIe* are discussed in this paper.

The heterocyclization *Ia* → *IIa*, recently accomplished by treatment of 1,5-dione *Ia* with methanolic methylamine for several days[6], has now been extended to the preparation of X,X-disubstituted derivatives *IIb* – *IIf*. We have tried to prepare starting and hitherto undescribed 1,5-diones *Ib* – *Ie* from 4-substituted acetophenones $XC_6H_4COCH_3$ and fluorenone by treatment with sodium amide, similarly, as in the known case with acetophenone itself[4]. From Table I it is evident that the yields (16 to 51%) of X,X-disubstituted 3,3-(biphenyl-2,2′-diyl)-1,5-diphenylpentane-1,5-diones *Ib* – *Ie* decrease in the order X = Cl > Br > F > CH_3. Attempts to prepare bis(methoxy)-1,5-dione *If* were unsuccessful and resulted in a mixture from which 2-(fluoren-9-yl)-1-(4-methoxyphenyl)ethanone (*III*) and 2-(fluoren-9-yliden)-1,4-bis(4-methoxyphenyl)butane-1,4-dione (*IV*) were isolated. We assume the origin of the products *III* and *IV* to be explained by the following reactions: In the first stage, α,β-unsaturated ketone *V* is formed from fluorenone and 4-methoxyacetophenone. The latter, after its conversion with sodium amide to the corresponding enolate, interacts with ketone *V* according to Eq. (*A*).

$$\text{4-MeOC}_6\text{H}_4\text{C(ONa)=CH}_2 \quad + \quad V \xrightarrow{\text{CT}} \text{4-MeOC}_6\text{H}_4\text{COCH}_2^{\bullet} \quad + \quad VI \xrightarrow{\text{recomb.}} VII \quad (A)$$

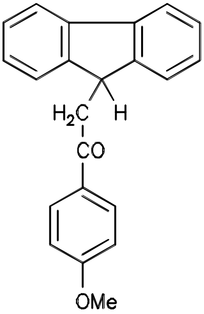


I

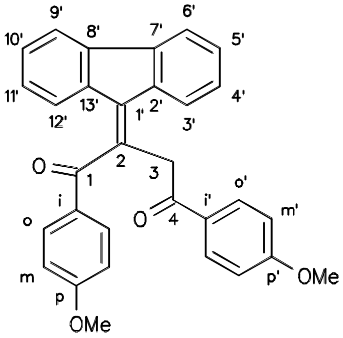


II

In formulae *I*, *II* : ***a***, X = H; ***b***, X = CH_3; ***c***, X = F;
d, X = Cl; ***e***, X = Br; ***f***, X = OCH_3



III



IV

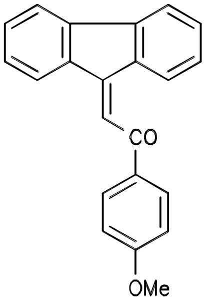
In the second stage, sodium salt *VII* undergoes its oxidation with another molecule of α,β-unsaturated intermediate *V* giving 1,4-dione *IV* and another sodium salt *VIII* (*VII* + *V* → *IV* + *VIII*). The isolated ketone *III* is probably formed by hydrolysis of the reaction mixture (*VIII* + H_2O → *III* + NaOH). In favour of the suggested reaction pathway via the radical-anion salt *VI* it was found that no ketolization affording 1,4-dione *IV* proceeded from fluorenone and diketone $(4\text{-}CH_3OC_6H_4COCH_2)_2$ under the same reaction conditions. Hence, an alternative recombination of the above mentioned radical ($4\text{-}MeOC_6H_4COCH_2^{\bullet} \rightarrow (4\text{-}MeOC_6H_4COCH_2)_2$) may hardly be involved in the path leading to the unexpected product *IV*.

TABLE I
New prepared 1,5-diones *Ib* – *Ie* and 1,4-dihydropyridines *IIb* – *IIe*

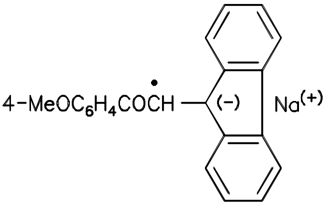
Compound	M.p., °C (Yield, %)	Formula (M.w.)	Calculated/Found			IR $\tilde{\nu}_{max}$, cm^{-1}
			% C	% H	% N	
Ib	166 – 170	$C_{31}H_{26}O_2$	86.48	6.09	–	1 608
	(16)	(430.5)	86.50	5.86	–	1 685[a]
Ic	134 – 135	$C_{29}H_{20}F_2O_2$	79.44	4.60	8.66[b]	1 599
	(26)	(438.5)	79.26	4.59	8.90[b]	1 690[a]
Id	147 – 148	$C_{29}H_{20}Cl_2O_2$	73.89	4.28	15.04[b]	1 590
	(51)	(471.4)	73.63	4.04	15.32[b]	1 691[a]
Ie	151 – 153	$C_{29}H_{20}Br_2O_2$	62.17	3.60	28.52[b]	1 586
	(29)	(560.3)	61.88	3.54	28.72[b]	1 690[a]
IIb	206 – 208	$C_{32}H_{27}N$	90.31	6.40	3.29	1 609[c]
	(76)	(425.6)	89.99	6.58	3.14	1 658[c]
IIc	175 – 178	$C_{30}H_{21}F_2N$	83.12	4.88	3.23	1 603[c]
	(72)	(433.5)	82.85	4.97	3.07	1 660[c]
IId	211 – 213	$C_{30}H_{21}Cl_2N$	77.26	4.54	3.00	1 613[c]
	(72)	(466.4)	76.90	4.42	2.93[d]	1 659[c]
IIe	213 – 216	$C_{30}H_{21}Br_2N$	64.89	3.81	2.52	1 611[c]
	(82)	(555.3)	64.99	3.69	2.43[e]	1 659[c]

[a] C=O Stretching vibration; [b] halogen content; [c] dihydropyridine ring vibrations; [d] calculated: 15.20% Cl, found: 15.42% Cl; [e] calculated: 28.78% Br, found: 28.89% Br.

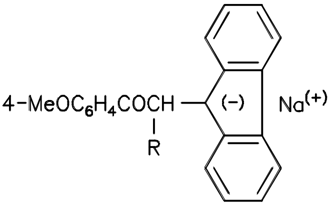
Molecular structure of all newly prepared compounds *Ib* – *Ie* and *IIb* – *IIe* (Table I) was prove by IR, NMR and mass spectroscopic methods similarly to the known[4,6] parent derivatives *Ia* and *IIa* (Tables II to IV).



V



VI



VII, R = 4-$MeOC_6H_4CO$

VIII, R = H

The ^1H NMR spectra of 1,5-diones *Ib* – *Ie* (Table II) contain four-proton singlet of CH_2 groups at about 3.85 δ, ABCD system of fluorene moiety and AA′BB′ system of a *para*-substituted benzene ring. The ABCD and AA′BB′ systems were identified using COSY spectra. Orientations of the substructures were established on the basis of NOESY spectra (correlation of 2H-2′ and H-*o* with CH_2 signal) and LR-HETCOR spectra (coupling between C-1′ and H-5′, C-*p* and H-*o*, as well as C-*i* and H-*m*). The assignments of ^{13}C NMR signals are given in Table III. Proton-bearing carbons were recognized from HETCOR experiments using the above mentioned interpretation procedures of ^1H NMR spectra. Signals of aliphatic quaternary carbons (about 50.5 ppm) and analogous carbons of conjugated carbonyl groups (197 to 198 ppm) were assigned considering their typical chemical shifts. The quaternary carbon C-1′ was assigned from the LR-HETCOR using its couplings with H-3′ and H-5′ and analogously the quaternary carbon C-6′ using its couplings with H-2′ and H-4′. Assignments of the C-*i* shifts followed from LR HETCOR experiments (coupling with H-*m* and H-2) and from the fine splitting of the signals in the coupled ^{13}C NMR spectra of halogen derivatives *Ic* – *Ie*.

The ^1H NMR spectra of 1,4-dihydropyridines *IIa* – *IIe* (Table III) contain three-proton singlet of the *N*-methyl group at about 2.8 ppm, two-proton singlet of the CH groups at about 4.8 ppm, the ABCD system of fluorene moiety and in spite of *IIa* the AA′BB′ system of *para*-substituted phenyl groups (in addition to the methyl signal of *IIb* at 2.39 ppm). The same procedures were used as in the case of compounds *Ib* – *Ie* for the ^{13}C NMR signals assignment (Table *III*). On the basis of multiplicity and chemical shift of the *N*-methyl group (about 39.9 ppm), the aliphatic quaternary carbon (about 52 ppm) and the olefinic methine (about 109.75 ppm) were assigned. The assignment of C-*i* was analogously based on the LR HETCOR results and the multiplicity considerations.

A complete interpretation of ^{1}H and ^{13}C NMR spectra of ketone *III* and 1,4-dione *IV* is given in the Experimental. The phenyl AA′BB′ system in *III* was analyzed by the LR HETCOR using the couplings of C-3 with H-3′ and H-*o*′ as well as of C-1 with C-*o*. The same procedure was used to assign quaternary carbons in diketone *IV*.

In the IR spectra (Table I) characteristic carbonyl bonds (1 685 – 1 691 cm^{-1}) for 1,5-diones *Ib* – *Ie* as well as heterocyclic ring vibrations[7] (1 604 – 1 613 and 1 658 – 1 660 cm^{-1}) for 1,4-dihydropyridines *IIb* – *IIe* were recognized.

TABLE II
^{1}H and ^{13}C NMR spectra of 1,5-diones *Ib* – *Ie*

Assignment[b]	*Ib*	*Ic*[a]	*Id*	*Ie*
H-2	3.90 s	3.90 s	3.85 s	3.85 s
H-2′	7.73 ddd	7.72 ddd	7.68 ddd	7.62 ddd
H-3′	7.22 ddd	7.25 ddd	7.23 ddd	7.23 ddd
H-4′	7.34 ddd	7.38 ddd	7.34 ddd	7.36 ddd
H-5′	7.77 ddd	7.77 ddd	7.74 ddd	7.74 ddd
H-Ar(*o*)	7.71 d	7.85 d	7.72 d	7.65 d
(*m*)	7.12 d	7.04 dd	7.32 d	7.49 d
CH_3	2.34 s	–	–	–
C-1	198.56	197.41	197.74	197.02
C-2	44.36	44.38	44.34	44.37
C-3	50.74	50.58	50.48	50.51
C-1′	150.91	150.46	150.33	150.33
C-2′	124.88	124.76	124.69	124.72
C-3′	127.46[c]	127.58	127.56	127.60
C-4′	127.56[c]	127.77	127.80	127.84
C-5′	119.93	120.03	120.01	120.06
C-6′	139.79	139.66	139.61	139.66
C-Ar(*i*)	143.50	133.95	135.76	136.23
(*o*)	128.15	130.66	129.40	129.56
(*m*)	129.02	115.43	128.63	131.68
(*p*)	135.25	165.57	139.27	128.08
CH_3	21.55	–	–	–

[a] *J*(F,H(*o*)) = 5.4, *J*(F,H(*m*)) = 8.3; *J*(F,C(*p*)) = 253, *J*(F,C(*m*)) = 21, *J*(F,C(*o*)) = 9.3 and *J*(F,C(*i*)) = 2.9; [b] all *J*(H,H) values for the fluorene and the phenyl parts in molecules *Ib* – *Ie* are identical: *J*(2′,3′) = *J*(3′,4′) = *J*(4′,5′) = 7.3, *J*(2′,4′) = *J*(3′,5′) = 1.4, *J*(2′,5′) = 0.7 and *J*(*o*,*m*) = 8.2; [c] assignments may be interchanged.

Mass spectrometric data for 1,4-dihydropyridines *IIa* – *IIe* are given in Table IV. The base peaks are all at the mass of molecular ions $M^{+\bullet}$ because they evidently involve isomeric radical ions *IX* and *X* in contrast to analogous 1,4-dihydropyridines without *ortho*-*ortho*-linking of 4,4-aryl groups[3]. Two other intensive ion species $[M-H]^+$ and $[M-C_6H_4X]^+$ may be formed by aromatization of radical ion *X* to pyridinium ions *XI* and *XII* resembling photochemical rearrangements[6] of compound *IIa* (cf. Scheme 1).

TABLE III
^1H and ^{13}C NMR spectra of 1,4-dihydropyridines *IIa* – *IIe*

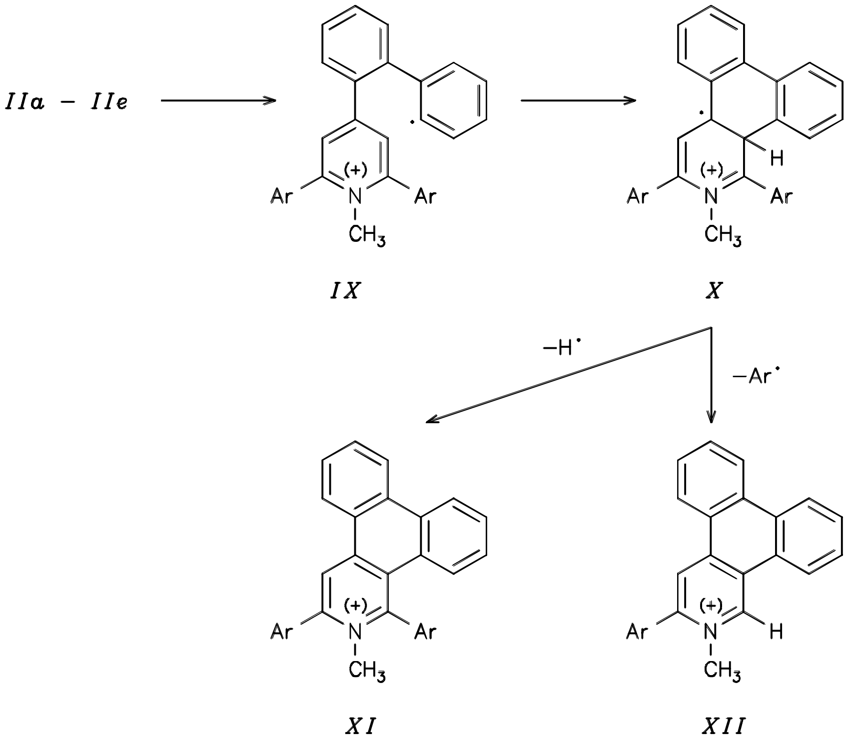
Assignment[c]	*IIa*	*IIb*[a]	*IIc*[b]	*IId*	*IIe*
H-3	4.79 s	4.79 s	4.79 s	4.81 s	4.82 s
H-2′	7.52 ddd	7.54 ddd	7.52 ddd	7.50 ddd	7.49 ddd
H-3′	7.33 ddd[d]	7.35 ddd	7.36 ddd	7.35 ddd	7.35 ddd
H-4′	7.34 ddd[d]	7.39 ddd	7.40 ddd	7.39 ddd	7.39 ddd
H-5′	7.72 ddd	7.75 ddd	7.76 ddd	7.75 ddd	7.75 ddd
H-Ar(*o*)	7.52 m	7.44 d	7.50 dd	7.45 d	7.39 d
(*m*)	7.35 m	7.19 d	7.07 dd	7.24 d	7.50 d
(*p*)	7.31 m	–	–	–	–
C-2	145.77	145.71	144.77	144.76	144.80
C-3	109.76	109.05	109.98	110.57	110.64
C-4	52.29	52.66	52.44	52.46	52.46
C-1′	154.75	155.01	154.47	154.31	154.26
C-2′	126.27	126.28	126.13	126.14	126.13
C-3′	127.76	127.72	127.82	127.86	127.87
C-4′	127.46	127.36	127.59	127.68	127.69
C-5′	119.56	119.50	119.65	119.69	119.70
C-6′	138.83	138.83	138.85	138.91	138.92
C-Ar(*i*)	137.87	135.16	133.75	136.20	136.66
(*o*)	127.69	127.64	129.25	128.91	129.23
(*m*)	128.27	128.93	115.22	128.55	131.53
(*p*)	127.92	137.67	162.59	133.84	121.97
H_3CN	39.97	39.87	39.90	40.01	40.03

[a] Additional signals: 2.39 s, 3 H (H_3CC) and 21.16 q (CH_3); [b] *J*(F,H(*o*)) = 5.4, *J*(F,H(*m*)) = 8.8, *J*(F,C(*p*)) = 245.6, *J*(F,C(*m*)) = 21.3, *J*(F,C(*o*)) = 8.1 and *J*(F,C(*i*)) = 3.1; [c] all *J*(H,H) values for compounds *IIa* – *IIe* are identical: *J*(2′,3′) = *J*(3′,4′) = *J*(4′,5′) = 7.3, *J*(2′,4′) = *J*(3′,5′) = 1.4, *J*(2′,5′) = 0.7 and *J*(*o*,*m*) = 8.2; [d] assignments may be interchanged.

All spirocyclic 1,4-dihydropyridines *IIb* – *IIe* were found to exhibit the UV-photocoloration with two new absorption maxima at 620 – 650 nm thus showing the expected “bridge-effect”. Hence, there is no reason to consider any different mechanism of this photoprocess than that postulated earlier[6].

EXPERIMENTAL

Melting points were determined on a Boetius block and are uncorrected. IR spectra (in cm^{-1}) were measured on a Perkin–Elmer 325 spectrometer in KBr pellets. NMR spectra (given in δ ppm, *J* in Hz) were recorded on a Varian VXR-400 spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C) in $CDCl_3$ at 25 °C with TMS as internal standard. UV-VIS spectra were measured on a Perkin–Elmer Hitachi instrument, the polycrystalline powders by the diffuse reflectance under argon in the same way as in preceding paper[6]. Positive electron-impact MS were recorded on a double sector instrument (Finnigan MAT 90) of BE geometry (70 eV, source temperature 250 °C, emission current 1 mA, accelerating voltage 5 kV, direct inlet), DIP temperature 170 °C.



SCHEME 1

3,3-(Biphenyl-2,2′-diyl)-1,5-di-(4-X-phenyl)pentane-1,5-diones (*Ia* – *Ie*)

Sodium amide (0.038 mol) was added to a solution of 0.0222 mol fluorenone and 0.045 mol X-substituted acetophenone in 30 ml ether. The mixtures became brownish-red and after stirring for 10 h at 20 °C were decomposed with 20 ml water. The precipitates were filtered off, washed with water, 10% H_2SO_4, once more with water and finally with 50 ml EtOH. Crystallizations from toluene–ethanol mixtures yielded colourless 1,5-diones *Ia* – *Ie* as shown in Table I.

TABLE IV
Mass spectra of 1,4-dihydropyridines *IIa* – *IIe*

Ion species	*IIa*	*IIb*	*IIc*	*IId*	*IIe*
	m/*z* (relative intensity)				
$M^{+\bullet}$	397 (100)	425 (100)	433 (100)	456 (100)	555 (98)
$[M–H]^+$	396 (95)	424 (81)	432 (86)	464 (92)	554 (100)
$[M–XC_6H_4CNR]^+$	279 (2)	293 (1)	297 (2)	313 (1)	357 (w)[a]
$[XC_6H_4CNR]^+$	118 (13)	132 (3)	136 (8)	152 (6)	196 (4)
$[M–R]^+$	382 (2)	410 (3)	418 (2)	450 (6)	538 (w)[a]
$[M–C_6H_4X]^+$	320 (49)	334 (36)	338 (45)	354 (61)	398 (40)
$[M–X]^+$	[b]	410[c] (3)	414 (w)[a]	430 (4)	474 (5)
$[M–C_{13}H_9]^+$	232 (2)	260 (2)	268 (3)	300 (2)	388 (w)[a]
$[M–C_6H_5]^+$	[d]	348 (1)	356 (2)	388 (2)	476[e] (5)

[a] Weak, r.i. lower than 1%; [b] undistinguishable from $[M–H]^+$; [c] alternative generation also from $CH_3–N$ fragment; [d] undistinguishable from $[M–C_6H_4X]^+$; [e] possible isotropic ion to *m*/*z* 474.

4,4-(Biphenyl-2,2′-diyl)-2,6-di-(4-X-phenyl)-1-methyl-1,4-dihydropyridines (*IIa* – *IIe*)

Methylamine hydrochloride (0.370 mol) was added to a sodium methanolate solution prepared from 0.304 mol Na and 250 ml MeOH. The suspension was then shaken with corresponding 1,5-dione *Ia* – *Ie* for 7 days at 20 °C and evaporated in vacuo. Solid residues were mixed with water (250 ml) and extracted with toluene (300 ml). Collected organic layers were dried by potassium carbonate, evaporated in vacuo and the residues were chromatographed on a column (30 g silica gel, toluene). The first fractions afforded crude products *IIa* – *IIe* as colorless crystals (from acetone–ethanol mixtures, see Table I) which exhibited typical color changes to green after UV-illumination. Visible photochromic spectra (MgO powder), λ_{max} (absorbance, %) *IIb*: 466 (0.260), 620 (0.455); *IIc*: 460 (0.280), 620 (0.455); *IId*: 452 (0.375), 635 (0.540); *IIe*: 462 (0.425), 650 (0.580).

Reaction of Fluorenone with 4-Methoxyacetophenone

The reaction of sodium amide (0.0513 mol) with fluorenone (0.0222 mol) and 4-methoxyacetophenone (0.0450 mol) in 30 ml ether was carried out in the same way as for the preparation of 1,5-diones *Ib* – *Ie*. Crystallization of the crude product from a toluene–ethanol mixture gave 2.6 g (26%) of 1,4-dione *IV*, yellowish crystals m.p. 207 – 209 °C. For $C_{31}H_{24}O_4$ (460.5) calculated: 80.85% C, 5.25% H; found: 80.84% C, 5.26% H. ^{1}H NMR spectrum: 3.83 s, 3 H ($H_3'CO$); 3.88 s, 3 H (H_3CO); 4.75 s, 2 H (H_2C-3); 6.91 d, 2 H (*J*(*o*′,*m*′) = 9.1, H-*m*′); 6.95 ddd, 1 H (*J*(9′,11′) = 1.2, *J*(10′,11′) = 7.5, *J*(11′,12′) = 7.8, H-11′); 6.96 d, 2 H (*J*(*o*,*m*) = 9.0, H-*m*); 7.176 ddd, 1 H (*J*(9′,12′) = 0.8, *J*(10′,12′) = 1.2, *J*(11′,12′) = 7.8, H-12′); 7.182 ddd, 1 H (*J*(4′,6′) = 1.2, *J*(4′,5′) = 7.5, *J*(3′,4′) = 7.6 H-4′); 7.22 ddd, 1 H (*J* = 1.2, *J*(10′,11′) = *J*(9′,10′) = 7.5, H-10′); 7.36 ddd, 1 H (*J*(3′,5′) = 0.8, *J*(4′,5′) = *J*(5′,6′) = 7.5, H-5′); 7.52 ddd, 1 H (*J*(3′,5′) = *J*(3′,6′) = 0.8, *J*(3′,4′) = 7.8, H-3′); 7.65 ddd, 1 H ((9′,12′) = 0.8, *J*(9′,11′) = 1.2, *J*(9′,10′) = 7.6, H-9′); 7.73 ddd, 1 H ((3′,6′) = 0.8, *J*(4′,6′) = 1.2 (*J*(5′,6′) = 7.6, H-6′); 8.02 d, 2 H (*J* = 9.1, H-*o*′). ^{13} C NMR spectrum: 43.58 CH_2 (C-3); 55.44 CH_3O; 55.52 $CH_3'O$; 113.95 2 × CH (C-*m*′); 114.09 2 × CH (C-*m*); 119.36 CH (C-9′); 119.87 CH (C-6′); 124.88 CH (C-3′); 125.64 CH (C-12′); 127.06 CH (C-11′); 127.37 CH (C-4′); 128.19 CH (C-10′); 128.76 C (C-*i*); 128.84 CH (C-5′); 129.43 (C-*i*′); 130.63 2 × CH (C-*o*′); 132.84 2 × CH (C-*o*); 134.02 C (C-2); 136.52 C (C-2′); 137.24 C (C-13′); 137.86 C (C-1′); 140.19 C (C-8′); 141.22 C (C-7′); 163.88 C (C-*p*′), 164.28 C (C-*p*); 193.22 CO (C-1); 198.22 CO (C-4). The residue obtained by evaporation of the filtrates was chromatographed on a column of silica gel (150 g, toluene–ethylacetate 9 : 10) and gave ketone *III* (300 mg), m.p. 104 – 106 °C (EtOH). For $C_{22}H_{18}O_2$ (314.2) calculated: 84.07% C, 5.73% H; found: 84.20% C, 6.06% H. ^{1}H NMR spectrum: 2.42 d, 2 H (*J*(2,3) = 6.8, H-2); 3.86 s, 3 H (H_3CO); 4.81 dtt, 1 H (*J*(2′,3) = 0.9, *J*(3,3′) = 0.8, H-3); 6.94 d, 2 H (*J*(*o*,*m*) = 9.0, H-*m*); 7.29 ddd, 2 H (*J*(2′,3′) = *J*(3′,4′) = 7.5, *J*(3′,5′) = 1.2, H-3′); 7.39 dddd, 2 H (*J*(4′,5′) = *J*(3′,4′) = 7.5, *J*(2′,4′) = 1.2, *J*(3,4′) = 0.8, H-4′); 7.53 dddd, 2 H (*J*(2′,3′) = 7.5, *J*(2′,4′) = 1.2, *J*(2′,5′) = 0.8, *J*(2′,3) = 0.9, H-2′); 7.79 ddd, 2 H (*J*(4′,5′) = 7.5, *J*(3′,5′) = 1.2, *J*(2′,5′) = 0.8, H-5′); 7.98 d, 2 H (*J*(*o*,*m*) = 9.0, H-*o*). ^{13}C NMR spectrum: 42.77 CH (C-3); 42.95 CH_2 (C-2); 55.51 CH_3 (CH_3O); 113.76 2 × CH (C-*m*); 119.79 2 × CH (C-5′); 124.67 2 × CH (C-2′); 127.08 2 × CH (C-3′); 127.20 2 × CH (C-4′); 130.10 C (C-*i*); 130.44 2 × CH (C-*o*); 140.77 2 × C (C-6′); 147.31 2 × C (C-1′); 163.60 2 × C (C-*p*); 197.22 CO (C-1).

Other Attempts at Preparation of 1,4-Dione *IV*

The reaction of sodium amide (0.0256 mol) with 4-methoxyacetophenone (0.0111 mol) in 10 ml ether under argon led to a suspension to which fluorenone (0.0111 mol) in 10 ml ether was added. After 30 min stirring another portion of the ketone (0.0111 mol) in 10 ml ether was added and after 24 h at 20 °C the reaction mixture was worked up as in the above mentioned procedure. Yield 1.73 g

(34%) 1,4-dione *IV*, m.p. 207 – 210 °C (toluene–ethanol). In another experiment sodium amide (1.538 mmol) was added to a suspension of bis(4-methoxyphenyl)butane-1, 4-dione[8] (1.006 mmol) and fluorenone (1.665 mmol) in 15 ml ether and the mixture was stirred at 20 °C and monitored by TLC. No traces of 1,4-dione *IV* were detected in 7 days.

This work was supported by the grant No. 0202. The authors thank Dr M. Adamec (Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic) for the UV-VIS measurements. Elemental analysis and IR spectra measurements were performed in the Central Laboratories of Prague Institute of Chemical Technology.

REFERENCES

1. Peres de Carvalho A.: Ann. Chim. (Paris) *4*, 449 (1935).
2. Maeda K., Nakamura M.: J. Photochem. *17*, 87 (1981).
3. Kurfurst A., Zeleny J., Schwarz M., Kuthan J.: Chem. Papers *41*, 623 (1987).
4. Shibuya J., Nabashima M., Nagano H., Maeda K.: J. Chem. Soc., Perkin Trans. 2 *1988*, 1607.
5. Nespurek S., Schwarz M., Bohm S., Kuthan J.: J. Photochem. Photobiol., A *60*, 345 (1990).
6. Bohm S., Hocek M., Nespurek S., Kuthan J.: Collect. Czech. Chem. Commun. *59*, 262 (1994).
7. Schwarz M., Trska P., Kuthan J.: Collect. Czech. Chem. Commun. *54*, 1854 (1989).
8. Buchta E., Schaefer G.: Justus Liebigs Ann. Chem. *597*, 129 (1955).

Translated by the author (J. K.).