

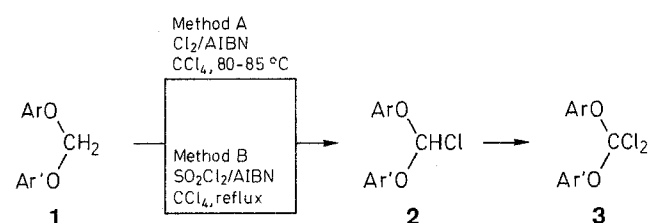
Synthesis of Bis(aryloxy)chloromethanes via Radical-Induced Chlorinations of Formaldehyde Diaryl Acetals

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Bis(aryloxy)chloromethanes **2** and bis(aryloxy)dichloromethanes **3** are prepared via radical-induced chlorination of the formaldehyde diaryl acetals **1** with chlorine or sulfuryl chloride.

The chlorinated acetals **2** and **3**, derivatives of formic and of carbonic acid, respectively, are useful reagents in organic synthesis (**2**,¹⁻⁶ **3**⁷⁻¹²) and various methods for their preparation have been published (**2**,^{2-5,13,14} **3**^{8,10,15-18}). We report now that these compounds can more easily be prepared via radical-initiated chlorination of the formaldehyde acetals **1**,¹⁹ though treatment of **1c** with chlorine in acetic acid was reported to proceed with electrophilic aromatic substitution, and the reaction of **1c** with sulfuryl chloride gave only 46% of **3c**.¹⁶



1-3	Ar	Ar'	1-3	Ar	Ar'
a	Ph	Ph	c		
b	4-ClC ₆ H ₄	4-ClC ₆ H ₄			

When chlorine was passed through refluxing solutions of **1a-c** and traces of 2,2'-azobisisobutyronitrile (AIBN) in tetrachloromethane the dichlorinated compounds **3a-c** were formed in 95-96% yield. Since **1a, b** react considerably faster than **2a, b**, the intermediate monochlorinated compounds **2a, b** can be

Table. Radical-Induced Chlorinations of Formaldehyde Diaryl Acetals **1a-c**

Prod-uct	Me-thod	Reaction Time (min)	Yield (%)	bp (°C/mbar)	Lit. bp (°C/mbar)	mp ^a (°C) (solvent)
2a	A	30	72	120-122/0.1	128-130/0.2 ²	
2b	A	30	73	145-150/0.1	170/0.8 ³	65-67.5 (pentane)
	B	90	73			
3a	A	120	95	100-105/0.07	183-185/16 ¹⁵	40-42 ^d
3b^b	A	120	96	170-175/0.4		30.5-31.5 (pentane)
	B	270	96			
	C ^c	20	95			
3c	A	210	95	83-86/20	82-89/16 ¹⁵	

^a mp uncorrected.

^b C₁₃H₈Cl₄O₂; calc. C 46.19, H 2.39; found C 46.30, H 2.46.

^c Reaction with Cl₂ at ambient temperature; irradiation with UV lamps (300 nm).

^d Lit. mp (°C) 42-44^{8,15}.

isolated with > 70% yield when the reaction is monitored (e.g., ¹H-NMR) and interrupted after the signals of **1a, b** have disappeared. This method has not been successful for an efficient preparation of **2c**. As shown for the synthesis of **3b**, the chlorinations can also be carried out at ambient temperature when the chlorine radicals are generated photolytically. In analogy to radical-induced chlorinations of alkanes, sulfuryl chloride can be employed in place of chlorine, whereby similar yields of the compounds **2b** and **3b** have been obtained.

Since the formaldehyde diaryl acetals **1** can be prepared via phase-transfer-catalyzed reactions of phenols with dichloromethane,²⁰ the title compounds are now readily available. Publications on further applications of these compounds in organic synthesis are in preparation.

Bis(aryloxy)chloromethanes **2** and Bis(aryloxy)dichloromethanes **3**; General Procedure:

Both procedures are carried out in a flask flushed with dry nitrogen.

Method A: Chlorine is passed through a solution of formaldehyde diaryl acetal **1** (30 mmol) and AIBN (0.45 mmol) in dry CCl₄ (50 mL) at 80-85 °C until the wanted degree of chlorination is achieved (spectroscopic control). After evaporation of the solvent, the residue is distilled.

Method B: Compound **1** (20 mmol), sulfuryl chloride (2 equivalents per hydrogen to be substituted), and AIBN (0.30 mmol) in dry CCl₄ (30 mL) are heated under reflux until the wanted degree of chlorination is achieved (1.5-4.5 h, spectroscopic control). After evaporation of the solvent, the residue is distilled.

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