

The Hurtley reaction III. A reactivity study of copper(I) 2-halobenzoates either as pure reagents, or under Hurtley reaction conditions, and as a part of mixed (benzoato)(mesityl)copper(I) clusters[#]

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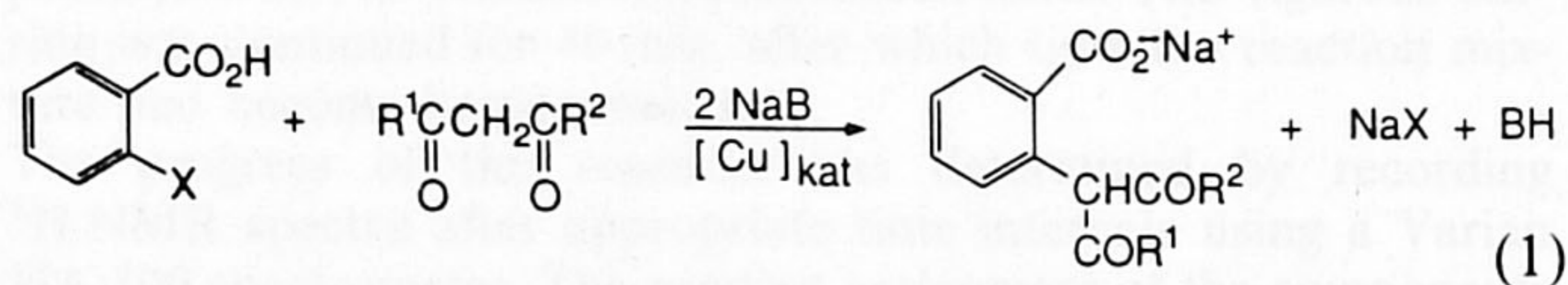
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Abstract. The reactivity of pure isolated copper(I) 2-halobenzoates has been studied at 20 and 80°C either with or without oxidizing agents (O₂ and CuBr₂). Furthermore, these complexes have been reacted at 80°C either alone or in combination with sodium acetylacetonate, *i.e.* under “Hurtley reaction conditions”. Corresponding reactivity of the mixed (2-halobenzoato)(mesityl)copper(I) clusters, wherein the mesityl fragment can be considered as an intramolecularly bonded nucleophile, has also been studied.

The organic products of these reactions and their distribution, measured by combined gas chromatography–mass spectrometry (GC–MS) and gas–liquid chromatography (GLC), for both types of reactions showed remarkable similarities. The principal products of these reactions, *e.g.* biaryls, methyl 2-(1-acetyl-2-oxopropyl)benzoate and 2-mesitylbenzoate derivatives, are formed by a halogen substitution reaction. Compared to the chlorobenzoate derivatives, the more reactive bromo species generate more by-products. The presence of a coordinating solvent, such as acetylacetonate, proved to be necessary in order to obtain a good yield from the condensation reaction between the copper(I) 2-halobenzoates and sodium acetylacetonate. A detailed mechanism involving dinuclear copper(I) intermediates is proposed for the Hurtley reaction.

Introduction

Recently, we have begun a study of the mechanism of the Hurtley reaction^{1,2}, *i.e.* the copper-catalysed condensation of 2-halobenzoic acids with various β-dicarbonyls (1,3-diketones) in water, alcohols or the β-dicarbonyl itself in the presence of a strong base (*e.g.* NaOH or NaH), see Eqn. 1.



X = Cl, Br; B = base

The proposed mechanisms^{3–6} all have the following characteristics; (a) a copper(I) benzoate as the essential intermediate and (b) polarization of the C–X (X = halogen) bond which is augmented by coordination of the halogen to the copper(I) atom (see Fig. 1). It is particularly the exact nature of the copper(I)–halogen interaction that is uncertain. Moreover, with the proposed mechanisms, the high reactivity of 8-bromonaphthoic acid is not in agreement with the mesomerism in the proposed intermediates. Our strategy to investigate the Hurtley reaction was: (i) to isolate the postulated intermediates [copper(I) 2-halobenzoates] and (ii) to study the reactivity of these intermediates in stoichiometric reactions with β-dicarbonyl compounds.

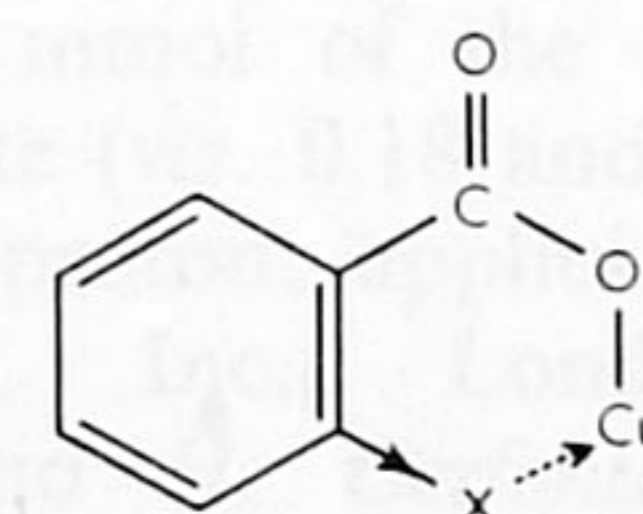


Fig. 1. Postulated polarization of the carbon–halogen bond augmented by coordination to copper(I) in the Hurtley reaction.

[#] Dedicated to Prof. Dr. W. Drenth on the occasion of his retirement from the Chair of Physical Organic Chemistry at the University of Utrecht.

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Our first goal was reached with the synthesis of copper(I) 2-chlorobenzoate (**1**) and copper(I) 2-bromobenzoate (**2**)⁷. The reactions of these benzoates with disubstituted alkynes (dimethyl or diethyl acetylenedicarboxylate and diphenylacetylene) indicated that their structures are tetrameric and similar to that of non-substituted copper(I) benzoate^{1,8}, see Figure 2. Copper(I) 2-halobenzoates were found to react with mesitylcopper(I) to afford novel mixed trinuclear (benzoato)(mesityl)copper(I) compounds⁷, see Figure 3.

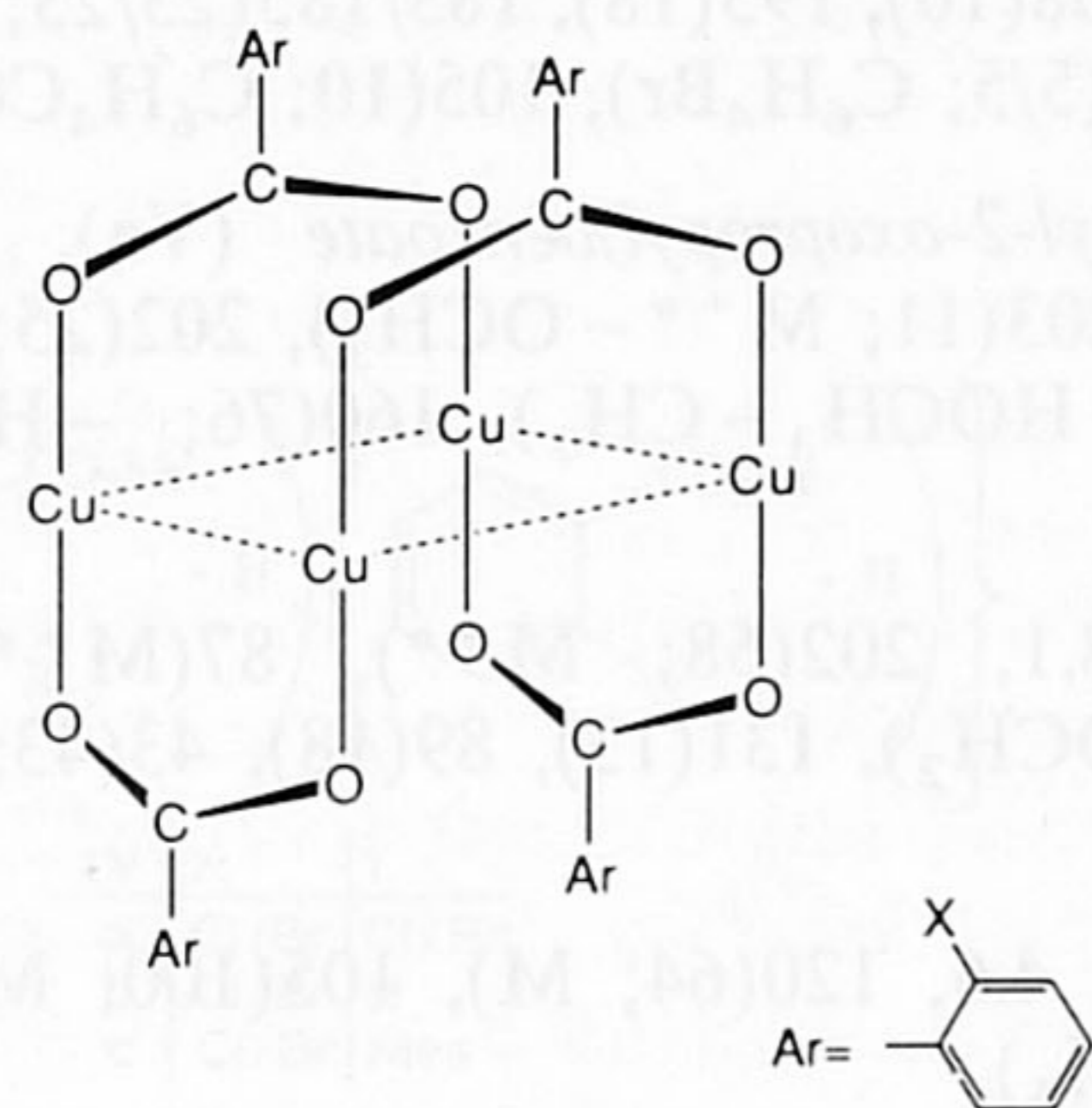


Fig. 2. Schematic representation of the structure of copper(I) benzoates; (**1**) $X = Cl$, (**2**) $X = Br$.

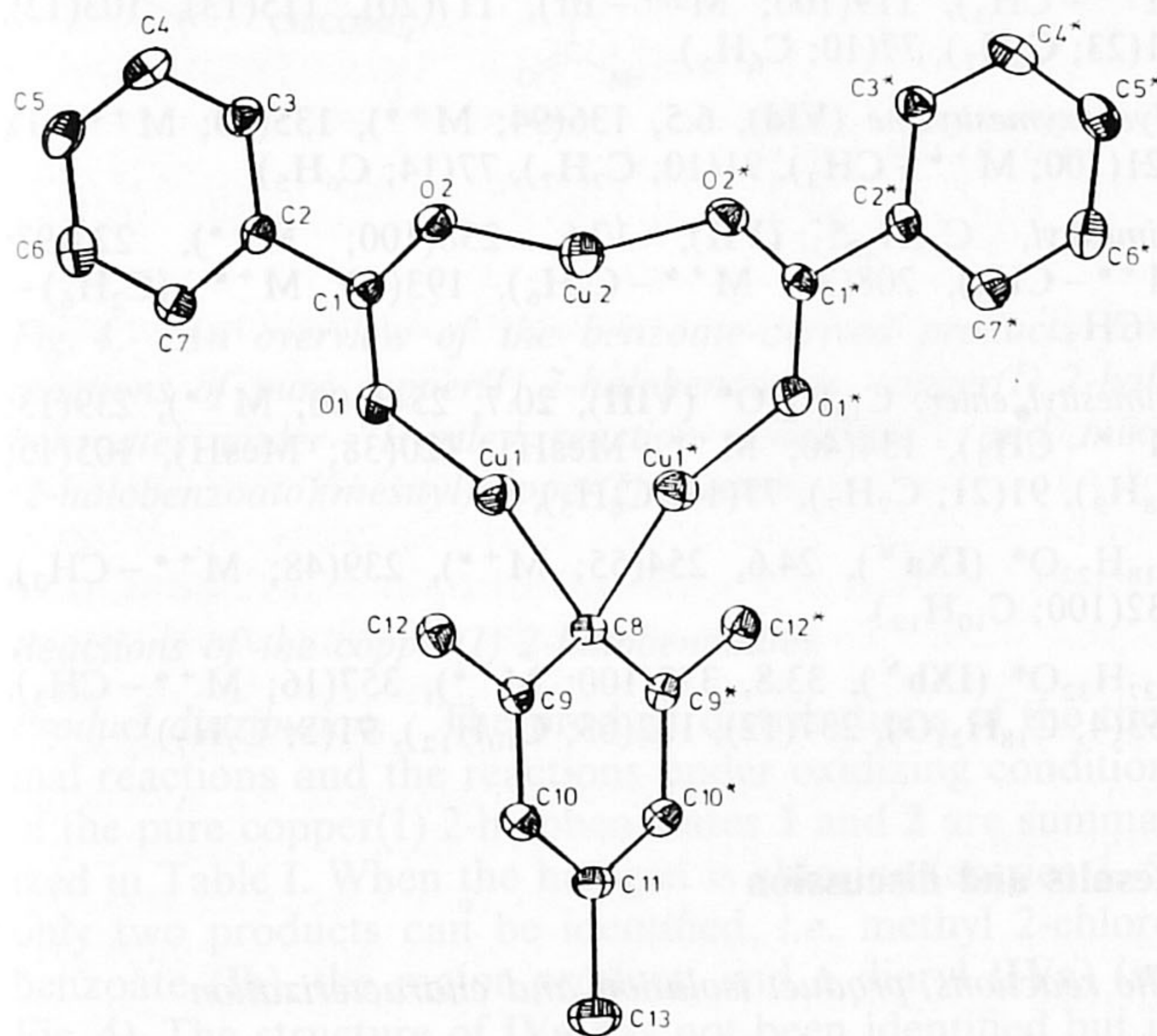


Fig. 3. Structure of $[Cu_3(C_6H_2Me_3-2,4,6)(\mu-O_2CC_6H_5)_2]$.

The present study is an investigation of the reactivity of copper(I) 2-halobenzoates at 80°C and under "Hurtley reaction conditions", *i.e.* in the presence of sodium acetylacetonate and/or acetylacetone*. A comparison of the products and their distribution provides new information on the intermediates in the Hurtley reaction enabling a consistent mechanism for this reaction to be proposed.

The reactivity of the mixed (2-halobenzoato)(mesityl)copper(I) compounds has also been investigated since this type of mixed (organic)(organo)copper(I) species can be seen as a model for a possible Hurtley reaction intermediate in which the nucleophile and the 2-halobenzoate are brought together in a polynuclear copper species.

For both the pure copper(I) 2-halobenzoates and the mixed (benzoato)(mesityl)copper(I) species, the influence of oxidizing agents (O_2 and $CuBr_2$) was also studied because of

the possible effect they are known to have on copper-catalysed reactions^{5,6,9,10}.

Experimental

General

All reactions were carried out under dry oxygen-free nitrogen using standard Schlenk techniques and serum caps unless stated otherwise. Solvents were carefully dried and distilled prior to use. Sodium acetylacetonate¹¹, $[Cu(\mu-O_2CC_6H_4X-2)]_4$ ⁷ ($X = Cl$, **1**; $X = Br$, **2**) and mesitylcopper(I)¹² were synthesized according to literature procedures.

The GC-MS analyses of organic products were performed on a Kratos MS 80 combined gas-chromatograph-mass-spectrometer. The mass spectra were recorded at an ionizing voltage of 40 eV. Gas-liquid chromatographic (CLC) analyses were performed on a Varian Aerograph 144010-01 gas chromatograph equipped with a Shimadzu Chromatopac C-R2AX integrator. Yields were calculated from peak areas using internal standard techniques. The relative response factors were calculated based on the effective carbon contributions of the different carbon atoms¹³ present in the products.

General procedures

Introduction of oxidizing reagents. (a) The preformed copper(I) 2-halobenzoate was exposed for 3 min to the air. (b) Pure oxygen was bubbled through the reaction mixture throughout the entire reaction period. (c) 1.1 equivalent of copper(II) bromide [relative to Cu(I)] was added to the reaction mixture.

Reactions of the copper(I) 2-halobenzoates. The preformed copper(I) compound (2 mmol; based on the monomeric unit) was added to toluene (8 ml) and the oxidizing reagent (when used, see Table I) at 20 or 80°C (see Table I) contained in a two-necked Schlenk-tube equipped with a condenser. After 1 h, the reaction was stopped by cooling to 0°C and by acidification.

Reactions of the copper(I) 2-halobenzoates under "Hurtley reaction conditions". The preformed copper(I) compound (2 mmol; based on the monomeric unit) was added to toluene (10 ml), acetylacetone (10 ml; when used see Table II), sodium acetylacetonate (269 mg, 2.2 mmol; when used see Table II) and the oxidizing reagent (when used, see Table II) at 80°C contained in a two-necked Schlenk-tube equipped with a condenser. After 15 min or 1 h (see Table II), the reaction was stopped by cooling to 0°C and by acidification.

Reactions of the mixed (benzoato)(mesityl)copper(I) complexes. To a suspension of copper(I) 2-halobenzoate (2 mmol; based on the monomeric unit) in toluene (10 ml) was added a 10 ml toluene solution containing mesitylcopper(I) (1.8 mmol based on the monomeric unit) and the reaction mixture was stirred for 30 min at room temperature. The oxidizing reagent (when used, see Table III, IV) was then introduced and, when the reaction was carried out at high temperature (see Table III, IV), the Schlenk tube was quickly placed in an oil bath at 80°C. After 2 h, the reaction was stopped by cooling to 0°C followed by acidification.

Analysis of products

The product mixture was prepared for qualitative or quantitative analysis by acidification using a slight excess (1.1 equivalent) of a 1.2N HCl solution in diethyl ether. The copper salts were filtered off and washed with diethyl ether. The combined filtrate and washings were evaporated *in vacuo*. The residual benzoic acids were redissolved in diethyl ether and treated with CH_2N_2 ¹⁴.

The copper salts still remaining were removed by a washing procedure using aqueous potassium cyanide. The aqueous washings were extracted with diethyl ether. The combined ethereal fractions were dried over magnesium sulfate and the organic products isolated by removal of the solvent *in vacuo*. When the products were to be analyzed quantitatively, 2-methylbenzoic acid was added as an internal standard to the reaction mixture prior to work-up.

GLC quantitative analyses were performed using a Cp-Sil 5 column (Chrompack, 25 m × 0.22 m × 0.32 mm). The nitrogen

* IUPAC name: 2,4-pentanedione.

flow rate was 6 ml/min; the initial column temperature was 80°C with a programmed rise of 6°C/min to 300°C. Yields were always at least 90% and the product percentages given have an accuracy of 5 rel %.

The qualitative GC-MS analyses were conducted on a BP 1 column (S.G.E.; 25 m × 0.33 mm × 0.5 μ; flow 2 ml/min; split various) using a temperature program similar to that of the GLC analysis. Products were identified by comparison of the mass-spectroscopic data with those of reference compounds and based on expected chemical reactivities. Exact mass data of several compounds were also measured.

Combined GLC and GC-MS data for the isolated products:
compound, retention time (min), *m/z* (%), fragment

The *m/z* peaks with a relative intensity below 10 are omitted, unless important. Mes = mesityl = C₆H₂Me₃-2,4,6; @ = 20 times enhanced; * = confirmed by high-resolution mass spectra; † = structure not assigned; Dimer = -2H.

Methyl benzoate (Ia), 5.4, 136(31; M⁺•), 105(100; M⁺• - OCH₃), 77(48; C₆H₅), 51(12).

Methyl 2-chlorobenzoate (Ib), 8.3, 170/172(31/11; M⁺•), 139/141(100/33; M⁺• - OCH₃), 111/113(31/10; M⁺• - COCH₃), 75(19; C₆H₃).

Methyl 2-bromobenzoate (Ic), 10.8, 214/216(44/44; M⁺•), 183/185(100/100; M⁺• - OCH₃), 155/157(31/31; M⁺• - CO₂CH₃), 76(32; C₆H₄), 75(30; C₆H₃), 50(24).

Methyl 2-hydroxybenzoate (Id), 7.3, 152(42; M⁺•), 121(18; M⁺• - OCH₃), 120(100; M⁺• - HOCH₃), 105(21; C₇H₅O), 92(46; C₆H₅O), 77(10; C₆H₅), 65(17), 39(12).

Methyl 2-mesitylbenzoate, C₁₇H₁₈O₂ (Ie)*, 20.0, 254(53; M⁺•), 222(100; M⁺• - HOCH₃), 207(21; M⁺• - HOCH₃ - CH₃), 194(17; C₁₅H₁₄), 179(58; C₁₄H₁₁), 178(30; C₁₄H₁₀), 165(21; C₁₃H₉), 89(10).

Mesityl 2-mesitylbenzoate, C₂₅H₂₆O₂ (If)*, 30.8, 358(4; M⁺•), 223(100; M⁺• - OMes), 195(15; M⁺• - CO₂Mes), 180(20), 179(17; C₁₄H₁₁), 178(13; C₁₄H₁₀), 165(23; C₁₃H₉).

Mesityl 2-chlorobenzoate, C₁₆H₁₅ClO₂ (Ig')*, 24.5, 274/276(5/2; M⁺•), 139/141(100/34; M⁺• - OMes), 111/113(15/6; C₆H₄Cl).

Mesityl 2-bromobenzoate, C₁₆H₁₅BrO₂ (Ig'')*, 25.6, 318/320(6/6; M⁺•), 183/185(100/100; M⁺• - OMes), 155/157(14/14; C₆H₄Br), 91(10; C₇H₇).

Dimethyl biphenyl-2,2'-dicarboxylate (IIa), 20.8, 270(30; M⁺•), 239(36@; M⁺• - OCH₃), 211(100; M⁺• - CO₂CH₃), 180(13), 152(12), 76(12; C₆H₄).

Mesityl methyl biphenyl-2,2'-dicarboxylate (IIb), 22.8, 374(1@; M⁺•), 343(4@; M⁺• - OCH₃), 239(100; M⁺• - OMes), 195(68), 180(32), 165(10), 152(19); 59(13; CO₂CH₃).

2-(Methoxycarbonyl)phenyl 2-chlorobenzoate (III'), C₁₅H₁₁ClO₄* 22.9, 290/292(43@; M⁺•), 259/261(37@/11@; M⁺• - OCH₃), 139/141(100/31; C₇H₄OCl), 111/113(17/6; PhCl), 75(8; C₆H₃).

2-(Methoxycarbonyl)phenyl 2-bromobenzoate (III''), 23.8, 334/336(40@/40@; M⁺•), 303/305(28@/28@; M⁺• - OCH₃), 183/185(100/100; C₇H₄OBr), 155/157(18/18; C₆H₄Br), 76(14; C₆H₄).

C₁₆H₁₂Cl₂O₄* (IVa'), dimer of methyl 2-chlorobenzoate†, 30.3, 338/340/342(24@/16@/2@; C₁₆H₁₂O₄Cl₂), 295(10@; M⁺• - COCH₃), 183/185(45@/15@; C₉H₈O₂Cl), 180/182(5@/15@; C₉H₇O₂Cl), 139/141(100/31; C₇H₄OCl), 111/113(7/22; C₆H₄Cl), 75(10; C₆H₃).

C₁₆H₁₂Br₂O₄* (IVa''), dimer of methyl 2-bromobenzoate†, 32.0, 426/428/430(16@/32@/16@; C₁₆H₁₂O₄Br₂), 227/229(44@/44@; C₉H₈O₂Br), 183/185(100/100; C₇H₄OBr), 155/157(12/12; C₆H₄Br), 76(15; C₆H₄).

C₁₆H₁₃ClO₄* (IVb'), dimer of methyl 2-chlorobenzoate with one chlorine substituted by hydrogen†, 28.0, 304/306(30@/10@; M⁺•), 261/263(82@/27@; M⁺• - COCH₃), 139/141(83/30; C₇H₄OCl), 111/113(17/6; C₇H₄Cl), 105(100; C₆H₅CO), 77(23; C₆H₅).

C₁₆H₁₃BrO₄* (IVb''), dimer of methyl 2-bromobenzoate with one

bromine substituted by hydrogen†, 29.1, 348/350(1/1; M⁺•), 183/185(30/30; C₇H₄OBr), 155/157(6/6; C₆H₄Br), 105(100; C₆H₄CO), 77(15; C₆H₅).

C₂₅H₂₃ClO₄* (IVc'), dimer of methyl 2-chlorobenzoate with one chlorine substituted by mesitylene†, 35.6, 422/424(6/2; M⁺•), 222(100; (Mes)PhCO), 183/185(51/16; C₉H₈O₂Cl), 182(16@; C₉H₇O₂Cl), 156(8; C₇H₅O₂Cl), 139/141(75/25; C₇H₄OCl), 111/113(12/4; C₆H₄Cl), 77(5; C₆H₅).

C₂₅H₂₃BrO₄* (IVc''), dimer of methyl 2-bromobenzoate with one bromine substituted by mesitylene†, 37.2, 466/468(7/7; M⁺•), 266(3; C₇H₅O₂Br), 227/229(24/24; C₉H₉BrO₂), 222(100; MesC₆H₄CO), 208(10), 195(18), 183/185(23/23; C₇H₄OBr), 165(8; C₁₃H₉), 155/157(5/5; C₆H₄Br), 105(10; C₆H₄CO), 77(2; C₆H₅).

Methyl 2-(1-acetyl-2-oxopropyl)benzoate (Va), C₁₃H₁₄O₄* 15.5, 234(40; M⁺•), 203(11; M⁺• - OCH₃), 202(25; M⁺• - HOCH₃), 187(100; M⁺• - HOCH₃ - CH₃), 160(76; -HOCH₃ - COCH₂), 43(72; COCH₃).

Lactone Vb, 18.1, 202(58; M⁺•), 87(M⁺• - CH₃), 145(21; M⁺• - CH₃ - COCH₂), 131(13), 89(18), 43(43; COCH₃), 28(52; CO).

Mesitylene (VIa), 4.6, 120(64; M), 105(100; M⁺• - CH₃), 91(8; C₇H₇), 77(9; C₆H₅).

Chloromesitylene (VIb), 5.3, 154/156(48/16; M⁺•), 139/141(14/5; M⁺• - CH₃), 119(100; M⁺• - Cl), 117(15), 115(14), 103(10), 91(17; C₇H₇), 77(12; C₆H₅).

Bromomesitylene (VIc), 7.8, 198/200(57/57; M⁺•), 183/185(6/6; M⁺• - CH₃), 119(100; M⁺• - Br), 117(20), 115(13), 103(12), 91(23; C₇H₇), 77(10; C₆H₅).

Hydroxymesitylene (VI'd), 6.5, 136(94; M⁺•), 135(30; M⁺• - 1), 121(100; M⁺• - CH₃), 91(10; C₇H₇), 77(14; C₆H₅).

Bimesityl, C₁₈H₂₂ (VII)*, 17.6, 238(100; M⁺•), 223(97; M⁺• - CH₃), 208(37; M⁺• - C₂H₆), 193(29; M⁺• - (C₂H₆) - CH₃).

Dimesityl ether, C₁₈H₂₂O (VIII)*, 20.7, 254(100; M⁺•), 239(13; M⁺• - CH₃), 134(40; M⁺• - MesH), 120(38; MesH), 105(15; C₈H₉), 91(21; C₇H₇), 77(10; C₆H₅).

C₁₈H₂₂O* (IXa†), 24.6, 254(55; M⁺•), 239(48; M⁺• - CH₃), 132(100; C₁₀H₁₂).

C₂₇H₃₂O* (IXb†), 33.8, 372(100; M⁺•), 357(16; M⁺• - CH₃), 253(4; C₁₈H₂₁O), 237(12), 132(63; C₁₀H₁₂), 91(5; C₇H₇).

Results and discussion

The reactions, product isolation and characterization

The reactivity of isolated copper(I) 2-halobenzoates [Cu(μ-O₂CC₆H₄Cl-2)]₄ (**1**) and [Cu(μ-O₂CC₆H₄Br-2)]₄ (**2**) has been studied in toluene at 20 or 80°C either with or without oxidizing agents (O₂, CuBr₂). These complexes have also been studied under "Hurtley reaction conditions", *i.e.* at 80°C with sodium acetylacetonate and/or acetylacetone. The corresponding reactivity of the mixed (2-halobenzoato)(mesityl)copper(I) clusters [Cu_{*m*}(2,4,6-Me₃C₆H₂)_{*n*}(μ-O₂CC₆H₄X-2)_{*o*}] (*m* = *n* + *o*; X = Cl, **3**; X = Br, **4**) were also investigated under similar conditions.

The products and by-products of these reactions (see Fig. 4 for an overview of the benzoate-derived products formed) have been qualitatively and quantitatively analysed by combined GLC and GC-MS techniques. To aid GLC separation, the product mixtures were treated with CH₂N₂ to convert all carboxylate fragments into the corresponding methyl esters. For quantitative GLC results, 2-methylbenzoic acid was used as an internal standard (see Experimental). Product characterization by GC-MS was based on fragmentation patterns and on exact mass data. In the case of coupling products **Id-f**, **II**, **III** and **Va-b**, it is assumed that new C-C or C-O bonds are situated *ortho* to

the carboxylate moiety, *i.e.* that C–C or C–O bond formation has resulted from an *ipso* halogen substitution reaction.

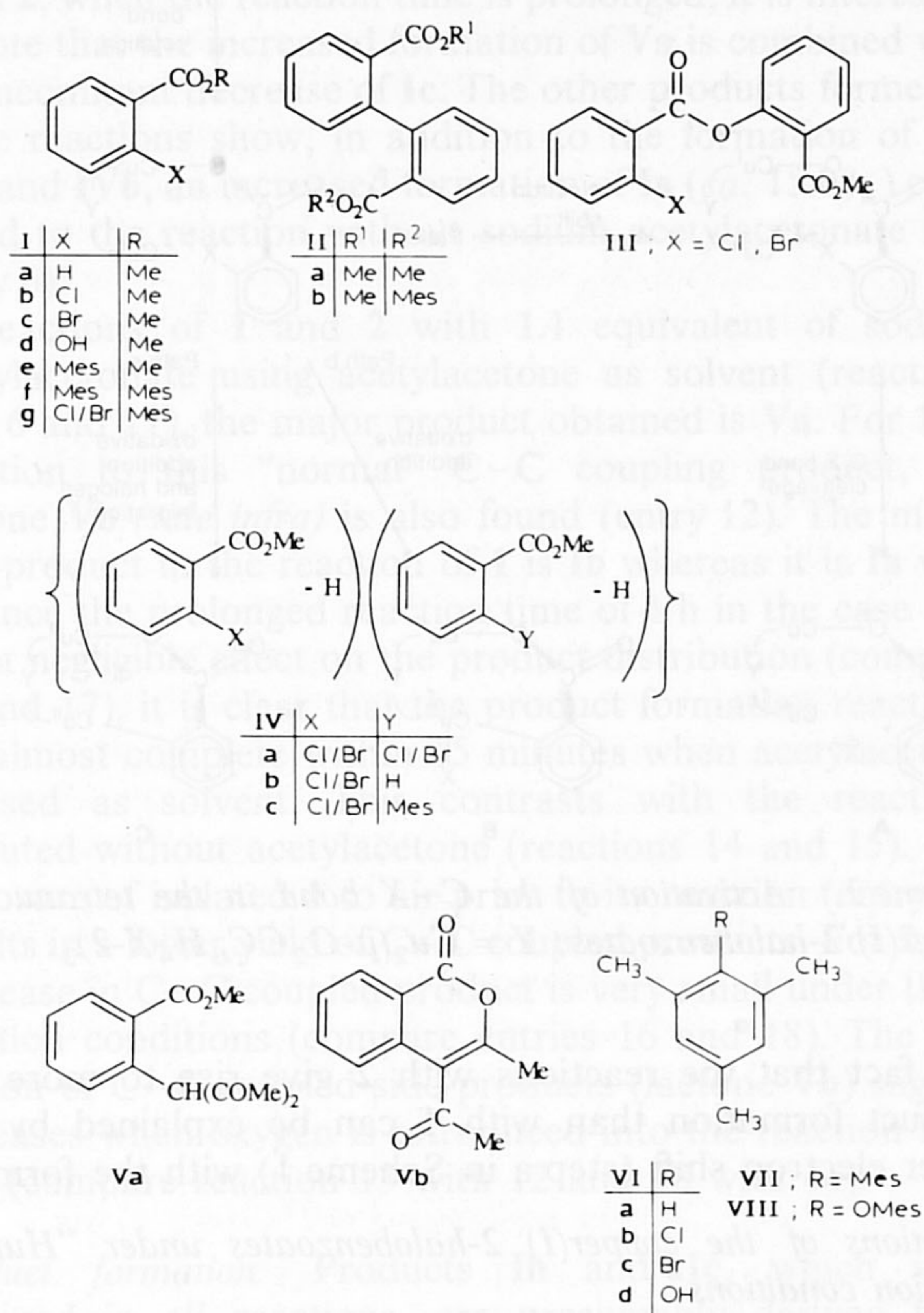


Fig. 4. An overview of the benzoate-derived products from reactions of pure copper(I) 2-halobenzoates, copper(I) 2-halobenzoates under "Hurtley reaction conditions", and mixed (2-halobenzoato)(mesityl)copper(I) clusters.

Reactions of the copper(I) 2-halobenzoates

Product distribution. The product distributions of the thermal reactions and the reactions under oxidizing conditions of the pure copper(I) 2-halobenzoates **1** and **2** are summarized in Table I. When the halogen is chlorine (entries 1–5), only two products can be identified, *i.e.* methyl 2-chlorobenzoate (**Ib**), the major product, and a diaryl (**IVa**) (see Fig. 4). The structure of **IVa** has not been identified but its composition, based on high-resolution mass spectra, is C₁₆H₁₂Cl₂O₄. This composition suggests that **Va** consists of two coupled methyl 2-halobenzoate units.

Table I The distribution of organic products from the reactions of pure copper(I) 2-halobenzoates^a.

	Reaction variables				Reaction products (%)					
	X	T (°C)	O ₂ ^b	CuBr ₂	Ia	Ib/Ic	Id	IIa	III	IVa
1	Cl	80				92.5			^c	7.5
2	Cl	20	+			98.3				1.7
3	Cl	20		+		88.7				11.3
4	Cl	80	+			70.4				29.6
5	Cl	80		+		85.2				14.8
6	Br	80			0.5	78.4		10.3	7.7	3.1
7	Br	20	+		0.8	94.2	3.0	0.2		1.8
8	Br	80	+			91.5	1.7	0.8	0.2	5.8

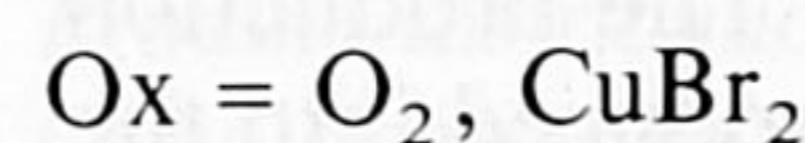
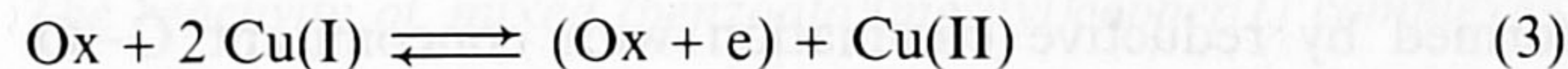
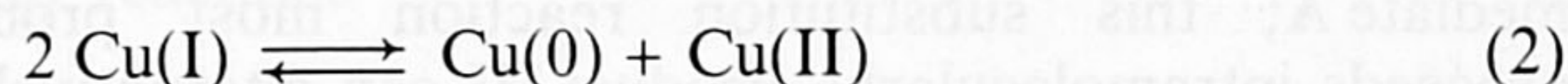
^a Relative percentages. Total amount of identified products obtained, was always > 90%. ^b Method *b* was used. ^c Only observed by GC-MS analysis.

With bromine as the halogen, in addition to methyl 2-bromobenzoate (**Ic**) (the major product) and **IVa**, significant amounts of other products were always present in the reaction mixture. In these by-products, *i.e.* **Ia**, **Id**, **IIa** and **III** (see Fig. 4), the bromine atom originally present in **2** has been replaced. This implies that the C–Br bond has been activated in the reaction sequence.

The formation of products **IIa** and **III**, which are the result of a C–C and a C–O coupling reaction, respectively, is especially favoured in the thermal reaction of **2** (entry 6). Their formation is considerably reduced when oxygen is introduced (for **IIa** from 10.3% to 0.8% and for **III** from 7.7 to 0.2%; compare entries 6 and 8).

Product **IVa** is formed in all the reactions of the pure copper(I) 2-halobenzoates studied but especially in reactions where X = Cl. The formation of **IVa** particularly increases when, at 80°C, oxidizing reagents are introduced (compare entry 1 with entries 4 and 5).

Product formation. Prior to discussing the origin of the various products it is worthwhile summarizing some important aspects of the copper(I) 2-halobenzoates **1** and **2**. Firstly, they are believed to have tetrameric structures (see Fig. 2) in which there is no interaction of the C–X bond with the copper(I) centre¹. Secondly, solvents such as toluene are not able to break the tetranuclear cluster down into smaller units. Finally, these copper(I) species can generate copper(II) benzoates by either of two routes; (i) valence disproportionation [Eqn. 2; the equilibrium moves to the side of Cu(0)/Cu(II) with increasing temperature]⁷ and (ii) oxidation (by O₂ or CuBr₂), Eqn. 3.



The origin of the major product from the reaction of **1** (*i.e.* **Ib**) and **2** (*i.e.* **Ic**) is straightforward. These products can be derived (after work-up) either from unreacted starting compound or from copper(II) benzoates formed in the reactions outlined above. The products **Ia**, **Id**, **IIa** and **III** all clearly result from C–X bond activation and our proposed mechanism for this, starting from the tetrameric clusters, is shown in Scheme 1. Step *i* involves an initial Cu–O bond breaking reaction which is followed (step *ii*) by a rotation around the C–O and the C_{carboxylate}–C_{aryl} bond which brings the halogen atom close to the copper atom. This positioning gives rise to either (a) a facile electron shift from the copper(I) atom to the halogen atom, thereby generating an intermediate wherein the C–X bond is easily broken to

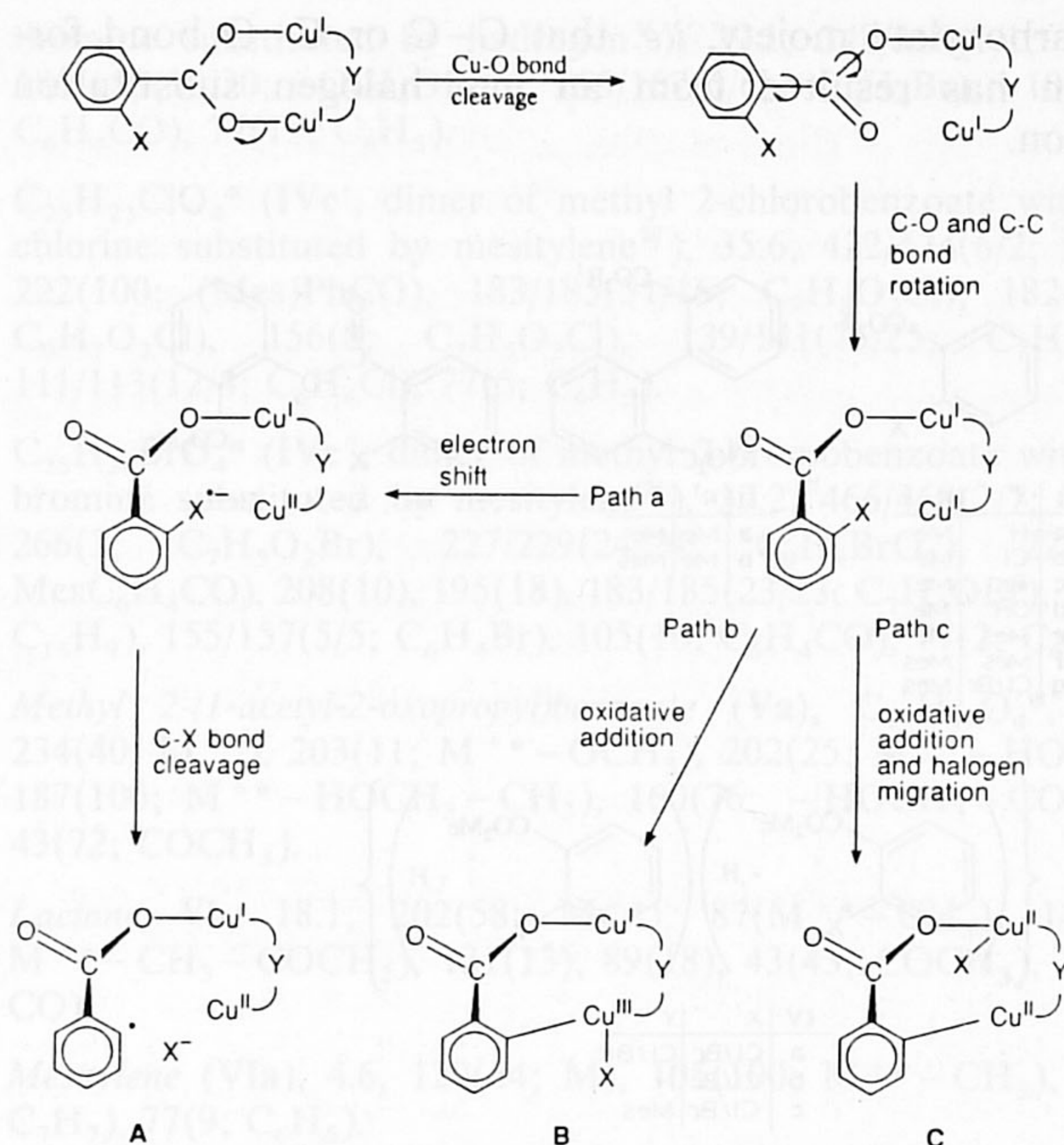
afford an aryl radical and an halide anion (intermediate **A**), (b) an oxidative addition of the C–X bond to the nearby copper(I) atom, thereby generating a dinuclear Cu(I)/Cu(III) intermediate (**B**), or (c) an oxidative addition of the C–X bond with concomitant migration of the halogen atom to an adjacent copper(I) atom, thereby generating intermediate **C** containing two copper(II) atoms. Radical intermediate **A** is able to react further to intermediate **B** or **C** by Cu–C and Cu–X bond formation.

It is on the basis of intermediates **A**, **B** and **C** that we can now explain the organic products formed in the reactions of copper 2-halobenzoates. Reactions of these intermediates with a hydrogen atom of a solvent molecule is responsible for the formation of methyl benzoate (**Ia**). The formation of methyl 2-hydroxybenzoate (**Id**) is due to a reaction of **A**, **B** or **C** with oxygen¹⁵, whereafter the carbon-bonded oxygen may either abstract a proton from the solvent or, more likely, becomes protonated during the work-up procedure.

We assume that product **IIa** is generated either via an intramolecular coupling on a tetranuclear cluster of two simultaneously formed aryl radicals (intermediates **A**) or via intramolecular coupling of two simultaneously formed organocopper fragments (intermediates **B** or **C**). Inter-molecular mechanisms are unlikely since interaction of the radical and organocopper intermediates with solvent molecules would be anticipated to yield **Ia**. The formation of biaryl products in reactions of organocopper(I) compounds having a Cu–C bond is a well known phenomenon¹⁶.

The C–O coupling product **III** can be formed by intramolecular attack of a carboxylate moiety, acting as a nucleophile, on the activated C-2 position in radical intermediate **A**; this substitution reaction most probably proceeds intramolecularly. Product **III** can alternatively be formed by reductive elimination with concomitant C–O bond formation from intermediates **B** or **C**. The production of **IIa** and **III** decreases when oxygen is introduced into the reaction mixture. This indicates either that formation of the key intermediates (**A**, **B** or **C**) is thwarted or that competing reactions are accelerated by oxygen (e.g. the oxidation reaction, Eqn. 3).

Since the structure of **IVa** has not been determined, a detailed discussion of its formation in the reactions of the pure copper(I) 2-halobenzoates is not advisable. However, since the yield of **IVa** is increased by both O₂ and copper(II) bromide (Table II), it is likely to be formed by an oxidative reaction mechanism. The formation of **IVa** in the reactions where the pure copper(I) 2-halobenzoates are only thermally activated (entries 1 and 6) is most likely due to the prior *in situ* formation of Cu(II) atoms by the disproportionation reaction (eq 2).



Scheme 1. Activation of the C–X bond in the tetranuclear copper(I) 2-halobenzoates; $Y = \text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{X-2})_3$.

The fact that the reactions with **2** give rise to more by-product formation than with **1** can be explained by the easier electron shift (step a in Scheme 1) with the former.

Reactions of the copper(I) 2-halobenzoates under "Hurtley reaction conditions"

Product distribution. The product distributions of the reactions of the copper(I) 2-halobenzoates, **1** and **2**, under "Hurtley reaction conditions" (i.e. at 80°C with acetylacetone, sodium acetylacetonate, and/or oxygen) are summarized in Table II.

When **1** is reacted in the absence of sodium acetylacetonate (entries 9 and 10), in addition to the major products methyl 2-chlorobenzoate (**Ib**) and methyl benzoate (**Ia**), no products due to a C–C coupling reaction between acetylacetone and 2-chlorobenzoic acid are found.

In reactions of **1** and **2** with sodium acetylacetonate (without acetylacetone) in toluene (entries 11, 14 and 15), poor formation of the desired C–C coupling product between acetylacetonate and 2-halobenzoic acid, i.e. **Va** occurs; the major product is methyl 2-halobenzoate (**Ib/Ic**). With **1**, the other products which are obtained in this reaction are **Ia**, **IIa** and **IVa**. Of these compounds **IVa** is

Table II The distribution of organic products from the reactions of pure copper(I) 2-halobenzoates under Hurtley reaction conditions^a.

	Reaction variables					Reaction products (%)									
	X	NaAcac	HAcac	O ₂ ^b	t (min)	^c	Ia	Ib	Ic	IIa	IVa	IVb	Va	Vb	
9	Cl		+		15	0.6	3.4	96.6							
10	Cl		+	+	15	0.3	3.0	97.0							
11	Cl	+			15	1.8	1.5	84.4		5.1	2.3		6.7		
12	Cl	+	+		15	5.3	4.1	39.3					51.3	3.2	
13	Cl	+	+	+	15	7.3	8.9	50.0					34.4	5.7	
14	Br	+			15		15.0		67.9	4.6	2.9	1.7	7.9		
15	Br	+			60		14.2		41.9	18.4			25.5		
16	Br	+	+		15		35.0		4.7	2.0			56.9		
17	Br	+	+		60	1.7	30.6		6.1	2.6			60.7		
18	Br	+	+	+	15	0.2	41.0		1.7	1.2			55.4	0.5	

^a Relative percentages. Total amount of identified products obtained, was always > 90%. ^b Method a was used. ^c Unidentified products.

also found in the reactions of **1** in the absence of sodium acetylacetonate (compare reaction 1 with 11) and therefore formation of **Ia** and **IIa** must be due to the presence of sodium acetylacetonate.

With **2**, when the reaction time is prolonged, it is interesting to note that the increased formation of **Va** is combined with a concomitant decrease of **Ic**. The other products formed in these reactions show, in addition to the formation of **IIa**, **IVa** and **IVb**, an increased formation of **Ia** (ca. 15.0%) compared to the reaction without sodium acetylacetonate (see entry 6).

In reactions of **1** and **2** with 1.1 equivalent of sodium acetylacetonate using acetylacetone as solvent (reactions 12, 16 and 17), the major product obtained is **Va**. For **1**, in addition to this "normal" C–C coupling product, the lactone **Vb** (*vide infra*) is also found (entry 12). The major side-product in the reaction of **1** is **Ib** whereas it is **Ia** with **2**. Since the prolonged reaction time of 1 h in the case of **2** has a negligible effect on the product distribution (compare 16 and 17), it is clear that the product formation reactions are almost complete within 15 minutes when acetylacetone is used as solvent. This contrasts with the reactions executed without acetylacetone (reactions 14 and 15).

Exposure of isolated **1** to air prior to its reaction (entry 13) results in a lower yield of C–C coupled products. For **2**, the decrease in C–C coupled product is very small under these reaction conditions (compare entries 16 and 18). The formation of C–C-coupled side-products (lactone **Vb**) slightly increases when oxygen is introduced into the reaction mixture (compare reaction 13 with 12 and 18 with 16).

Product formation. Products **Ib** and **Ic**, which were obtained in all reactions, are presumably derived from either non-reacted starting compound or Cu(II) benzoates formed by valence disproportionation or oxidation (*vide supra*). The increased formation of **Ib** in reaction 13 (compare to 12) must be due to the presence of oxygen and must therefore be associated with the oxidation reaction.

Ia is formed in every reaction of **1** and **2** under Hurltley reaction conditions and, as discussed above, its formation is due to solvent interaction with an intermediate in which the C–X bond is activated. In these reactions under Hurltley conditions (9–18), this interaction appears to be more important than in reactions without sodium acetylacetonate and acetylacetone (1–8).

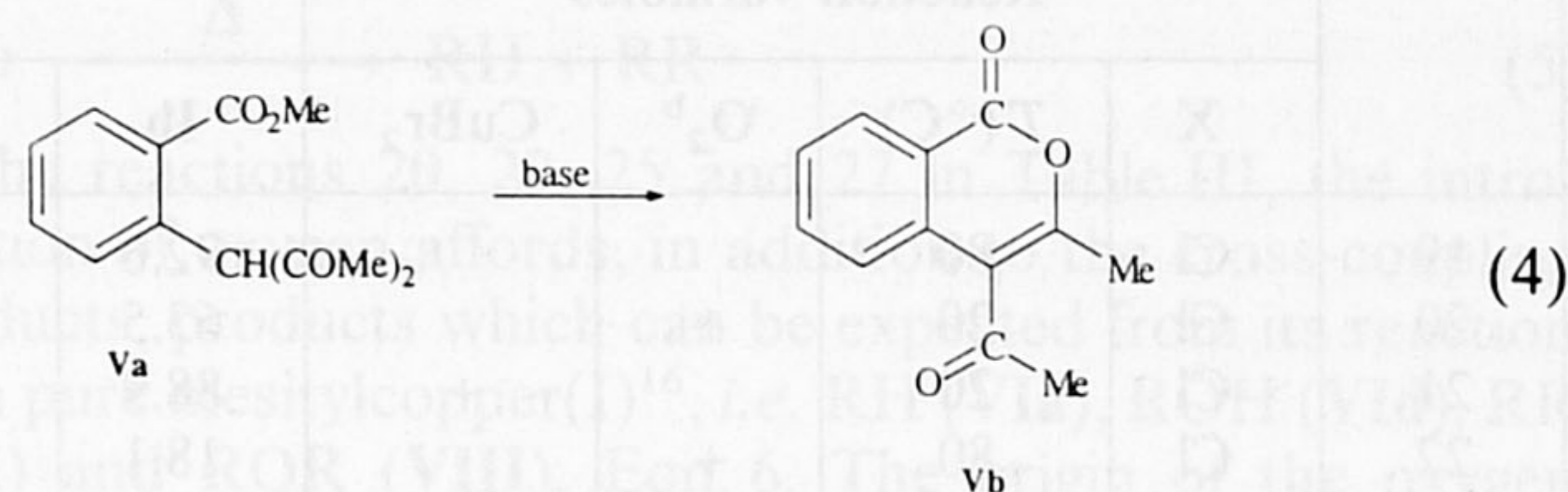
The increased formation of product **Ia** in reactions where acetylacetone rather than toluene is used as a solvent can be attributed to the higher acidity of acetylacetone which accelerates the reaction of the solvent with the activated C–X bond of the intermediate.

Since the desired C–C coupling product **Va** is only recovered when sodium acetylacetonate is present (entries 11–13 and 14–18), it can be concluded that this is the nucleophile in the Hurltley reaction. Furthermore, there is also a strong dependence of product **V** formation on the absence (poor yields) or presence of acetylacetone (reasonable yields) as solvent. The better coordinating ability of acetylacetone over that of toluene (the other solvent used) must therefore play an important role in the mechanism of the Hurltley reaction (*vide infra*).

The increased formation of **Va**, after a prolonged reaction time in the absence of acetylacetone (compare reactions 15 and 14), indicates that (i) reactive copper(I) 2-bromobenzoate is regenerated by the reversible disproportionation reaction or, more unlikely, that (ii) after a reaction period of 15 minutes, unreacted copper(I) 2-bromobenzoate is still present.

In addition to the "normal" C–C coupling product **Va**, the lactone **Vb** is also formed (entries 12, 13 and 18). **Vb** is

known to result from the reaction of **Va** with base⁶ (see eq 4), which in our case is sodium acetylacetonate.



The unknown side-product **IVa** is also recovered in these reactions under Hurltley conditions (entries 11 and 14) and, contrary to what was found with the pure copper(I) 2-halobenzoates, there is no correlation between the introduction of oxidizing agents and its formation.

The formation of the partly reduced product **IVb** indicates that the reduction of the carbon–halogen bond (normally yielding **Ia**) and the dimerization reaction (yielding product **IVa**) can proceed in sequential reaction steps on a copper cluster.

The influence of the halo atom on the reactivity of the copper(I) 2-halobenzoates is remarkable. Those reactions carried out with copper(I) 2-bromobenzoate always give rise to more products derived from reactions involving the carboxylate C_{ortho} atom (*i.e.* all products except **Ib** and **Ic**) than from the corresponding reactions with copper(I) 2-chlorobenzoate. This indicates that the activation of the C–X bond by an *ortho* copper(I) carboxylate moiety is more effective when X is Br than when X is Cl and is in agreement with the reactivity found for the copper catalysed Hurltley reactions^{5,6}.

The reactivity of mixed (benzoato)(mesityl)copper(I) complexes

Product distribution. The products derived from the mixed (2-halobenzoato)(mesityl)copper(I) complexes are summarized in Tables III and IV.

In all reactions of the mixed (2-halobenzoato)(mesityl)copper(I) clusters (except 24) [for both the chloro (**3**) and bromo (**4**) species], methyl 2-halobenzoate (**Ib/Ic**) is one of the major products.

Reactions with **3** (entries 19–23) afford only minor quantities of the C–C cross-coupling products, *i.e.* **Ie**, **If** and **IVc** (see supplementary material). Particularly when only thermal activation takes place (entry 19) is the product distribution similar to that of the reaction of pure copper(I) 2-chlorobenzoate (entry 1) and the influence of the mesityl-copper(I) unit seems to be minimal. This limited involvement of the mesitylcopper(I) fragments is reflected in the recovery of 95.5% of mesitylene (see Table IV) and very little bimesityl (**VII**).

Reactions of **3** in the presence of oxidizing agents lead to the formation of the C–O-cross-coupled product **Ig**, whose yield increases with thermal activation (compare reaction 20 with 22 and 21 with 23). Oxidizing activation with oxygen also affords substantial amounts of the unidentified self-coupling product **IVa** (entries 20 and 22).

Reactions of **4** carried out at room temperature (entries 25 and 26) yield almost no C–C cross-coupling products (**Ie**, **If** and **IVc**). However, with only thermal activation (entry 24), this bromo species affords C–C cross-coupling products for 87.6% of the benzoate fragments. When oxidizing reagents are introduced with thermal activation, the amount of these C–C coupled products decreases significantly [to 27.6% for oxygen (entry 27) and to 18.9% for copper(II) bromide (entry 28)]. Significantly, these latter conditions lead to an increase in the formation of C–O-cross-coupled products (mesityl esters **If**, **Ig** and **IIf**), which is also the case for reactions of **3** (*vide supra*).

Table III The distribution of benzoate-derived organic products from the reactions of the mixed (2-halobenzoato)(mesityl)copper(I) clusters^a.

	Reaction variables				Reaction products (%)									
	X	T (°C)	O ₂ ^b	CuBr ₂	Ib	Ic	Ie	If	Ig	IIa	IIb	IVa	IVc	C-C?
19	Cl	80			92.6		1.2		0.4			5.0	0.3	0.5
20	Cl	20	+		63.5				2.0			34.5		
21	Cl	20		+	88.9				11.0			0.1		
22	Cl	80	+		18.1				30.4			51.5		
23	Cl	80		+	75.8		0.1		24.1					
24	Br	80					64.1	16.7	3.5	7.8	1.1		6.8	
25	Br	20	+			33.3		0.4	6.6			56.9	2.8	
26	Br	20		+		73.6	0.4	0.4	19.3			5.5	0.8	
27	Br	80	+			11.0	0.6	23.8	46.5		8.5	6.4	3.2	
28	Br	80		+		54.2	12.3	5.8	22.0	4.2			0.8	0.7

^a Relative percentages. Total amount of identified products was always >90%. ^b Method *b* was used.

Table IV The distribution of the mesityl fragments from the reactions of the mixed (2-halobenzoato)(mesityl)copper(I) clusters^a.

	Reaction variables				Reaction products								
	X	T (°C)	O ₂ ^b	CuBr ₂	Mesityl coupled to benzoate fragment	RH VIa	RCl VIb	RBr VIc	ROH VIId	R ₂ VII	ROR VIII	IXa ^c	IXb ^d
19	Cl	80			3.0	95.5				1.5			
20		20	+		2.2	11.6	12.7			54.8	12.1	6.6	
21		20		+	12.2	22.8	7.4	33.2		21.8	2.3	0.3	
22		80	+		33.4	7.2				24.9	31.8		2.7
23		80		+	24.2	20.0	5.0	28.8		11.3	7.0		3.7
24	Br	80			97.9	^e				2.1			
25		20	+		11.2	21.1			^e	57.1	9.8	0.8	
26		20		+	23.0	18.0		29.2		27.9	1.9		
27		80	+		90.9	0.2				4.3	4.2		0.4
28		80		+	52.6	17.1		17.7		12.6			

^a Relative percentages. Total amount of identified products was always >90%. R = mesityl. ^b Method *b* was used. ^c Constitution by exact mass spectroscopy is C₁₈H₂₂O (two mesityl groups and an oxygen). ^d Constitution by exact mass spectroscopy is C₂₇H₃₃O (three mesityl groups and an oxygen). ^e Only observed by GC-MS.

The biaryl products **IIa** and **IIb** are only formed from the bromo derivative **4** (entries 24, 27 and 28).

With both **3** and **4**, the distribution of those products derived solely from mesitylene fragments is very dependent on the reaction conditions, particularly the presence or absence of oxidizing agents. For example, when oxygen is introduced at ambient temperature, for **3** as well as for **4** (entries 20 and 25, respectively), in addition to mesitylene (**VIa**; 11.6% and 21.1%), bimesityl (**VII**; 54.8% and 57.1%), dimesityl ether (**VIII**; 12.1% and 9.8%) and an unidentified product **IXa** (see supplementary material; 6.6% and 0.8%) are also formed; for **3**, chloromesitylene (12.7%) and for **4**, a minor quantity of hydroxymesitylene is also recovered. When copper(II) bromide, instead of oxygen, is introduced at ambient temperature (entries 21 and 26), formation of bromomesitylene, 33.2% and 29.2%, respectively, occurs at the expense of bimesityl and dimesityl ether (compare with entries 20 and 25).

With **3**, when oxygen is introduced together with thermal activation (entry 22), the formation of dimesityl ether increases, while the ratio of mesitylene to bimesityl formed remains comparable to that of the reaction at ambient temperature (1:3.45 for entry 22 and 1:4.7 for entry 20). With **4**, the mesityl fragments under these conditions give mainly (90.9%) coupling products with the benzoate fragments.

When, instead of oxygen, copper(II) bromide is introduced at 80°C for **3**, the yields of the major products are similar to those of the reaction at room temperature (compare

entries 21 and 23). Only the formation of bimesityl decreased (from 21.8% to 11.3%), while the amount of benzoate coupled product increased. For **4**, the formation of benzoate coupled products increases at the expense of the formation of **IVc**, **VII** and **VIII** (compare entry 28 with 26).

Thermal activation and the introduction of oxidizing reagents cause the coupling of an extra mesityl fragment to unknown **IXa**, thereby forming **IXb** (compare 20 and 21 with 22 and 23 and also 25 with 27).

Product formation. In the reactions of **3** and **4**, the formation of compounds **Ib**, **Ic**, **IIa** and **IVa** most likely follows the same paths as described above for **1** and **2**; the mesityl-copper(I) fragments do not seem to interfere with these product forming reactions. The activation of the C-X bond in reactions of these mixed copper(I) clusters, affording products **Ie**, **If**, **IIa**, **IIb**, **III** and **IVc**, is assumed to follow the pathway outlined above for the pure copper(I) 2-halobenzoates (Scheme 1).

Product **Ie** is formed by an intramolecular "Hurtley-like" C-C cross-coupling reaction of a mesityl fragment with an intermediately activated C-X bond which is analogous to the C-C cross-coupling reaction between sodium acetylacetonate and 2-halobenzoic acid or the biaryl-forming reaction (affording **IIa/IIb**).

Product **If**, a mesityl ester, is also formed after an initial C-C cross-coupling reaction (*vide supra*) whereafter

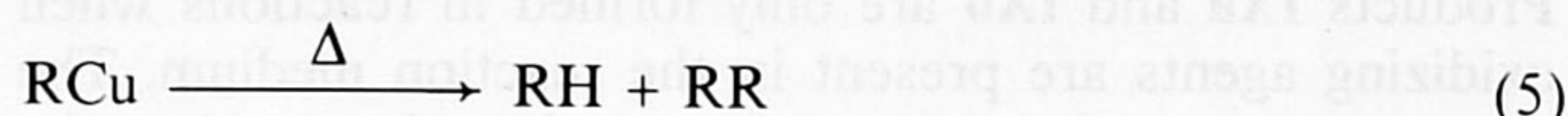
another mesitylene fragment couples with the benzoate carboxylate function. The C–C coupling reaction is assumed to take place first since, in the case of initial ester formation, the coordination to a copper cluster and subsequent activation of the C–X bond are most unlikely. Compound **IVc**, an unidentified dimer, is another C–C coupling product of a mesitylene fragment and the C-2 atom of a benzoate unit.

The mesityl esters (**If**, **Ig** and **Iib**), whose formation is aided by the introduction of oxidizing agents, are the result of the well-known Cu(II)-mediated ester formation reaction¹⁷. This reaction is made possible by the oxidation of a copper(I) atom which is bonded to a benzoate and a mesityl unit. It is interesting to note that this esterification reaction takes place after either the C–C coupling reaction or the biaryl coupling reaction, since otherwise **If** and **Iib** would not have been formed (*vide supra*).

Since, in the reactions of the pure copper(I) 2-bromobenzoates, the formation of the unidentified product **IVa** was never high, the increased formation of this product in a reaction of a mixed (2-bromobenzoato)(mesityl)copper(I) cluster in the presence of oxygen (entry 25) is noteworthy; we have no simple explanation for this result.

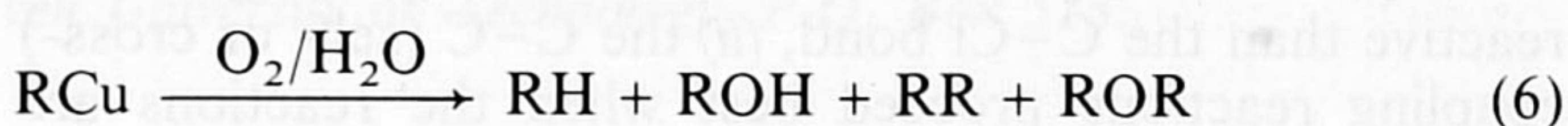
The formation of products which are solely due to mesitylene fragments shows that the reactions which normally take place with pure organocopper(I) compounds can also take place in mixed (benzoato)(mesityl)copper(I) clusters. In reaction 19, most of the mesitylene recovered is formed from unreacted mesityl units during the protic work-up procedure. However, in this thermal activation reaction of **3**, a small part of the mesitylene and all of the bimesityl is formed by thermolysis of the mixed cluster, similar to that of pure organocopper(I) compounds¹⁶, see Eqn. 5. The thermal activation reaction for **4** yielded very little

mesitylene, since most mesityl fragments were coupled with benzoate units (97.9%).

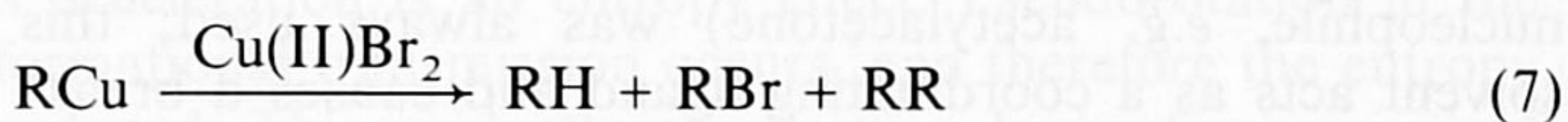


In the reactions 20, 22, 25 and 27 in Table III, the introduction of oxygen affords, in addition to the cross-coupling products, products which can be expected from its reaction with pure mesitylcopper(I)¹⁶, *i.e.* RH (**VIa**), ROH (**VIc**), RR (**VII**) and ROR (**VIII**), Eqn. 6. The origin of the oxygen atom involved in the formation of dimesityl ether (**VIII**) in reactions 21, 23 and 26 must be oxygen absorbed onto the surface of the copper(II) bromide introduced.

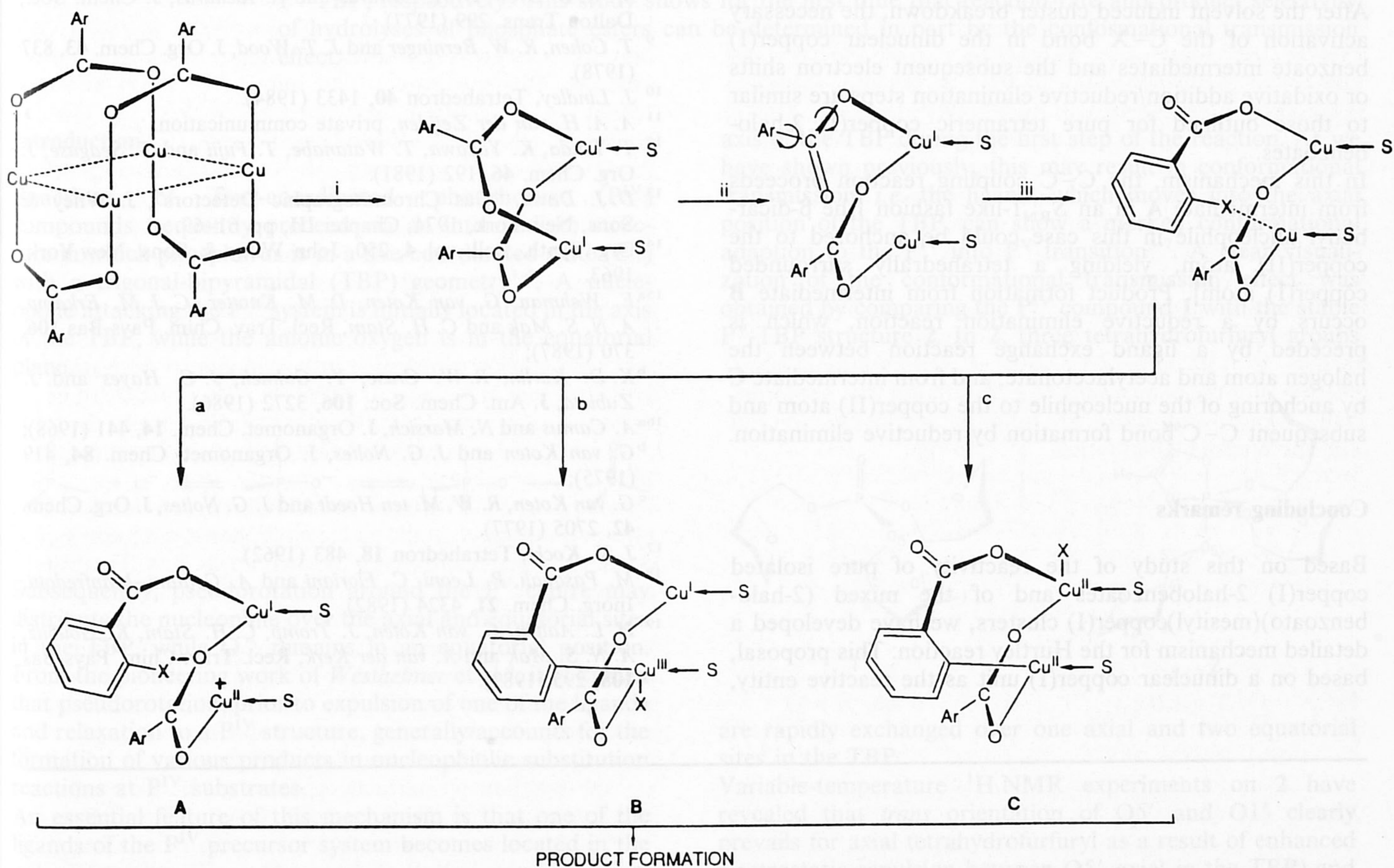
The product distribution in the thermal decomposition reactions of organocopper(I) compounds depends on the nature of the R group¹⁶. In our system, the outcome of these reactions also depends on the nature of the 2-halobenzoate. For instance, the formation of a minor quantity of **VIc** only occurs in the reaction of **4** where oxygen is introduced.



With the mixed clusters, the introduction of copper(II) bromide gives products derived from the mesityl fragment which are also of the type expected for pure organocopper(I) clusters with this reagent^{16b,c} (see Eqn. 7), *i.e.* RH (**VIa**), RBr (**VIc**) and RR (**VII**).



For **3**, the formation of mesityl chloride (**VIb**) in the reactions where oxidizing reagents are introduced (entries 20, 21 and 23) is due to the *in situ* formation of copper(II) chloride. The reason that **IVb** is not formed in reaction 22,



Scheme 2. Mechanism of the Hurtley reaction involving; i, solvent induced cluster breakdown; ii, C–O bond cleavage; iii, C–O and C–C bond rotation; path a, initial electron shift; path b, oxidative addition; path c, oxidative addition with concomitant halogen migration.

where *in situ* formation of copper(II) chloride is also possible, is due to the favoured formation of VIII.

Products IXa and IXb are only formed in reactions when oxidizing agents are present in the reaction medium. The exact structure of these compounds is unknown but the mesitylene fragments are most likely coupled to each other by a methylene bridge, *i.e.* a C–H bond has been activated in the reaction sequence.

The mechanism of the Hurtley reaction

Our results strengthen the literature proposal³⁻⁶ that copper(I) 2-halobenzoates are the key intermediates in the copper-catalysed condensation reaction between 2-halobenzoates and β -dicarbonyl compounds. Their intermediacy is confirmed by the completed product formation within 15 minutes in the reaction of copper(I) 2-bromobenzoate with sodium acetylacetonate and acetylacetonate (entry 17). In our reactivity study, there are many parallels found with the Hurtley reaction, *i.e.* (i) the C–Br bond is always more reactive than the C–Cl bond, (ii) the C–C (self- or cross-) coupling reactions proceed best when the reactions are executed in the absence of oxidizing reagents, and (iii) a coordinating solvent (such as acetylacetonate) is needed to promote the C–C cross-coupling reaction between a 2-halobenzoic acid and acetylacetonate.

In published Hurtley reactions, an O-donor solvent (water, methanol or the conjugated acid of the β -dicarbonyl nucleophile, *e.g.* acetylacetonate) was always used; this solvent acts as a coordinating ligand and causes a breakdown of the tetrameric cluster. Since methanol is known to break down a tetrameric copper(I) benzoate cluster into a dinuclear unit^{1,18}, we propose a mechanism for the Hurtley reaction which involves dinuclear copper(I) 2-halobenzoates as intermediates (see Scheme 2).

After the solvent induced cluster breakdown, the necessary activation of the C–X bond in the dinuclear copper(I) benzoate intermediates and the subsequent electron shifts or oxidative addition/reductive elimination steps are similar to those outlined for pure tetrameric copper(I) 2-halobenzoates.

In this mechanism, the C–C coupling reaction proceeds from intermediate A in an $S_{RN}1$ -like fashion [the β -dicarbonyl nucleophile in this case could be anchored to the copper(II) atom, yielding a tetrahedrally surrounded copper(I) atom]. Product formation from intermediate B occurs by a reductive elimination reaction, which is preceded by a ligand exchange reaction between the halogen atom and acetylacetonate, and from intermediate C by anchoring of the nucleophile to the copper(II) atom and subsequent C–C bond formation by reductive elimination.

Concluding remarks

Based on this study of the reactivity of pure isolated copper(I) 2-halobenzoates and of the mixed (2-halobenzoato)(mesityl)copper(I) clusters, we have developed a detailed mechanism for the Hurtley reaction. This proposal, based on a dinuclear copper(I) unit as the reactive entity,

explains the necessity of O-donor solvents for this reaction. The activation of the C–X bond [initiated by Cu–O bond breaking and rotation around C–O and C–C bonds, followed by an interaction with a copper(I) atom of a dinuclear copper cluster in the Hurtley reaction] is similar to that proposed for the activation of the C–C bond in the copper-assisted decarboxylation reaction¹⁹.

The high reactivity of 8-bromonaphthoic acid in the Hurtley reaction can now be readily explained. A CPK model study shows that, in a dinuclear copper(I) cluster of this acid, the bromo atom is always close to a copper atom which can activate the C–Br bond.

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References

- ¹ H. L. Aalten, G. van Koten, E. Riethorst and C. H. Stam, *Inorg. Chem.*, in the press.
- ² W. R. H. Hurtley, *J. Chem. Soc.* 1870 (1929).
- ³ A. A. Goldberg, *J. Chem. Soc.* 4368 (1952).
- ⁴ W. Mayer and R. Fikentscher, *Chem. Ber.* **91**, 1536 (1958).
- ⁵ K. A. Cirigottis, E. Ritchie and W. C. Taylor, *Austral. J. Chem.* **27**, 2209 (1974).
- ⁶ A. Bruggink and A. McKillop, *Tetrahedron* **31**, 2607 (1975).
- ⁷ H. L. Aalten, G. van Koten, K. Goubitz and C. H. Stam, *Organometallics* **8**, 2293 (1989).
- ⁸ M. G. B. Drew, D. A. Edwards and R. Richards, *J. Chem. Soc., Dalton Trans.* 299 (1977).
- ⁹ T. Cohen, R. W. Berninger and J. T. Wood, *J. Org. Chem.* **43**, 837 (1978).
- ¹⁰ J. Lindley, *Tetrahedron* **40**, 1433 (1984).
- ¹¹ A. A. H. van der Zeijden, private communication.
- ¹² T. Tsuda, K. Yazawa, T. Watanabe, T. Fujii and T. Seaguse, *J. Org. Chem.* **46**, 192 (1981).
- ¹³ D. J. David, "Gas Chromatographic Detectors", J. Wiley & Sons, New York, 1974, Chapter III, pp. 61–69.
- ¹⁴ *Org. Synth.*, coll. vol. **4**, 250, John Wiley & Sons, New York, 1963.
- ^{15a} E. Wehman, G. van Koten, D. M. Knotter, C. J. M. Erkamp, A. N. S. Mak and C. H. Stam, *Recl. Trav. Chim. Pays-Bas* **106**, 370 (1987);
- ^b K. D. Karlin, R. W. Cruse, Y. Gultneh, J. C. Hayes and J. Zubieta, *J. Am. Chem. Soc.* **106**, 3272 (1986).
- ^{16a} A. Camus and N. Marsich, *J. Organomet. Chem.* **14**, 441 (1968);
- ^b G. van Koten and J. G. Noltes, *J. Organomet. Chem.* **84**, 419 (1975);
- ^c G. van Koten, R. W. M. ten Hoedt and J. G. Noltes, *J. Org. Chem.* **42**, 2705 (1977).
- ¹⁷ J. K. Kochi, *Tetrahedron* **18**, 483 (1962).
- ¹⁸ M. Pasquali, P. Leoni, C. Floriani and A. Geatani-Manfredotti, *Inorg. Chem.* **21**, 4324 (1982).
- ¹⁹ H. L. Aalten, G. van Koten, J. Tromp, C. H. Stam, K. Goubitz, A. N. S. Mak and A. van der Kerk, *Recl. Trav. Chim. Pays-Bas* **108**, 295 (1989).