SYNTHESIS OF 1-[4-(3-CHLOROPROPANOYL)PHENYL]--2-PHENYLETHANEDIONE

Ivan LUKÁČ[a] and Gour K. DAS MOHAPATRA[b]

[a] *Polymer Institute, Slovak Academy of Sciences, 842 36 Bratislava, Czechoslovakia*
[b] *Department of Chemistry, Jadavpur University, Calcutta — 700 032, India*

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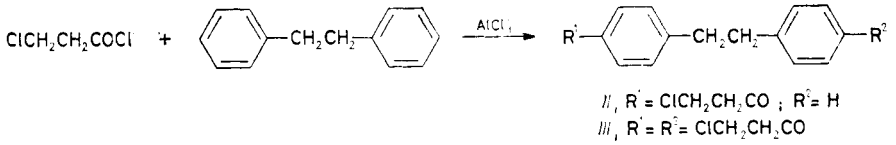
1-[4-(3-Chloropropanoyl)phenyl]-2-phenylethanedione (*I*) was prepared by Friedel–Crafts acylation of (3-chloropropyl)benzene with phenylacetyl chloride, oxidation with SeO_2 of the resulting 1-[4-(3-chloropropyl)phenyl]-2-phenyl-1-ethanone (*IV*) to 1-[4-(3-chloropropyl)phenyl]-2-phenylethanedione (*V*), and subsequent transformation of its benzyl CH_2 group to carbonyl, via bromo (*VI*), acetoxy (*VII*) and hydroxy (*VIII*) derivatives.

The photochemistry of poly(vinyl ketone)s have been attracting much attention[1,2]. Irradiation of these polymers by light of wavelength higher than 300 nm leads to an efficient decrease of the molecular mass. On introduction of another chromophore (benzophenone) into monomeric structure of vinyl ketone, more sensitive material is produced[3]. For further increase of spectral sensitivity we are interested in preparing poly(vinyl ketones) with benzil moiety in the constitutional repeating unit. The most suitable way of preparation of vinyl ketones is dehydrochlorination of 2-chloroethyl ketones, specifically for our purpose dehydrochlorination of 1-[4--(3-chloropropanoyl)phenyl]-2-phenylethanedione (*I*) which may lead to the required 4-acryloylbenzil.

4-Alkanoylbenzils are unknown except for the formyl derivative which was prepared from 4-bromomethylbenzil through a nitrone[4]. 4-Aroylbenzils were prepared by oxidation, mostly with bromine, of some heterocyclic compounds, mainly acylated 4,5-diphenyl-2-oxazolones[5,6]. However, the synthesis of *I* by this method may be somewhat limited due to the thermal instability of 3-chloropropanoyl structure in the acylation step and also its possible side reactions in the oxidation step.

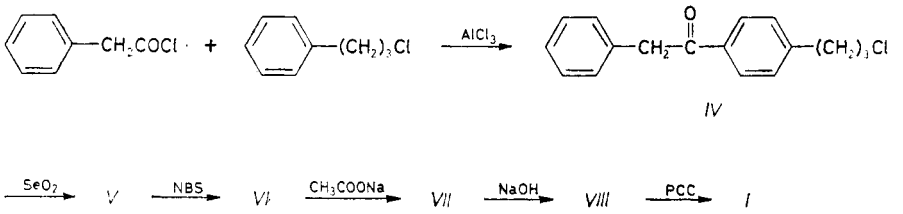
At first we tried to prepare 1-[4-(3-chloropropanoyl)phenyl]-2-phenylethanedione(*I*) by the oxidation of 1-[4-(3-chloropropanoyl)phenyl-2-phenylethane (*II*) prepared by the Friedel–Crafts acylation of 1,2-diphenylethane with 3-chloropropanoyl chloride (Scheme 1). In this reaction, 1,2-bis[4-(3-chloropropanoyl)phenyl]ethane (*III*) is formed as a by-product. However, subsequent oxidation of one of benzyl CH_2 groups in *II* failed: oxidation of *II* with CrO_3 in acetic acid[3] leads to the products of extensive degradation which are soluble in aqueous alkali, the oxidation with

selenium dioxide or sodium dichromate[7] produces complex reaction mixtures. In both cases we failed to isolate *I*.



SCHEME 1

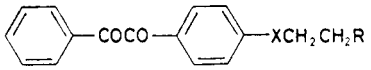
To overcome these difficulties we at first prepared benzil moiety with subsequent introduction and mild oxidation of alcoholic group in the 1-hydroxy-3-chloropropyl structure (Scheme 2).



SCHEME 2

In the first step we prepared 1-[4-(3-chloropropyl)phenyl]-2-phenyl-1-ethanone (*IV*) by the Friedel–Crafts acylation of (3-chloropropyl)benzene with phenylacetyl chloride. Compound *IV* was then oxidized with selenium dioxide to give 1-[4-(3--chloropropyl)phenyl]-2-phenylethanedione (*V*) which, on the bromination in benzylic position with N-bromosuccinimide[8], produced *VI*. Unfortunately, the treatment of *VI* with various bases does not give alcohol *VIII*. Therefore, bromide *VI* was transformed to acetate *VII* and then hydrolyzed . Since, in addition to monoacetoxy derivative *VII*, also 1-[4-(1,3-diacetyloxypropyl)phenyl]-2-phenylethanedione (*IX*) arises, we had to find conditions under which the formation of *IX* was suppressed. The content of *IX* increases with the increasing reaction time; on extending the reaction time to 9 h, *IX* is the main reaction product. Small amounts of 1-[4-(3--acetyloxypropyl)phenyl]-2-phenylethanedione (*X*) and 1-[4-(3-acetyloxy-1-hydroxypropyl)phenyl]-2-phenylethanedione (*XI*) were also isolated from the reaction mixture. The use of barium acetate instead of potassium acetate gives somewhat better results but isolation is tedious. The hydrolysis of *VII* to 1-[4-(1-hydroxy-3-chloropropyl)phenyl]-2-phenylethanedione (*VIII*) strongly depends on reaction conditions. Extension of the reaction time yields a number of by-products which have

not been isolated. For preparative purposes, chromatographic separation of *VIII* instead of *VII* is reasonable. In the final step, mild oxidation of alcohol *VIII* with pyridinium chlorochromate[9] gave *I* and small amount of methyl 4-(3-chloropropanoyl)benzoate (*XII*) as a product of deeper oxidation.



Compoud	X	R
I	CO	Cl
V	CH_2	Cl
VI	CHBr	Cl
VII	CHOAc	Cl
VIII	CHOH	Cl
IX	CHOAc	OAc
X	CH_2	OAc
XI	CHOH	OAc

The yields of the first three steps in Scheme 2 are nearly quantitative. Greater problems, however, arose in the formation of ester *VII* and its hydrolysis. The overall yield of *I* starting from *IV* is 11%. Preparation of the monomer 1-(4-propenoylphenyl)-2-phenylethanedione from *I* and photochemical study of its polymers will be described in another paper.

EXPERIMENTAL

Infrared and ultraviolet spectra were measured on an IR-75 and Specord M 40 spectrometers (Zeiss, Jena, F.R.G.), respectively. NMR spectra were taken at 30°C on an AM-300 (Bruker, F.R.G.) instrument in deuteriochloroform with tetramethylsilane as internal standard. Mass spectra were recorded on a JMFD 100 (JEOL, Japan) spectrometer. For spectral data see Table I and II. Melting points were determined on a Boetius instrument and are uncorrected.

Purity of the products was followed by TLC on Silufol UV 254 (Kavalier, ČSFR) and by liquid chromatography on Separon SE (250 × 4 mm column, eluent methanol, detection at 254 nm).

1-[4-(3-Chloropropanoyl)phenyl]-2-phenylethane (*II*)

3-Chloropropanoyl chloride (25·1 g, 0·2 mol) was added to a suspension of anhydrous $AlCl_3$ (26·7 g, 0·2 mol) in CCl_4 (60 ml) at −5°C. The reaction mixture was then cooled to −30°C and a solution of 1,2-diphenylethane (36·1 g, 0·2 mol) in CCl_4 (120 ml) was added. The temperature of the reaction mixture was allowed to rise gradually up to −5°C and then stirred for 1 h. The mixture was poured into dilute HCl (10 ml concentrated HCl and 400 ml H_2O), extracted with $CHCl_3$ and concentrated in vacuo. The residue was separated by chromatography on silica gel using elution with benzene–hexane (9 : 1) and benzene–acetone (9 : 1). First fractions gave *II*, (11 g, 20%), m.p. 51–55°C (benzene). For $C_{17}H_{17}ClO$ (272·8) calculated: 74·86% C, 6·28% H; found: 75·58% C, 6·59% H.

1,2-*Bis*[4-(3-*chloropropanoyl*)*phenyl*]*ethane* (III) was isolated from the last chromatographic fractions in the preparation of *II* in the yield of 5·5 g, m.p. 156–159°C (benzene). For $C_{20}H_{20}Cl_2O_2$ (363·2) calculated: 66·12% C, 5·55% H; found: 66·61% C, 5·51% H.

1-[4-(3-Chloropropyl)phenyl]-2-phenyl-1-ethanone (*IV*)

Phenylacetyl chloride (74·1 g, 0·48 mol) was added to the stirred suspension of anhydrous $AlCl_3$ (69·5 g, 0·52 mol) in CCl_4 (290 ml) at 0°C. Then 1-chloro-3-phenylpropane (80·8 g, 0·52 mol) was added dropwise to the mixture at such a rate that the temperature of 3–8°C was maintained. After that, the temperature was allowed to rise to 20°C and the reaction mixture was poured into the mixture of concentrated HCl and ice, extracted with $CHCl_3$ and concentrated in vacuo. Yield 123 g (94%), m.p. 78–80°C (ethanol). For $C_{17}H_{17}ClO$ (272·8) calculated: 74·86% C, 6·28% H; found: 75·22% C, 6·27% H. UV data ($CHCl_3$; λ_{max}; log ε): 315 nm (2·66).

1-[4-(3-Chloropropyl)phenyl]-2-phenylethanedione (*V*)

SeO_2 (54·7 g, 0·49 mol) was added to the stirred solution of *IV* (82 g, 0·3 mol) in 70% acetic acid

TABLE I
IR and MS data of 4-substituted benzils and related compounds

Compound	IR[a], cm^{-1}		MS, *m/e*
	$\tilde{\nu}$(C=O)	$\tilde{\nu}$(arom)	
I	1 680	1 590	300 (M^+), 264, 195, 149, 131, 105, 77
II	1 660[b]	1 590[b]	272 (M^+), 236, 209, 181, 118, 91, 65
III	1 660[c]	1 590[c]	326 (M^+ – HCl), 299, 290, 263, 145, 118
IV	1 670[d]	1 600[d]	272 (M^+), 181, 153, 91
V	1 660	1 590	286 (M^+), 181, 105
VI			261, 180, 121, 105, 77
VII	1 660 1 730[e]	1 590	239 (M – PhCO), 105
VIII			199, 197, 175, 105, 77
IX			263 (M – PhCO), 203, 161, 149, 144, 115, 105
X			310 (M^+), 205, 145, 105, 77
XI			221 (M – PhCO), 161, 122, 105, 77
XII	1 680 1 720[e]		226 (M^+), 195, 191, 190, 165, 164, 135, 104, 103, 77

[a] in $CHCl_3 : CCl_4 = 1 : 1$; [b] in $CHCl_3 : CCl_4 = 1 : 2$; [c] in $CHCl_3$; [d] in CCl_4; [e] ester.

(1 500 ml) at room temperature and then stirred at 90°C for 11 h. The solvent was removed at reduced pressure, the residue was extracted with ether and the solution dried over anhydrous Na_2SO_4. Ether was evaporated in vacuo and the residue dissolved in benzene was filtered through a short silica gel column. After evaporating the solvent 76·6 g (89%) of the product was obtained.

TABLE II

^1H NMR and ^{13}C NMR chemical shifts (δ, ppm) of 4-substituted benzils and related compounds

Compound	CH_2R CH_2X	CH_2Ar CHAr	CH_3	*o*-H[a]	*m*-H[a] *p*-H[a]
I	3·49 t	—	—	7·96–8·12 m[b]	7·51–7·58 m
	3·93 t	—		—	7·66–7·73 m
II	3·36 t	2·83–2·98 m[c]	—	7·81 d[d]	7·07–7·26 m[e]
	3·85 t	—		—	—
III	3·44 t[c]	3·01 s[c]	—	7·87 d[c]	7·23 d[c]
	3·92 t[c]	—		—	—
IV	3·52 t	2·83 t	—	7·90–8·04 m[d]	7·17–7·43 m[e]
	2·00–2·19 m	4·27 s[f]		—	—
V[g]	3·52 t	2·87 t	—	7·89–8·00 m[c]	7·48–7·53 m[d] 7·31–7·37 m[d,h]
	2·06–2·17 m	—		—	7·62–7·69 m
VI[i]	3·47–3·77 m	—	—	7·82–7·96 m[c]	7·30–7·66 m[j]
	2·32–2·68 m	5·13–5·19 m		—	—
VII	3·32–3·58 m	—	2·04 s	7·84–8·00 m[c]	7·37–7·65 m[j]
	1·96–2·40 m	5·88–5·98 m		—	—
IX[k]	4·03–4·22 m	—	1·97 s	7·59–7·68 m[c]	7·96–8·20 m
	2·22–2·32 m	5·90–5·96 q	2·10 s	—	7·73–7·82 m
X[k]	4·07 t	2·82 t	1·98 s	7·88–8·02 m[c]	7·56–7·64 m[d] 7·44–7·51 m[d,h]
	2·00–2·09 m	—		—	7·69–7·80 m
XI[k]	4·09–4·30 m	—	1·97 s	7·93–8·03 m[c]	7·56–7·70 m[c]
	2·00–2·12 m	4·92–5·02 q	4·63–4·82 br[l]	—	7·73–7·82 m
XII[m]	3·48 t	—	3·97 s	8·03 d[d]	—
	3·94 t	—		8·14 d[d]	—

[a] to CO; [b] 6 H; [c] 4 H; [d] 2 H; [e] 7 H; [f] CH_2CO; [g] ^{13}C NMR (δ, ppm): 33·2 (CH_2), 33·6 (Ar—CH_2), 43·8 (CH_2Cl), 129·0, 129·2, 129·8, 130·2 (*o*- and *m*-C to CO), 131·3, 133·3 ($C_{ar}CO$), 134·9 (*p*-C in Ph), 148·7 ($C_{ar}CH_2$), 194·1 and 194·7 (CO); [h] *ortho* to CH_2; [i] ^{13}C NMR: 33·2 (CH_2), 33·6 (Ar—CH_2), 43·8 (CH_2Cl), 129·0, 129·2, 129·8, 130·2 (*o*- and *m*-C to CO), 131·3, 133·0 ($C_{ar}CO$), 134·9 (*p*-C in Ph), 148·7 ($C_{ar}CHBr$), 194·1 and 194·7 (CO); [j] 5 H; [k] in CD_3COCD_3; [l] OH; [m] ^{13}C NMR: 38·35 (CH_2CO), 41·58 (CH_2Cl), 52·49 (CH_3), 127·91 and 129·90 ($C_{ar}H$), 134·24 and 139·41 (C_{ar}—C), 169·99 (COOMe), 196·14 (CO).

1-[4-(-Bromo-3-chloropropyl)phenyl]-2-phenylethanedione (*VI*)

It was prepared from *V* and N-bromosuccinimide according to the described procedure[8]. The reaction mixture in benzene was filtered through a short silica gel column and concentrated in vacuo.

1-[4-(1-Acetyloxy-3-chloropropyl)phenyl]-2-phenylethanedione (*VII*)

A) A mixture of *VI* (58·6 g, 0·16 mol), anhydrous $Ba(OCOCH_3)_2$ (351·6 g, 1·38 mol) and 80% acetic acid (590 ml) was refluxed for 4 h. The mixture was evaporated in vacuo and the residue was extracted with ether and concentrated. Yield 50 g.

B) A mixture of *VI* (3·0 g, 8·2 mol) and anhydrous CH_3COOK (4·85 g, 0·05 mol) was refluxed in 99% acetic acid (16 ml) for 30–60 min. After evaporation of the solvent water (20 ml) was added and the residue extracted with $CHCl_3$. The extract was dried over anhydrous Na_2SO_4 and concentrated. Yield 2·9 g. For analysis, crude *VII* was chromatographed on silica gel with eluent benzene–hexane (9 : 1).

1-[4-(3-*Acetyloxypropyl*)*phenyl*]-2-*phenylethanedione* (X) was obtained from further fractions after repeated chromatography on silica gel with eluent $CHCl_3$–hexane–diethyl ether (45 : 45 : 10). For $C_{19}H_{18}O_4$ (310·4) calculated: 73·53% C, 5·85% H; found: 73·52% C, 6·01% H.

1-[4-(3-*Acetyloxy*-1-*hydroxypropyl*)*phenyl*-2-*phenylethanedione* (XI) was obtained after elution of the original column with benzene–acetone (9 : 1) and repeated separation on silica gel using $CHCl_3$, $CHCl_3$–diethyl ether (95 : 5 and 8 : 2), as eluents. For $C_{19}H_{18}O_5$ (326·4) calculated: 69·93% C, 5·56% H; found: 69·44% C, 5·80% H.

1-[4-(1,3-*Diacetyloxypropyl*)*phenyl*]-2-*phenylethanedione* (IX) is the main product if the boiling of the reaction mixture is prolonged to 9 h.

1-[4-(1-Hydroxy-3-chloropropyl)phenyl]-2-phenylethanedione (*VIII*)

Compound *VII* (50 g, 0·15 mol) was dissolved in methanol (770 ml) and treated with NaOH (40 g in 40 ml water) while stirring at room temperature for 10 min. After acidification with HCl, the solvent was evaporated in vacuo, the residue was extracted with ether and concentrated under diminished pressure. The product (40 g) was separated chromatographically on silica gel with the eluent benzene–hexane 4 : 1. The first fractions contained 28 g of *VIII*.

1-[4-(3-Chloropropionyl)phenyl]-2-phenylethanedione (*I*)

Pyridinium chlorochromate (30 g, 0·14 mol) in CH_2Cl_2 (160 ml) was stirred at room temperature for 10 min. The solution of *VIII* (28 g, 0·093 mol) in dry CH_2Cl_2 (50 ml) was added in one portion, stirred for 6·5 h and allowed to stand for further 15 h at room temperature[9]. The solvent was evaporated in vacuo, the residue was extracted with benzene and separated chromatographically on silica gel with the eluent benzene–hexane (1 : 1). Crystallization from hexane produced 9·5 g *I*, m.p. 73–75°C. The overall yield of *I* (starting from *IV*) is 10·6%. For $C_{17}H_{13}O_3$ (300·7) calculated: 67·89% C, 4·36% H; found: 67·27% C, 4·60% H. UV data (CH_3OH; λ_{max}, log ε): 385 nm (1·92), 267 nm (4·40).

1-(4-*Methoxycarbonylphenyl*)-3-*chloro*-1-*propanone* (XII) was obtained by repeated crystallization of the solid from mother liquor of *I* from hexane. Yield 0·4 g *XII*, m.p. 56–59°C. For $C_{11}H_{11}ClO_3$ (226·7) calculated: 58·29% C, 4·89% H; found: 57·35% C, 5·10% H.

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