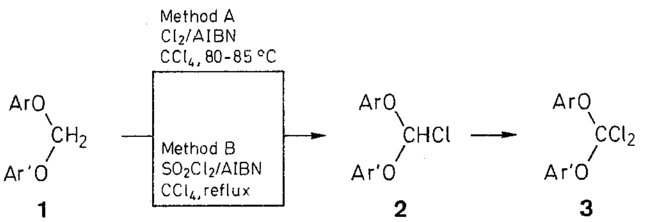
Synthesis of Bis(aryloxy)chloromethanes via Radical-Induced Chlorinations of Formaldehyde Diaryl Acetals

Anton Cambanis, Englbert Bäuml, Herbert Mayr*

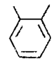
Institut für Chemie der Medizinischen Universität zu Lübeck, Ratzeburger Allee 160, D-2400 Lübeck 1, Federal Republic of Germany

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 **2** **3**

1–3	Ar	Ar′	1–3	Ar	Ar′
a	Ph	Ph	**c**		
b	4-ClC_6H_4	4-ClC_6H_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 isolated with > 70% yield when the reaction is monitored (e.g., ^{1}H-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.

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

Product	Method	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
	B	90	73			(pentane)
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
	B	270	96			(pentane)
	C[c]	20	95			
3c	A	210	95	83–86/20	82–89/16[15]	

[a] mp uncorrected.

[b] $C_{13}H_8Cl_4O_2$: calc. C 46.19, H 2.39; found C 46.30, H 2.46.

[c] Reaction with Cl_2 at ambient temperature; irradiation with UV lamps (300 nm).

[d] Lit. mp (°C) 42–44[8,15].

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 CCl_4 (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 CCl_4 (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.

We thank the Deutsche Forschungsgemeinschaft for support of this work.

Received: 20 September 1988

(1) Scheibler, H., Depner, M. *J. Prakt. Chem.* **1958**, *7*, 60.
(2) Böhme, H., Neidlein, R. *Chem. Ber.* **1962**, *95*, 1859.
(3) Scheeren, J.W., Staps, R.J.F.M., Nivard, R.J.F. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 11.
(4) Scheibler, H., Faass, U., Hadji-Walassis, B. *J. Prakt. Chem.* **1958**, *7*, 70.
(5) Costisella, B., Gross, H. *J. Prakt. Chem.* **1978**, *320*, 128.
(6) Wittig, G., Böll, W. *Chem. Ber.* **1962**, *95*, 2526.
(7) McDonald, R.N., Krueger, R.A. *J. Org. Chem.* **1965**, *30*, 4372.
(8) Webb, R.L., Labaw, C.S. *J. Heterocycl. Chem.* **1982**, *19*, 1205.
(9) Webb, R.L., Eggleston, D.S., Labaw, C.S., Lewis, J.J., Wert, K. *J. Heterocycl. Chem.* **1987**, *24*, 275.
(10) Gross, H., Rusche, J., Mirsch, M. *Chem. Ber.* **1963**, *96*, 1382.
(11) Mayr, H., von der Brüggen, U. *Chem. Ber.* **1988**, *121*, 339.
(12) Mues, P., Buysch, H.-J. *Ger. Patent* 3502106.3 (1986), Bayer AG, Leverkusen; *C.A.* **1986**, *105*, 191103.
(13) Scheibler, H., Depner, M. *Ber. Dtsch. Chem. Ges.* **1935**, *68*, 2151.
(14) Scheeren, J.W., van Melick, J.E.W., Nivard, R.J.F. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 1123.
(15) Gross, H., Rieche, A., Höft, E. *Chem. Ber.* **1961**, *94*, 544.
(16) Groß, H., Costisella, B. *Liebigs Ann. Chem.* **1968**, *720*, 146.
(17) Barger, G. *J. Chem. Soc.* **1908**, *93*, 563.
(18) Yagupol'skii, L.M., Klyushnik, G.I., Troitskaya, V.I. *Zh. Obshch. Khim.* **1964**, *34*, 307.
(19) Cambanis, A., Bäuml, E., Mayr, H. *D.O.S.* 3821130.0 Bayer AG, Leverkusen.
(20) Dehmlow, E.V., Schmidt, J. *Tetrahedron Lett.* **1976**, 95.