Synthesis of new 4,4′-bis(arylethynyl)benzophenones and 4,4′-bis(arylglyoxalyl)benzophenones based on chloral

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4,4′-Diiodobenzophenone was obtained by a three-stage synthesis from chloral and iodobenzene. 4,4′-Bis(arylethynyl)benzophenones were synthesized by cross-coupling of 4,4′-diiodobenzophenone with terminal arylethynes in the presence of a complex Pd catalyst; further oxidation of the products obtained in an iodine/DMSO medium afforded new bis(arylglyoxalyl)benzophenones.

Key words: chloral, 4,4′-diiodobenzophenone, cross-coupling reaction, 4,4′-bis(arylethynyl)benzophenones, bis(α-diketones).

A search for new fields of application of chloral, which are not associated with the involvement of chloral in the food chain, is an important problem. One way of solving this problem is to use chloral for preparing tetraketones, whose limited availability blocks developments in the field of promising polymers like polyphenylquinoxalines, polyphenylenes, and polyphenyltriazines.[1,2]

Therefore, our studies were directed toward the development of Scheme 1, which involves the synthesis of 2,2-di(4-iodophenyl)-1,1,1-trichloroethane (**1**) from iodobenzene and chloral, transformation of **1** to 4,4′-diiodobenzophenone (**3**) *via* dichloride (**2**), condensation of **3** with arylethynes (**4**), and oxidation of the bis(ethynyl)benzophenones **5a—e** formed to the corresponding bis(α-diketones) **6a—e**.

2,2-Di(4-iodophenyl)-1,1,1-trichloroethane **1** was synthesized from chloral and iodobenzene in sulfuric acid at 15 °C. Addition of oleum causes the yield of the desired product to increase from 50 to 92 %, whereas a rise in the reaction temperature (≥50 °C) decreases the yield to 45 %, which is, apparently, associated with the sulfonation of the compounds formed and with cleavage of the C—C bonds.[1] Dehydrochlorination of compound **1** with the formation of 2,2-di(4-iodophenyl)-1,1-di-

Scheme 1

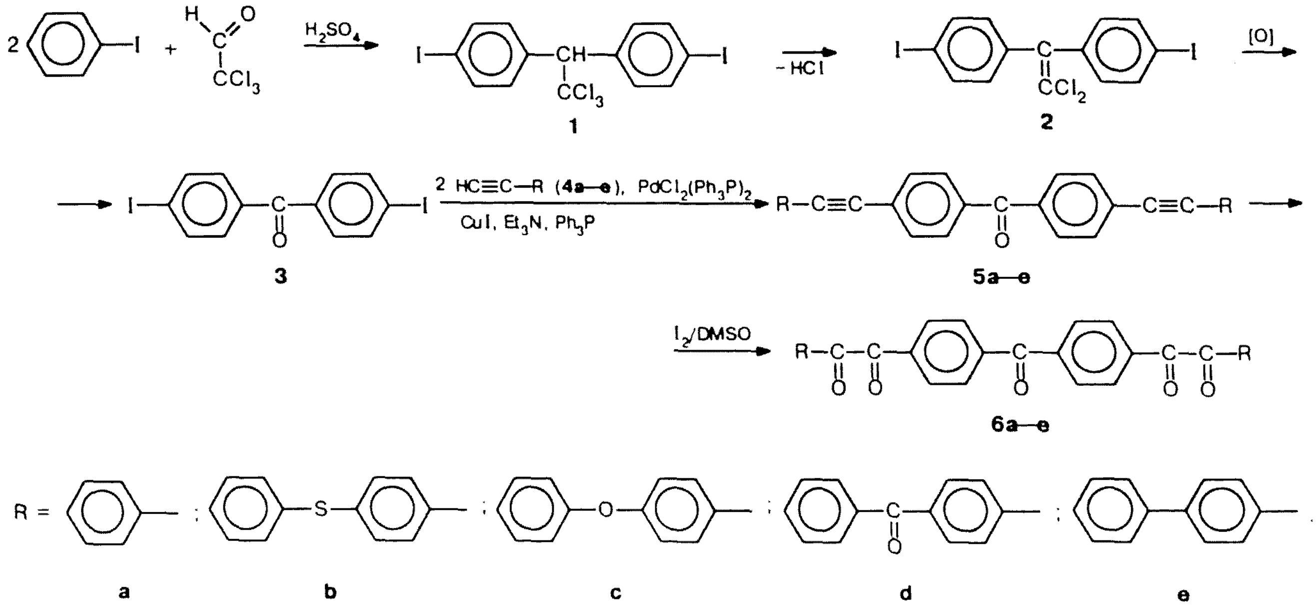

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Table 1. Selected characteristics of 4,4′-bis(arylethynyl)benzophenones **5a—e**

Compound	Yield (%)	M.p. °C	Empirical formula	Found/Calculated (%)			Raman spectra, ν(C≡C)/cm^{-1}
				C	H	S	
5a	90	234—235	$C_{29}H_{18}O$	89.70 90.08	4.79 4.74	— —	2214
5b	89	235—236	$C_{41}H_{26}OS_2$	82.11 82.24	4.29 4.37	10.48 10.69	2214
5c	91	260—261	$C_{41}H_{26}O_3$	86.36 86.90	4.77 4.62	— —	2217
5d	92	309—310	$C_{43}H_{26}O_3$	87.37 87.43	4.39 4.39	— —	2214
5e	88	336—337	$C_{41}H_{26}O$	92.01 92.11	4.87 4.90	— —	2214

Table 2. Selected characteristics of bis(α-diketones) **6a—e**

Compound	Yield (%)	M.p. °C	Empirical formula	Found/Calculated (%)		
				C	H	S
6a	93	130—131	$C_{29}H_{18}O$	78.11 78.01	4.12 4.06	— —
6b	89	155—157	$C_{41}H_{26}O_5S_2$	74.11 74.30	4.00 3.95	9.94 9.67
6c	90	171—172	$C_{41}H_{26}O_7$	77.97 78.08	4.30 4.15	— —
6d	84	195—196	$C_{43}H_{26}O_7$	79.08 78.89	3.95 4.00	— —
6e	70	204—205	$C_{41}H_{26}O_5$	82.23 82.25	4.36 4.37	— —

chloroethylene **2** and subsequent oxidation of **2** to 4,4′-diiodobenzophenone **3** were carried out according to the procedure reported in Ref. 3.

New 4,4′-bis(arylethynyl)benzophenones **5a—e** were obtained by cross-coupling of compound **3** with terminal arylethynes **4a—e** with the use of the complex Pd catalyst in DMF in the presence of Et_3N.[4] It is known that the mobility of halides in ethynylation reactions decreases in the order I > Br > Cl > F, and the rate constants for ethynylation of iodine derivatives are 800 times higher than those for bromine derivatives.[5,6] The presence of bridges in halogen-containing compounds substantially affect the rate and the direction of cross-coupling. Electron-withdrawing substituents accelerate the reaction, whereas electron-releasing substituents (which impair the solubility of arylhalides) slow down the reaction and decrease the yield of the desired products resulting in a mixture of mono- and disubstituted ethynes.[7] In this aspect, compound **3** exhibits an enhanced reactivity and is a suitable monomer for cross-coupling as a result of which the successive replacement of iodine with arylethynyl groups occurs. All compounds **4a—e**, which we used, were obtained by the known procedures.[8—10] Selected characteristics of 4,4′-bis(arylethynyl)benzophenones **5a—e** are given in Table 1.

Previously, a number of bis(α-diketones) were obtained by oxidation of bis(ethynyl) compounds with $KMnO_4$,[11] atmospheric oxygen, or ozone.[12] Note that attempts to oxidize some bis(ethynyl) compounds, in particular, compounds containing fragments of fused systems, terphenyls, or quaterphenyls with $KMnO_4$ failed because of insolubility of these compounds in acetone.[11] The efficient method of oxidation of ethynyl compounds to α-diketones in the iodine/DMSO system, which was recently proposed,[13] substantially enhances the possibilities of obtaining tetraketones with different structures. Bis(α-diketones) **6a—e** were synthesized by this method; the characteristics of these compounds are given in Table 2. Structures of tetraketones were confirmed by the results of elemental analysis and by spectra.

Experimental

Raman spectra were obtained on a U 1000 spectrometer; the Ar$^+$ laser excitation line of an ILA-2 laser was 5145 Å; the laser power was 100 mW. Solvents, iodobenzene, phenylacetylene, and chloral were purified by standard procedures.

1,1,1-Trichloro-2,2-di(4-iodophenyl)ethane (1). A mixture of sulfuric acid (37.5 mL) and oleum (12.5 mL) was added dropwise with stirring to a solution of iodobenzene (55.5 mL, 0.5 mol) and chloral (19.5 mL, 0.2 mol) at 15 °C over 30 min, and the mixture was stirred at this temperature for 2 h. Then the temperature was raised to 30 °C, and the reaction mass was stirred for 10 h (claret color), cooled, and poured onto ice. The precipitate formed was filtered off and washed with methanol and hexane. Compound **1** was obtained in 92 % yield, m.p. 172—174 °C (from hexane) (the data in the literature: m.p. 173 °C).[3]

1,1-Dichloro-2,2-di(4-iodophenyl)ethylene (2) and 4,4′-diiodobenzophenone (3) were prepared according to the procedure reported in Ref. 3.

4,4′-Bis(phenylethynyl)benzophenone (5a). A $PdCl_2(Ph_3P)_2$ complex (0.035 g, 0.05 mmol), Ph_3P (0.013 g, 0.05 mmol), CuI (0.019 g, 0.1 mmol), and Et_3N (6 ml) were added to a solution of 4,4′-diiodobenzophenone (2.17 g, 5 mmol) and phenylacetylene (1.02 g, 10 mmol) in 40 mL of DMF. The reaction mass was heated to 90 °C and kept at this temperature for 8 h; then the mixture was cooled to ~20 °C. The precipitate formed was filtered off, washed with a 10% HCl solution (2×50 mL), water (until the reaction mixture became neutral), and alcohol, and dried *in vacuo*. Compound **5a** was obtained in 90 % yield, m.p. 234—235 °C (from DMF) (the data in the literature: 235—235.5 °C).[11] Compounds **5b—e** were obtained in a similar manner with the use of other arylethynes (Table 1).

4,4′-Bis(phenylglyoxalyl)benzophenone (6a). Iodine (2.03 g, 8 mmol) was added to a solution of compound **5a** (1.79 g, 4 mmol) in 40 mL of DMSO; the reaction mass was heated with stirring, kept at 155 °C for 22 h, cooled to ~20 °C, and poured to a 10-fold excess of water. The precipitate formed was filtered off, washed with a 1% $Na_2S_2O_3$ (to neutralize excess I_2), with water (until the reaction became neutral), and with alcohol, and dried *in vacuo*. Compound **6a** was obtained in 93 % yield, m.p. 130—131 °C (from BuOH) (the data in the literature: m.p. 130—131 °C).[13]

Compounds **6b—e** were obtained in a similar manner (Table 2).

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References

1. V. V. Korshak and A. L. Rusanov, *Usp. Khim.*, 1989, **58**, 1005 [*Russ. Chem. Rev.*, 1989, **58** (Engl. Transl.)].
2. E. S. Krongauz, *Vysokomol. Soedin., Ser. A*, 1984, **26**, 227 [*Polym. Sci. USSR*, 1984, **26** (Engl. Transl.)].
3. J. Forrest, O. Stephenson, and W. Waters, *J. Chem. Soc.*, 1946, 333.
4. R. F. Heck, *Palladium Reagents in Organic Synthesis*, New York, London, 1985.
5. M. G. Grigor'ev, Cand. Sc. (Chem.) Thesis, Tomsk Polytechnical Institute, Tomsk, 1979 (in Russian).
6. C. Pugh and V. Percec, *J. Polym. Sci. A*, 1990, **28**, 1101.
7. M. Bochman and K. Kelly, *J. Polym. Sci., Part A*, 1992, **30**, 2503.
8. I. L. Kotlyarevskii, M. S. Shvartsberg, G. I. Volgina, and S. F. Vasilevskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 1704 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1965, **14** (Engl. Transl.)].
9. H. Tani, F. Toda, and K. Matsumya, *Bull. Chem. Soc. Jpn*, 1963, **4**, 391.
10. B. Delford and G. Lucotte, *J. Polym. Sci., Part A*, 1990, **28**, 2451.
11. N. M. Kofman, Cand. Sc. (Chem.) Thesis, A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 1977 (in Russian).
12. E. S. Krongauz, *Usp. Khim.*, 1977, **46**, 112 [*Russ. Chem. Rev.*, 1977, **46** (Engl. Transl.)].
13. M. S. Yusybov and V. D. Filimonov, *Synthesis*, 1991, 131.

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