Selective bromination of alkanes and arylalkanes with CBr_4

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The catalytic bromination of alkanes, cycloalkanes and arylalkanes with near 100% yields was performed using CBr_4 as a brominating agent in the presence of copper- and nickel-containing catalysts.

We performed the selective catalytic bromination of alkanes (decane and dodecane), cycloalkanes (cyclohexane) and arylalkanes (toluene and *p*-xylene) by CBr_4 in the presence of metal (Cu and Ni) complex catalysts for the first time.

Previously,[1] CBr_4 was used in a combination with sodium hydroxide for the bromination of alkanes and cycloalkanes in a two-phase system in the presence of a phase-transfer catalyst. However, this process is ineffective: the reaction time was as long as 90 h even for reactive substrates, and the product yields were no higher than 30–70%. Carbon tetrabromide as the constituent of a catalytic complex with $AlBr_3$ was also used for the bromination of alkanes and cycloalkanes.[2] In this case, the $CBr_4 \cdot 2AlBr_3$ complex can also serve as a brominating agent in the absence of molecular bromine.[3] A required twofold molar excess of aluminium bromide and the sensitivity of the brominating agent to moisture make this synthesis difficult to perform. Analogously, in a similar process[4] of alkane bromination with methylene bromide in the presence of SbF_5, large relative amounts of the metal halide were used (the molar ratio $CHBr_2{:}SbF_5$ was about two). The aim of this study was to develop a selective procedure for alkane bromination by CBr_4 in the presence of catalytic amounts of a transition metal.

Copper complexes prepared by the reactions of CuBr with quaternary ammonium bromides, for example, CuBr + Bu_4NBr (1:1) (catalyst **1**),† the $[(PhSiO_{1.5})_2CuO]_n$ metal-containing polyphenylsiloxane immobilised on silica (catalyst **2**)‡ and the related nickel derivative $\{[H_2N(CH_2)_3SiO_{1.5}]_2NiO\}_n$ (catalyst **3**)‡ were used as the catalysts. Previously,[5–7] copper chloride complexes similar to **1** and organometallic polysiloxanes (containing phenyl, alkyl and aminoalkyl substituents at silicon) grafted onto silica were used in the metathesis of C–Cl and C–H bonds in the CCl_4–alkane systems. These catalytic systems are stable, highly active and easy to use. Chloroform and monochloroalkanes were prepared with 98–99% selectivity at 50–80% conversion of the parent alkanes in reactions with the participation of CCl_4 and these catalysts.

Table 1 Bromination of alkanes by CBr_4.

Entry	Alkane (RH)	RH:CBr_4 molar ratio	Catalyst	*t*/h	*T*/°C	Yield of RBr (%) (on a CBr_4 basis)
1	$C_{12}H_{26}$	10:1	**1**[a]	2.5	180	67
2	$C_{10}H_{22}$	5:1	**1**	8	160	93
3	$C_{12}H_{26}$	10:1	**1**	5	180	95
4	cyclo-C_6H_{12}	10:1	**1**	10	180	86
5	$C_{12}H_{26}$	10:1	**2**	2.5	160	130[b]
6	$C_{12}H_{26}$	10:1	**2**	5	150	68
7	$C_{12}H_{26}$	2.2:1	**2**	5	150	61
8	$C_{12}H_{26}$	10:1	**2**	10	130	55
9	$C_{12}H_{26}$	10:1	**2**	10	98	28
10	$C_{10}H_{22}$	10:1	**2**	5	150	60
11	cyclo-C_6H_{12}	10:1	**2**	8	150	48
12	$C_{12}H_{26}$	10:1	**3**	2.5	150	155[b]
13	cyclo-C_6H_{12}	10:1	**3**	10	150	67
14	Toluene	10:1	**3**	10	150	160[b]
15	Toluene	5:1	**3**	10	150	145[b]
16	*p*-Xylene	10:1	**3**	5	150	135[b]

[a] Equimolar mixture of CuBr and Bu_4NBr (10 wt.% of the weight of reactants). [b] Yields higher than 100% indicate that more than one bromine atom from a molecule of CBr_4 took part in the formation of bromoalkanes.

The reactions of CBr_4 with alkanes and arylalkanes in the presence of **1**–**3** proceed at elevated temperatures (150–180°) in 100% (dodecane, decane, toluene and xylene) or near 100% (cyclohexane) yields of monobromoalkanes in terms of the initial CBr_4.§ An induction period was absent. Table 1 summarises the yields of reaction products at different conditions. The reaction is highly selective: cyclohexane gives only cyclohexyl bromide, and toluene and xylene, monobromides of the benzyl structure. Isomer mixtures of secondary bromoalkanes were obtained from decane and dodecane; 1-bromoalkanes and dibromo derivatives were absent from the products or occurred as traces. We failed to identify particular isomers by GC–MS because of the similarity of the mass spectra of linear secondary bromoalkane isomers. The bromination of *n*-dodecane at 150 °C in the presence of catalyst **1** gave five isomeric secondary bromides in the ratio 1.3:1.2:1.0:1.4:0.9 (to within ±0.1); the selectivity for particular isomers varied within narrow limits from 16 to 24% (±2%) in

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† Chemically pure carbon tetrabromide was triply recrystallised from ethanol. Dodecane, decane, cyclohexane, bromoform, and dodecyl bromide were distilled and thoroughly dried before use. Tetrabutylammonium bromide prepared by the interaction between tributylamine and *n*-bromobutane was azeotropically dried and twice recrystallised from benzene. The catalytic complex was prepared from chemically pure CuBr and the quaternary salt by dissolving the components in the reaction mixture on heating (40–50 °C).

‡ The cage organometallic siloxane oligomers were prepared by well-known methods.[10,11] The structure of the compounds was confirmed by the presence of absorption bands typical of Si–O–Si (1030–1100 cm^{-1}, **2** and **3**), Si–O–Cu (950–980 cm^{-1}, **2**), Ph–Si (1130 cm^{-1}, **2**) and NH_2 (750, 3380 cm^{-1}, **3**) groups in the IR spectra; a typical band at 750 nm in the electronic absorption spectrum of **2** (*d*–*d* transitions in the Cu^{2+} ion); and elemental analysis data. In all of the compounds, the Si:M atomic ratio was close to 2. For a precursor of **2** found (%): Cu, 18.2; Si, 16.4; C, 45.3; H, 2.7. $C_{12}H_{10}Si_2O_4Cu$ requires (%): Cu, 18.8; Si, 16.6; C, 45.6; H, 3.0. For a precursor of **3** found (%): Ni, 19.0; Si, 18.5; C, 24.7; H, 5.0. $C_6H_{16}N_2Si_2O_4Ni$ requires (%): Ni, 19.9; Si, 18.9; C, 24.4; H, 5.4. Catalysts supported on silica (Silochrome C-80) were prepared by sorption from toluene or toluene–DMF solutions. After the removal of the solvent, the catalysts were heated at 160 °C in a vacuum. The copper or nickel content of heterogeneous catalyst **2** or **3** was 0.11 or 0.16 wt.%, respectively.

§ The bromination was performed in sealed ampoules under temperature-controlled conditions with stirring. The amount of a catalyst was 2 mol% on a hydrocarbon basis for complex **1** or 1 g of a heterogeneous catalyst per 10 ml of the reaction mixture. Oxygen was removed by repeated freeze–pump–thaw cycles (the residual pressure was 10^{-3} mmHg). Products were analysed by GLC and GC–MS (a Finnigan MAT-212 instrument coupled with a Varian 3740 chromatograph). The mass spectra of monobromodecanes exhibited a peak of the $[M - Br]^+$ ion (*m*/*z* = 169) and a set of peaks corresponding to alkyl chain fragmentation (*m*/*z* = 43, 57, 71, 85, 113). The absence of a peak of the stable ion $C_4H_8Br^+$ (*m*/*z* = = 135, 137)[12] suggests that 1-bromodecane is not a reaction product. The released hydrogen bromide was determined by acid–base titration.

the absence of 1-bromododecane. Temperatures above 150 °C are required to obtain 100% yields in several hours. At 98–130 °C, the reaction rate decreases; however, as follows from Table 1 (entries 8 and 9), it remains measurable. This is a dissimilarity from analogous reactions with the participation of CCl_4, which proceed very slowly below 150 °C. The ratio between reactant has almost no effect on the yield (*cf.* entries 6, 7 and 14, 15 in Table 1).

Undoubtedly, the bromination in the presence of copper complexes has radical nature and can be represented by the following reaction scheme taking into account published data[5–9] concerning reactions with the participation of CCl_4 and CCl_3Br:

$$\{Cu^I\} + CBr_4 \longrightarrow \{Cu^{II}Br\} + CBr_3^{\bullet} \qquad (1)$$

$$CBr_3^{\bullet} + RH \longrightarrow CHBr_3 + R^{\bullet} \qquad (2)$$

$$R^{\bullet} + CBr_4 \longrightarrow RBr + CBr_3^{\bullet}, \qquad (3)$$

where $\{Cu^I\}$ and $\{Cu^{II}Br\}$ are bromide complexes of Cu^I and Cu^{II}.

It is likely that the reaction

$$\{Cu^{II}Br\} + R^{\bullet} \longrightarrow \{Cu^I\} + RBr \qquad (4)$$

is responsible for the catalytic character of the overall process. Reaction (4) leads to the target product and, simultaneously, to the regeneration of an active form of the catalyst. Only Cu^I rather than Cu^{II} was found in the reaction mixture after the reaction completed.

The reaction in the presence of homogeneous catalyst **1** corresponds to the equation

$$CBr_4 + R'H \longrightarrow CHBr_3 + R'Br$$

A material balance on bromine for entry 4 in Table 1 is written as follows: 3 mmol of CBr_4 gave 2.4 mmol of bromoform, 2.6 mmol of bromocyclohexane, 0.15 mmol of HBr, and 0.45 mmol of unreacted CBr_4. The discrepancy between the initial amount of bromine (12 mmol of Br atoms) and the value found from the chemical analysis of products (11.75 mmol) does not exceed the measurement error. Thus, a side reaction with the formation of HBr plays an insignificant role in the material balance. In contrast, in the presence of heterogenised catalysts **2** and **3**, comparable amounts of HBr (20–50% of the initial CBr_4) were found; methylene bromide was also detected at high conversions. More than 1 mol of a monobromoalkane per mole of parent CBr_4 can be obtained with the use of the most reactive hydrocarbons (dodecane and alkylbenzenes) and highly active catalysts **2** and **3** (Table 1, entries 5, 12, 14–16). This fact, as well as the formation of CH_2Br_2 and the yields of bromoalkanes higher than that of bromoform by 10–20% in some experiments with catalyst **1**, can be explained by the participation of $CHBr_3$ in the reaction. It is likely that the following reactions occur in the system in the presence of CBr_4 and catalysts **2** and **3**:

$$R^{\bullet} + CHBr_3 \longrightarrow CHBr_2^{\bullet} + RBr \qquad (4a)$$

$$CHBr_2^{\bullet} + RH \longrightarrow CH_2Br_2 + R^{\bullet}. \qquad (3a)$$

The role of these reactions increases with the conversion of CBr_4 and hence with the $CHBr_3$:CBr_4 ratio. As a result, the yield of bromoform on **2** and **3** at high conversions was lower than that of a monobromoalkane by 30–50%. We found in special experiments with a mixture of CBr_4 and $CHBr_3$ in place of initial CBr_4 that bromoform was really consumed in the presence of CBr_4. Thus, a mixture of dodecane, $CHBr_3$ and CBr_4 in the molar ratio 10:3.5:1 (150 °C, the reaction time 2.5 h) gave a mixture of secondary monobromododecanes in 59% yield referred to parent CBr_4. In this case, the RH:$CHBr_3$:CBr_4 ratio after the reaction was 9.4:3.2:0.7 rather than 9.4:3.5:0.4 expected for the process with no participation of bromoform. In the absence of CBr_4, which takes part in chain initiation, bromoform reacts with alkanes and arylalkanes very slowly on all of the catalysts.

Thus, the results suggest that the reaction with CBr_4 is an effective and convenient method for alkane and arylalkane functionalisation. Its advantages are high conversion of parent CBr_4, near 100% selectivity for secondary bromoalkanes and bromocycloalkanes, and the absence of hazardous and toxic reagents.

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