KO\textsuperscript{t}Bu as a Single Electron Donor? Revisiting the Halogenation of Alkanes with CBr\textsubscript{4} and CCl\textsubscript{4}

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Abstract: The search for reactions where KO\textsuperscript{t}Bu and other tert-alkoxides might behave as single electron donors led us to explore their reactions with tetrahalomethanes, CX\textsubscript{4}, in the presence of adamantane. We recently reported the halogenation of adamantane under these conditions. These reactions appeared to mirror the analogous known reaction of NaOH with CBr\textsubscript{4} under phase-transfer conditions, where initiation features single electron transfer from a hydroxide ion to CBr\textsubscript{4}. We now report evidence from experimental and computational studies that KO\textsuperscript{t}Bu and other alkoxide reagents do not go through an analogous electron transfer. Rather, the alkoxides form hypohalites upon reacting with CBr\textsubscript{4} or CCl\textsubscript{4}, and homolytic decomposition of appropriate hypohalites initiates the halogenation of adamantane.

Keywords: halogenation; potassium tert-butoxide; alkanes; dihalocarbenes; hypohalite

1. Introduction

Recent reports have described transition-metal-free reactions, such as the coupling of haloarenes with arenes [1–4], that are promoted by a combination of KO\textsuperscript{t}Bu and an organic additive. The reactions proceed by a radical mechanism, with a single electron transfer (SET) step initiating the formation of the radicals. It has previously been reported that KO\textsuperscript{t}Bu is capable of reductively activating a range of substrates via single electron transfer [5,6], and this led some authors to propose that tert-butoxide anion is responsible for the initiation of these coupling reactions, either alone or in complexation with an additive, such as 1,10-phenanthroline, in the ground state [2,3,7–11]. However, recent publications have shown that the KO\textsuperscript{t}Bu base reacts with the organic additive to form an electron donor in situ. SET from this electron donor then initiates the radical chain mechanism, not SET from tert-butoxide anion [12–14]. The investigations begged the question: “under what circumstances would KO\textsuperscript{t}Bu behave as a single electron donor?” To answer that question, we were drawn to the research of Schreiner and Fokin et al., who reduced CBr\textsubscript{4} using aqueous NaOH and a phase-transfer catalyst in a two-phase system that led to the bromination of adamantane [15,16]. They demonstrated that reaction of hydroxide anion with CBr\textsubscript{4} led to the tribromomethyl radical 4, and concluded that this reflected direct electron transfer from hydroxide to CBr\textsubscript{4} (Scheme 1). This tribromomethyl radical 4 undergoes a chain reaction, where it abstracts a hydrogen atom from adamantane 5 to form the alkyl radical 7 and bromoform 6. The adamantyl radical 7 abstracts a bromine atom from CBr\textsubscript{4}, forming adamantyl bromide 8 and regenerating the tribromomethyl radical 4 [15]. The reactions of the tribromomethyl radical show diagnostic high selectivities for abstracting tertiary CH hydrogen atoms (to ultimately form 1-bromoadamantane) over secondary (CH\textsubscript{2}) counterparts (which would ultimately form 2-bromoadamantane).
Recently, we showed that KOt-Bu reacts with CBr₄ and adamantane (40 °C, 96 h) to afford bromoadamantane—in a reaction that appears to mirror the work of Schreiner and Fokin et al.—with NaOH, although phase-transfer conditions were not used [17]. The oxidation potential of KOt-Bu in DMF (0.10 V vs. SCE) [8] is not too different from the reduction potential of CBr₄ in DMF (−0.31 V vs. SCE) [18]. It was therefore proposed that KOt-Bu might reduce CBr₄ through an electron transfer mechanism, but the door was left open to further investigation. The aim of this paper is to explore the chemistry of KOt-Bu and related tertiary alkoxides in this context.

![Scheme 1](image1)

**Scheme 1.** The Schreiner–Fokin mechanism for the bromination of alkanes from reaction of hydroxide with carbon tetrabromide [15].

### 2. Results

The analogy of the proposed reaction of KOt-Bu with CBr₄ or CCl₄ (Scheme 2) to the Schreiner–Fokin reaction of NaOH with this halide is striking (Scheme 1). Upon donation of an electron, the alkoxide anion 9 would form the corresponding alkoxyl radical 10, which can undergo either hydrogen atom transfer (HAT) to form 11, or β-scission to form the derived ketone 12 (for appropriate R). Either the alkoxyl radical 10 or the methyl radical can abstract a hydrogen atom from adamantane; the adamantyl radical would then propagate the reaction in Scheme 1. In order to detect the product from the β-scission of the alkoxyl radical 10, and bearing in mind the volatility of acetone from β-scission of tert-butoxyl radicals, we synthesized potassium 2-phenylpropan-2-olate 14 and used it as a base to explore a range of reaction conditions (Table 1).

![Scheme 2](image2)

**Scheme 2.** The proposed mechanism for single electron transfer (SET) from tert-alkoxides to CBr₄.

Surprisingly, and in contrast to the case for KOt-Bu, exposure of 14 to CBr₄ in dichloromethane solvent at 40 °C led to no bromination of adamantane (Table 1, entry 1). The products (2,2-dibromo-
1-methylcyclopropyl)benzene 16, methylstyrene 17 and (2,2-dichloro-1-methylcyclo-propyl)benzene 19 were observed, in addition to 2-phenylpropanol 15 and unreacted adamantane 18 (Table 1, entry 1). To avoid the complexity of having compounds bearing different halogens in the reaction mixture, the reaction was repeated in dichloromethane using CCl₄ as the reagent, instead of CBr₄ (Table 1, entry 2). Although we had no evidence of light-sensitivity, we conducted this and all future experiments in foil-covered flasks [19]. The reaction yielded (2,2-dichloro-1-methylcyclopropyl)-benzene 19 as the major product. Note that a blank reaction in dichloromethane (absence of CX₄) resulted in the formation of product, bis((2-phenylpropan-2-yl)oxy)methane (20, 52%) (Table 1, entry 3) [20].

**Table 1.** The reaction of the potassium 2-phenylpropan-2-olate 14 in dichloromethane at 40 °C.

| Entry | Substrate 18 (mmol)/Additive (mmol) | 16 (%) | 17 (%) | 18 (%) | 19 (%) | 20 (%) |
|-------|-----------------------------------|--------|--------|--------|--------|--------|
|       | Yields Based on 0.5 mmol | Yields Based on [14] 2 mmol |        |        |        |        |
| 1     | 18 (0.5)/CBr₄ (0.5) | 31     | 10     | 82     | 14     | 82     |
| 2     | 18 (0.5)/CCl₄ (0.5) | -      | 3      | 76     | 50     | 67     |
| 3     | 18 (0.5)/-          | 2      | 90     | -      | -      | 55     |

All yields are calculated using 1,3,5-trimethoxybenzene as the standard internal (10 mol %) in ¹H-NMR unless stated in the experimental information. As a precaution, reactions were conducted in foil-covered flasks. The yields of 16–19 were calculated using adamantane 18 as the limiting reagent (0.5 mmol). However, the yields of 15 and 20 were calculated based on the alkoxide 14 used (2 mmol).

We propose that both (2,2-dibromo-1-methylcyclopropyl)-benzene 16 and (2,2-dichloro-1-methylcyclopropyl)benzene 19 are formed from methylstyrene 17. The formation of methylstyrene is therefore greatly encouraged in the presence of CBr₄, consistent with the conversion of the alkoxide to a leaving group (i.e., a hypobromite) (Scheme 3A). It is known that hypobromites are formed from reaction of KO'Bu with halogens, X₂ [21] (and that hypohalites are precursors to alkene halogenation by radical mechanisms [21,22]), so this reaction shows that they also form from reaction with tetrahalomethanes. The potassium 2-phenylpropan-2-olate 14 nucleophilically attacks a molecule of CBr₄ to form the hypobromite 21 and eliminate a CBr₃ anion 22. The hypobromite 21 then undergoes an elimination to form methylstyrene 17. The formation of (2,2-dibromo-1-methylcyclopropyl)benzene 16 occurs by decomposition of the tribromomethyl anion to CBr₂ 23, which attacks methylstyrene 17 (Scheme 3A).

Analogous to the formation of (2,2-dibromo-1-methylcyclopropyl)benzene 16, the isolation of (2,2-dichloro-1-methylcyclo-propyl)benzene 19 means that carbenes (in this case, CCl₂ 27) are formed under the reaction conditions (Scheme 3B). The carbene 27 forms when the potassium 2-phenylpropan-2-olate 14 deprotonates the solvent, CH₂Cl₂, and the resulting CHCl₂ anion 24 undergoes halogen exchange with CBr₄ to form bromodichloromethane 25. A second deprotonation would lead to the bromodichloromethyl anion 26, and decomposition of this anion would lead to the dichlorocarbene 27.

In the blank reaction (without CBr₄) (Table 1, entry 3), bis((2-phenylpropan-2-yl)oxy)methane 20 is formed by the nucleophilic displacement of chloride from dichloromethane by two molecules of potassium 2-phenylpropan-2-olate 14 (Scheme 4) [23,24]. The fact that bis((2-phenylpropan-2-yl)oxy)methane 20 is only observed in the absence of CBr₄ suggests that the reaction of potassium 2-phenylpropan-2-olate 14 with dichloromethane is slower than the reaction with CBr₄.
was used. Interception could occur if methylstyrene (1 equiv., Scheme 5).

Computationally, the competition between methylstyrene and adamantane as a source of H atoms suggests that it can shut down the radical mechanism, perhaps by acting as a preferential source of hydrogen atoms, relative to adamantane (the ratio of adamantane \( \Delta G^\circ \)) was determined to be 39:3.3:1 \([17]\), this suggests that either the two alkoxide bases do not react with CBr\(_4\) through analogous mechanisms, or that the halogenation reaction was intercepted and inhibited when \( t\)-Bu was used as the alkoxide.

The addition of methylstyrene \( 17 \)—formed in the reaction from potassium 2-phenylpropan-2-olate \( 14 \)—shuts down the radical chain pathway. To probe this possibility, the reaction of KO\(^t\)-Bu with CBr\(_4\) and adamantane \( 18 \) was repeated in the presence of methylstyrene \( 17 \) (1 equiv., Scheme 5).

The addition of methylstyrene \( 17 \) completely inhibited the bromination of adamantane, which suggests that it can shut down the radical mechanism, perhaps by acting as a preferential source of hydrogen atoms, relative to adamantane \( 18 \), for the radical intermediates in the reaction. Computationally, the competition between methylstyrene and adamantane as a source of H atoms is shown by the scheme below:

**Scheme 3.** (A) The proposed mechanism for the formation of methylstyrene \( 17 \) and (2,2-dibromo-1-methylcyclopropyl)-benzene \( 16 \) and (B) the CCl\(_2\) carbene \( 27 \), that is used to form (2,2-dichloro-1-methylcyclopropyl)benzene \( 19 \) (not shown).

**Scheme 4.** Formation of bis((2-phenylpropan-2-yl)oxy)methane \( 20 \).
was modeled using CBr₃ radicals, which showed that hydrogen atom abstraction by the CBr₃ radical from methylstyrene 17 (ΔG°⁺ = 10.7 kcal/mol and ΔGₐₙ = −7.7 kcal/mol) is thermodynamically and kinetically more favorable than from adamantane 18 (ΔG°⁺ = 13.9 kcal/mol and ΔGₐₙ = 1.1 kcal/mol) (see Supplementary Materials).

![Scheme 5. Using methylstyrene 17 to block the bromination of adamantane.](image)

All yields were calculated using 1,3,5-trimethoxybenzene as the internal standard (10 mol %) in the ¹H-NMR. The yield of 18 was calculated based on recovery of adamantane 18, the yield of 16 and 19 was calculated based on CBr₄. (Note that alkoxide (4 eq.) is capable of forming methylstyrene 17.)

With the knowledge that methylstyrene 17 is capable of preventing bromination of adamantane, why does bromination succeed when KOᵢBu 29 + CBr₄ alone are used? The two hypobromites, tert-buty1 hypobromite and 21, may undergo elimination at different rates; additionally, 2-methylpropene (b.p. −6.9 °C) exists as a gas at the reaction temperature. Such a volatile product would likely be found principally in the headspace above the reaction, rather than in solution, and therefore halogenation of adamantane 18 could occur.

As mentioned earlier, Wirth et al. [19] used tert-buty1 hypobromite to achieve the bromination of alkanes (while Walling [20] used tert-buty1 hypochlorite to achieve chlorination) and proposed that the mechanism was initiated via homolysis of the O–Br bond of tert-buty1 hypobromite. Either the bromine radical or the tert-butoxyl radical could abstract the H atom from adamantane. Propagation could then occur when the adamantyl radical abstracts a Br atom from CBr₄ [13] or from tert-buty1 hypobromite [23].

To gain further information on mechanism, an alternative alkoxide, potassium triphenylmethanolate 30, was prepared and subjected to the reaction conditions with CBr₄ and adamantane 18 (Table 2).

### Table 2. The reaction of potassium triphenylmethanolate 30 in dichloromethane at 40 °C.

| Entry | Additive (mmol) | 18 (%) | 31 (%) | 33 (%) | 34 (%) | 32 (%) |
|-------|----------------|--------|--------|--------|--------|--------|
| 1     | 18 (0.5) CBr₄ (0.5) | 49     | 7      | 5      | 12     | 88     |
| 2     | 18 (0.5)        | 87     | 0      | 1      | 0      | 81     |

ₐ All yields were calculated using 1,3,5-trimethoxybenzene as the internal standard (10 mol %) in the ¹H-NMR unless stated in the experimental information. The yields of 18, 31, 33, 34 were calculated using adamantane 18 as the limiting reagent. However, the yield of 32 was calculated based on the alkoxide 30.

Reaction of potassium triphenylmethanolate 30 with adamantane in the presence of CBr₄ afforded products 1-bromoadamantane 31 (7%) and triphenylmethanol 32 (88%), as well as two additional products, benzophenone 33 (5%) and 4-benzhydrylphenol 34 (12%) (Table 2, entry 1). When CBr₄ was not present in the reaction mixture, triphenylmethanol 32 (81%) was isolated following workup, together with a trace (1%) of benzophenone 33 (Table 2, entry 2). Further analysis of the starting
material showed trace amounts of 33 present in the commercially supplied triphenylmethanol 32. Background formation of benzophenone 33, in trace amounts from heterolytic fragmentation of similar tertiary alkoxides with expulsion of a phenyl anion, is also preceded [25,26].

The important difference between the reaction in the presence of CBr₄ and in its absence (Table 2, entry 1 and entry 2, respectively) is the formation of 4-benzhydrylphenol 34, which can arise through the hypobromite 35 (Scheme 6). Potassium triphenylmethanolate 30 reacts with CBr₄ to generate the hypobromite 35. This hypobromite can react by three pathways (1) the OBr anion leaves to form the stabilized cation 36; (2) the O–Br bond fragments ionically with simultaneous migration of a phenyl moiety to form cation 38; or (3) the O–Br bond undergoes homolysis to form alkoxyl radical 40 and a bromine radical, for which there is literature precedent [23]. If pathway (1) is followed, the carbocation 36 is attacked by another molecule of potassium triphenylmethanolate 30 and, due to steric effects, the alkoxide attacks at the para position of one of the benzene rings. In doing so, the species 37 is formed, which, following tautomerism and hydrolytic workup, leads to 34. Alternatively, 36 affords triphenylmethanol 32 on workup. Pathways (2) and (3) ultimately lead to the formation of benzophenone 33; pathway (2) involves the formation of intermediate 38, which reacts with water on workup to form 39 and, ultimately, benzophenone 33. Pathway (3) involves formation of the alkoxyl radical 40, which could form via O–Br homolysis of 35 or, alternatively, by SET from potassium triphenylmethanolate 30 to a molecule of CBr₄. This alkoxyl radical might undergo β-scission to form benzophenone 33. However, alternatively, the radical 40 could undergo a neopentylic rearrangement to form radical 41 (Scheme 6) [27]. The product 43 forms when the radical 42 abstracts a bromine atom from either CBr₄ or the hypobromite 35, and 43, in turn, upon workup, undergoes a hydrolytic conversion to benzophenone 33. Previous fragmentations of related alkoxyl radicals have been studied [28–32]. The enhanced formation of benzophenone 33 in the presence of CBr₄ could occur through either β-scission of the alkoxyl radical 40 (Scheme 6B), or the ionic mechanism (Scheme 6A).

![Scheme 6](image_url)

Scheme 6. Proposed pathway for the formation of 32, 33 and 34 from 30: (A) through ionic intermediates and (B) through radical intermediates.

The study above provides evidence for significant formation of hypohalites from alkoxides 14 and 30. However, it might be possible for the O⁻Bu anion in KO⁻Bu to behave differently. The absence
of electron-withdrawing aryl groups would render it more electron-rich, and, therefore, it might be a better candidate than the other alkoxides to undergo electron transfer.

To probe the ability of alkoxides to donate a single electron, computational modeling was implemented to calculate the energy profile for the SET from both KOtBu and potassium 2-phenylpropan-2-olate 14 to CBr4 in dichloromethane (Figure 1) [33]. Our previous calculations had been based on the classical Nelsen four-point method [34], but, since that time, we published a more accurate complexation method [33] for predicting the activation free energy and the relative free energy of reactions. (The calculations were conducted using the M06-2X functional [35,36] with the 6-311++G(d,p) basis set [37–41] on all atoms, except for the bromine. Bromine was modeled with the MWB28 relativistic pseudo-potential and associated basis set [42]. All calculations were carried out using the C-PCM implicit solvent model [43,44] with the dielectric constant for dichloromethane (ε = 8.93) or carbon tetrachloride (ε = 2.228) as appropriate. All calculations were performed in Gaussian09 [45]).

![Figure 1](image_url)

**Figure 1.** Computational modelling of SET from alkoxides, KOtBu and potassium 2-phenylpropan-2-olate 14 to CBr4 in dichloromethane.

The energy barriers for SET from either KOtBu or potassium 2-phenylpropan-2-olate 14, to a molecule of CBr4 were calculated to be ΔG‡ = +35.4 kcal/mol and +36.1 kcal/mol, respectively (while the corresponding ΔGrxn values were +13.9 and +18.9 kcal/mol) (Figure 1). When the energy barrier was calculated for the reactions with CCl4, a similar energy profile was obtained for the SET from either of the two alkoxides to a molecule of CCl4 (see Supplementary Materials). The energy barriers calculated were ΔG‡ = 42.5 kcal/mol and 44.5 kcal/mol for SET to CCl4 from KOtBu and potassium 2-phenylpropan-2-olate 14, respectively. These barriers for reactions of both CBr4 and CCl4 are not accessible for a reaction performed at 40 °C, even as an initiation step. These computationally derived
energy profiles for the SET step indicate that the initiation for this halogenation of adamantane 18 is not via SET from the alkoxide; the likely alternative radical pathway arises through homolysis of the hypohalite intermediate [19]. (Importantly, our computation predicts a barrierless, but endergonic, profile for homolysis of the O–Br bond in tertBuO–Br with ΔG_{rxn} = +27.6 kcal/mol [34]. This is a highly endergonic reaction, but as it is simply an initiation step, few tertBuO–Br molecules are required to undergo homolysis).

3. Experimental Section

3.1. Computational Methods

The calculations were run using the M06-2X functional [35,36] with the 6-311++G(d,p) basis set [37–41] on all atoms except bromine. Bromine was modeled with the MWB28 relativistic pseudo-potential and associated basis set [42]. All calculations were carried out using the C-PCM implicit solvent model [43,44] as implemented in Gaussian09 [45].

3.2. General Experimental Information

All reagents were bought from commercial suppliers and used without further purification unless stated otherwise. All the reactions were carried out under argon atmosphere. Diethyl ether, tetrahydrofuran, dichloromethane and hexane were dried with a Pure-Solv 400 solvent purification system, marketed by Innovative Technology Inc. (Herndon, VA, USA). Organic extracts were, in general, dried over anhydrous sodium sulfate (Na₂SO₄). A Büchi rotary evaporator was used to concentrate the reaction mixtures. Thin layer chromatography (TLC) was performed using aluminium-backed sheets of silica gel and visualized under a UV lamp (254 nm). The plates were developed using phosphomolybdic acid or KMnO₄ solution. Column chromatography was performed to purify compounds by using silica gel 60 (200–400 mesh).

The electron transfer reactions were carried out within a glove box (Innovative Technology Inc.) under nitrogen atmosphere, and performed in an oven-dried or flame-dried apparatus using anhydrous solvents, which were degassed under reduced pressure, then purged with argon and dried over activated molecular sieves (3 Å), prior to being sealed and transferred to the glovebox. All solvent or samples placed into the glovebox were transferred through the port, which was evacuated and purged with nitrogen 10 times before entry. When the reaction mixtures were prepared, the reaction vessel was removed from the glove box and the rest of the reaction was performed in a fume hood.

Proton (¹H) NMR spectra were recorded at 400.13, 400.03 and 500.16 MHz on Bruker AV3, AV400 and AV500 spectrometers, respectively. Carbon (¹³C) NMR spectra were recorded using broadband decoupled mode at 100.61, 100.59 and 125.75 MHz on Bruker AV3, AV400 and AV500 spectrometers, respectively. Spectra were recorded in either deuterated chloroform (CDCl₃) or deuterated dimethyl sulfoxide (d⁶-DMSO), depending on the solubility of the compounds. The chemical shifts are reported in parts per million (ppm), calibrated on the residual non-deuterated solvent signal, and the coupling constants, J, are reported in Hertz (Hz). The peak multiplicities are denoted using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; sx, sextet; m, multiplet; br s, broad singlet; dd, doublet of doublets; dt, doublet of triplets; td, triplet of doublets.

Infrared spectra were recorded on an ATR-IR spectrometer. Melting points were determined on a Gallenkamp melting point apparatus. The mass spectra were recorded by either gas-phase chromatography (GCMS) or liquid-phase chromatography (LCMS), using various ionization techniques, as stated for each compound: atmospheric pressure chemical ionization (APCI), electron ionization (EI), electrospray ionization (ESI). GCMS data were recorded using an Agilent Technologies 7890A GC system coupled to a 5975C inert XL EI/CI MSD detector. Separation was performed using the DB5MS-UI column (30 m × 0.25 mm × 0.25 µm) at a temperature of 320 °C, using helium as the carrier gas. LCMS data were recorded using an Agilent 6130 Dual source mass spectrometer with Agilent 1200, Agilent Poroshell 120ECC 4.6 mm × 75 mm × 2.7 um column.
High-resolution mass spectrometry (HRMS) was performed at the University of Wales, Swansea, in the EPSRC National Mass Spectrometry Centre. Accurate mass was obtained using atmospheric pressure chemical ionization (APCI), chemical ionization (CI), electron ionization (EI), electrospray ionization (ESI) or nanospray ionization (NSI) with a LTQ Orbitrap XL mass spectrometer.

3.3. Synthesis of Alkoxide, Potassium 2-Phenylpropan-2-Olate 14

Potassium hydride (586 mg, 15 mmol, 1.0 eq.) was added to a flame-dried three-necked flask, equipped with a vacuum tap. Under an argon atmosphere, at −78 °C, a solution of 2-phenylpropanol 15 (2.04 g, 15 mmol) in anhydrous diethyl ether (20 mL), as added and the reaction mixture, was stirred at −78 °C for 1 h, then at RT overnight. The solvent was removed under vacuum and the crude material was dried for 1 h to obtain potassium 2-phenylpropan-2-olate 14 (2.46 g, 14.1 mmol, 93%) as an off-white solid m.p. 128–132 °C; (Found: (GCMS-EI) C$_9$H$_{11}$O (M-K) 135.08); $\nu$$_{max}$ (film)/cm$^{-1}$ 3503, 2972, 1663, 1444, 1433, 1236, 1161, 1067, 1029, 955, 881, 861, 764; $^1$H-NMR (400 MHz, d$_6$-DMSO) $\delta$ 1.41 (6 H, s, 2 × CH$_3$), 7.15–7.19 (1 H, m, ArH), 7.26–7.30 (2 H, m, ArH), 7.45–7.47 (2 H, m, ArH); $^{13}$C-NMR (100 MHz, d$_6$-DMSO) $\delta$ 31.9 (2 × CH$_3$), 70.5 (C), 124.4 (2 × CH), 125.8 (CH), 127.7 (2 × CH), 150.5 (C). The product was put under an argon atmosphere and transported into the glovebox immediately.

3.4. Blank Reaction (No KOtBu) of CBr$_4$ with Adamantane 18

Adamantane 18 (68 mg, 0.5 mmol), CBr$_4$ (166 mg, 0.5 mmol, 1.0 eq.) and dichloromethane (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture was stirred at 40 °C for 90 h in the dark. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with diethyl ether ($4 \times 10$ mL). The organic phases were combined, dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 1.76–1.75 (12 H, m, C$_7$H$_{14}$), 1.88 (4 H, br s, CH$_2$); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 28.5 (6 × CH$_2$), 37.9 (4 × CH). (The yield of adamantane 18 [46] (93%) was determined by adding 1,3,5-trimethoxybenzene to the crude mixture as an internal standard for $^1$H-NMR). These signals are consistent with the literature values and reference samples.

3.5. Reactions of Potassium 2-Phenylpropan-2-Olate 14 with Adamantane 18 and CBr$_4$/CCl$_4$

3.5.1. Table 1, Entry 1

Potassium 2-phenylpropan-2-olate 14 (349 mg, 2 mmol, 4.0 eq.), adamantane 18 (68 mg, 0.5 mmol), CBr$_4$ (166 mg, 0.5 mmol, 1.0 eq.) and dichloromethane (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture was stirred at 40 °C for 90 h. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with diethyl ether ($4 \times 10$ mL). The organic phases were combined, dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The yield of 2-phenylpropanol 15 (66%), (2,2-dibromo-1-methylcyclopropyl)benzene 16 (33%), methylstyrene 17 (18%), adamantane 18 (91%) and (2,2-dichloro-1-methylcyclopropyl)benzene 19 (17%) were determined by adding 1,3,5-trimethoxybenzene to the crude mixture as an internal standard for $^1$H-NMR. The products were identified by the following characteristic signals; $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 1.60 (6 H, s) for 2-phenylpropanol 15; $\delta$ 1.72 (3 H, s), 1.78 (1 H, d, J = 7.6 Hz), 2.17 (1 H, d, J = 7.6 Hz) for (2,2-dibromo-1-methylcyclopropyl)benzene 16; $\delta$ 2.16 (3 H, s), 5.09 (1 H, s), 5.37 (1 H, s) for methylstyrene 17; $\delta$ 1.75–1.77 (12 H, m), 1.88 (4 H, br s) for adamantane 18; $\delta$ 1.68 (3 H, s), 1.96 (1 H, d, J = 7.2 Hz) for (2,2-dichloro-1-methylcyclopropyl)benzene 19; $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 31.9, 72.7, 124.5, 126.8, 128.4 for 2-phenylpropanol 15; $\delta$ 27.9, 33.9, 128.5, 128.6 for (2,2-dibromo-1-methylcyclopropyl)benzene 16; $\delta$ 22.0, 112.5 for methylstyrene 17; $\delta$ 28.5, 37.9 for adamantane 18; $\delta$ 25.7, 36.6 for (2,2-dichloro-1-methylcyclopropyl)benzene 19. These signals are consistent with the literature values and reference samples. The compounds 16 and 19 were inseparable, so pure samples of 16 and 19 were prepared for comparison—see below.
3.5.2. Preparation of 16

KO' Bu 29 (224 mg, 2 mmol, 4.0 eq.), HCBR3 (0.04 mL, 0.5 mmol, 1.0 eq.) and methylstyrene 17 (0.07 mL, 0.5 mmol) were added to an oven-dried pressure tube. Dichloromethane (3.13 mL) was added and the reaction mixture was stirred at 40 °C for 90 h. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with diethyl ether (4 × 10 mL). The organic phases were combined, dried over Na2SO4, filtered and concentrated in vacuo. The crude material was purified by column chromatography (100% hexane) to give (2,2-dibromo-1-methylocyclopropyl)benzene 16 [18] (82.4 mg, 57%) as a colorless oil [Found: (GCMS) C16H10Br2 + (M + H)+ 288.7]; νmax (film/cm−1) 1496, 1445, 1426, 1060, 1019, 763, 691; ¹H-NMR (400 MHz, CDCl3) δ 1.72 (3 H, s, CH3), 1.78 (1 H, d, J = 7.6 Hz, CH2), 2.17 (1 H, d, J = 7.6 Hz, CH2), 7.29–7.38 (5 H, m, ArH); ¹³C¹H¹-NMR (100 MHz, CDCl3) δ 27.9 (CH3), 33.8 (CH2), 35.9 (C), 36.9 (C), 127.4 (CH), 128.5 (2 × CH), 128.6 (2 × CH), 142.5 (C); m/z (Cl) 292.6 [(M + H)+, 81Br²Br, 61%], 290.6 [(M + H)+, 79Br²Br, 100], 288.7 [(M + H)+, 79Br²Br, 70%].

3.5.3. Preparation of 19

KO' Bu 29 (224 mg, 2 mmol, 4.0 eq.), HCCl3 (0.04 mL, 0.5 mmol, 1.0 eq.) and methylstyrene 17 (0.07 mL, 0.5 mmol) were added to an oven-dried pressure tube. Dichloromethane (3.13 mL) was added and the reaction mixture was stirred at 40 °C for 90 h. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with diethyl ether (4 × 10 mL). The organic phases were combined, dried over Na2SO4, filtered and concentrated in vacuo. The crude material was purified by column chromatography (100% hexane) to give (2,2-dichloro-1-methylocyclopropyl)benzene 19 [18] (63.7 mg, 63%) as a colorless oil [Found: (HRMS-EI) 200.0157. C20H12Cl2 (M)++ requires 200.0160]; νmax (film/cm−1) 1497, 1446, 1425, 1075, 1033, 1026, 936, 868, 772, 754, 697, 595; ¹H-NMR (400 MHz, CDCl3) δ 1.60 (1 H, d, J = 7.2 Hz, CH2), 1.68 (3 H, s, CH3), 1.96 (1 H, d, J = 7.2 Hz, CH2), 7.27–7.38 (5 H, m, ArH); ¹³C¹H¹-NMR (100 MHz, CDCl3) δ 25.7 (CH3), 32.0 (CH2), 36.6 (C), 66.0 (C), 127.4 (CH), 128.6 (2 × CH), 128.7 (2 × CH), 141.4 (C); m/z (Cl) 203.9 (M)++, δ 37Cl 12%, 201.9 (M)++, 35Cl 7%, 199.9 (M)++, 35Cl 5%, 100].

3.5.4. Table 1, Entry 2

Potassium 2-phenylpropan-2-olate 14 (349 mg, 2 mmol, 4.0 eq.), adamantane 18 (68 mg, 0.5 mmol), CCl4 (0.05 mL, 0.5 mmol, 1.0 eq.) and dichloromethane (3.13 mL) were added to an oven-dried pressure tube of 1H-NMR. The products were identified by the following characteristic signals; ¹H-NMR (100 MHz, CDCl3) δ 1.60 (6 H, s) for 2-phenylpropanol 15; δ 2.17 (3 H, s), 5.10 (1 H, s), 5.38 (1 H, s) for methylstyrene 17; δ 1.76–1.78 (12 H, m), 1.89 (4 H, br s) for adamantane 18; δ 1.68 (3 H, s), 1.97 (1 H, d, J = 7.2 Hz) for (2,2-dichloro-1-methylocyclopropyl)benzene 19; δ 4.51 (2 H, s), 7.20–7.24 (2 H, m) for bis(2-phenylpropan-2-yl)oxy)methane 20; ¹³C-NMR (100 MHz, CDCl3) δ 31.9, 72.7, 124.5, 126.8, 128.4 for 2-phenylpropanol 15; δ 22.0, 112.6 for methylstyrene 17; δ 28.5, 37.9 for adamantane 18; δ 25.6, 36.6 for (2,2-dichloro-1-methylocyclopropyl)benzene 19. These signals are consistent with the literature values and reference samples.

3.5.5. Table 1, Entry 3

Potassium 2-phenylpropan-2-olate 14 (349 mg, 2 mmol, 4.0 eq.), adamantane 18 (68 mg, 0.5 mmol) and dichloromethane (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture
was stirred at 40 °C for 90 h in the dark. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with diethyl ether (4 × 10 mL). The organic phases were combined, dried over Na₂SO₄, filtered and concentrated in vacuo. The yield of 2-phenylpropanol 15 (39%), methylstyrene 17 (1%), adamantane 18 (84%) and bis(2-phenylpropan-2-yl)oxy)methane 20 (52%) were determined by adding 1,3,5-trimethoxybenzene to the crude mixture as an internal standard for ¹H-NMR. The products were identified by the following characteristic signals; ¹H-NMR (400 MHz, CDCl₃) δ 1.60 (6 H, s) for 2-phenylpropanol 15; δ 2.16 (3 H, s), 5.09 (1 H, s), 5.37 (1 H, s) for methylstyrene 17; δ 1.75–1.77 (12 H, m), 1.88 (4 H, br s) for adamantane 18; δ 4.51 (2 H, s), 7.20–7.24 (2 H, m) for bis(2-phenylpropan-2-yl)oxy)methane 20; ¹³C-NMR (100 MHz, CDCl₃) δ 31.9, 72.7, 124.5, 149.2 for 2-phenyl-2-propanol 15; δ 28.5, 37.9 for adamantane 18; δ 29.5, 77.7, 86.8, 146.9 for bis(2-phenylpropan-2-yl)oxy)methane 20. These signals are consistent with the literature values and reference samples. This crude material was purified by column chromatography (0–5% ethyl acetate in hexane) to give bis((2-phenylpropan-2-yl)oxy)methane 20 (44.7 mg, 26%) as a colorless oil (Found: (HRMS-ESI) 302.2118. C₂₀H₂₂O₄ requires 302.2115); νmax (film)/cm⁻¹ 2978, 2934, 1493, 1447, 1381, 1365, 1258, 1153, 1072, 1018, 918, 762; ¹H-NMR (400 MHz, CDCl₃) δ 1.59 (12 H, s, 4 × CH₃), 4.50 (2 H, s, CH₂), 7.20–7.23 (2 H, m, ArH), 7.27–7.31 (4 H, m, ArH), 7.38–7.40 (4 H, m, ArH). These signals are consistent with the literature values and reference samples [49,50].

3.6. Reaction of KO⁴Bu in Dichloromethane

KO⁴Bu 29 (224 mg, 2 mmol, 4.0 eq.), CBr₄ (166 mg, 0.5 mmol, 1.0 eq.), adamantane 18 (68 mg, 0.5 mmol) and dichloromethane (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture was stirred at 40 °C for 90 h in the dark. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with diethyl ether (4 × 10 mL). The organic phases were combined, dried over Na₂SO₄, filtered and concentrated in vacuo. The ratio of adamantane 18:1-bromoadamantane 31:2-bromoadamantane 51 was determined to be 39:3.3:1 from the ¹H-NMR spectrum of the crude mixture. The products were identified by the following characteristic signals; ¹H-NMR (400 MHz, CDCl₃) δ 1.74–1.76 (12 H, m, CH₂ × 2), 1.84 (8 H, br s, CH × 4) for adamantane 18; δ 1.73 (6 H, m, CH₂ × 3), 2.10 (3 H, br s, CH × 3), 2.36 (6 H, m, CH₂ × 3) for 1-bromoadamantane 31 [47]; δ 1.96–2.00 (2 H, m, CH₂), 2.15 (2 H, br s, CH × 2), 2.33 (2 H, br s, CH × 2), 4.68 (1 H, br s, CH) for 2-bromoadamantane 51 [48]; ¹³C-NMR (100 MHz, CDCl₃) δ 28.5, 37.9 adamantane 18; δ 32.8, 35.7, 49.5 for 1-bromoadamantane 31; 36.6, 39.1 for 2-bromoadamantane 51. These signals are consistent with the literature values and reference samples.

3.7. Reactions of Adamantane 18 with CBr₄, Methylstyrene 17 and KO⁴Bu 29 (Scheme 5)

KO⁴Bu 29 (224 mg, 2 mmol, 4.0 eq.), CBr₄ (166 mg, 0.5 mmol, 1.0 eq.), methylstyrene 17 (0.07 mL, 0.5 mmol, 1.0 eq.), adamantane 18 (68 mg, 0.5 mmol) and dichloromethane (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture was stirred at 40 °C for 90 h in the dark. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with diethyl ether (4 × 10 mL). The organic phases were combined, dried over Na₂SO₄, filtered and concentrated in vacuo. The yield of (2,2-dibromo-1-methylcyclopropyl)benzene 16 (59%), methylstyrene 17 (3%), adamantane 18 (75%) and (2,2-dichloro-1-methylcyclopropyl)benzene 19 (40%) were determined by adding 1,3,5-trimethoxybenzene to the crude mixture as an internal standard for ¹H-NMR. The products were identified by the following characteristic signals; ¹H-NMR (400 MHz, CDCl₃) δ 1.72 (3 H, s), 1.78 (1 H, d, J = 7.6 Hz) for (2,2-dibromo-1-methylcyclopropyl)benzene 16; δ 5.09 (1 H, s), 5.37 (1 H, s) for methylstyrene 17; δ 1.75–1.78 (12 H, m), 1.88 (4 H, br s) for adamantane 18; δ 1.60 (1 H, d, J = 7.2 Hz), 1.69 (3 H, s), 1.97 (1 H, d, J = 7.2 Hz) for (2,2-dichloro-1-methylcyclopropyl)benzene 19; ¹³C-NMR (100 MHz, CDCl₃) δ 27.9, 33.9, 36.9, 142.5 for (2,2-dibromo-1-methylcyclopropyl)benzene 16; δ 28.5, 37.9 for adamantane 18; δ 25.7, 32.0, 36.6, 141.4 for (2,2-dichloro-1-methylcyclopropyl)benzene 19. These signals are consistent with the literature values and reference samples [49,50].
3.8. Synthesis of Alkoxide, Potassium Triphenylmethanolate 30

Potassium hydride (802 mg, 20 mmol, 1.0 eq.) was added to a flame-dried three-necked flask, equipped with a vacuum tap. Under an argon atmosphere, at –78 °C, a solution of triphenylmethanol 32 (5.21 g, 20 mmol) in anhydrous tetrahydrofuran (25 mL) was added and the reaction mixture was stirred at –78 °C for 1 h, then at RT overnight. The solvent was removed on the house vacuum line and the crude material was dried for 1 h to give potassium triphenylmethanolate 30 (5.07 g, 17 mmol, 85%) as a off-white solid, m.p. 238 °C (dec.). (Found: (GCMS-EI) C_{19}H_{15}O (M)** 260.1 (under the MS analysis 30 is protonated to the alcohol)); ν_{max} (film)/cm^{-1} 3057, 3022, 1595, 1487, 1443, 1414, 1329, 1155, 1053, 1009, 891, 756; ^1H-NMR (400 MHz, d^6-DMSO) δ 6.93–6.98 (3 H, m, ArH), 7.04–7.08 (6 H, m, ArH), 7.34–7.37 (6 H, m, ArH); ^13C-NMR (100 MHz, d^6-DMSO) δ 84.7 (C), 123.6 (3 × CH), 126.0 (6 × CH), 157.6 (3 × C). The product was put under an argon atmosphere and transported into the glove box immediately.

3.9. Reactions of Potassium Triphenylmethanolate 30 at 40 °C

3.9.1. Table 2, Entry 1

Potassium triphenylmethanolate 30 (597 mg, 2 mmol, 4.0 eq.), CBr₄ (166 mg, 0.5 mmol, 1.0 eq.), adamantane 18 (68 mg, 0.5 mmol) and dichloromethane (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture was stirred at 40 °C for 90 h in the dark. The reaction mixture was cooled to RT and quenched with aqueous hydrochloric acid (1 M, 5 mL) and extracted with diethyl ether (4 × 10 mL). The organic phases were combined, dried over Na₂SO₄, filtered and concentrated in vacuo. The yield of adamantane 18 (49%), 1-bromoadamantane 31 (7%), triphenylmethanol 32 (88%), benzophenone 33 (5%) and 4-benzhydrylphenol 34 (12%) were determined by adding 1,3,5-trimethoxybenzene to the crude mixture as an internal standard for ^1H-NMR. The products were identified by the following characteristic signals; ^1H-NMR (400 MHz, CDCl₃) δ 1.75–1.78 (12 H, m), 1.88 (4 H, br s) for adamantane 18; δ 1.74 (6 H, m), 2.12 (3 H, br s), 2.38 (6 H, m) for 1-bromoadamantane 31 [47]; δ 7.27–7.34 (15 H, m) for triphenylmethanol 32; δ 7.49 (4 H, d, J = 8.0 Hz), 7.60 (2 H, d, J = 8.0 Hz), 7.82 (4 H, d, J = 8.0 Hz) for benzophenone 33 [51]; δ 5.49 (1 H, s), 6.73–6.77 (2 H, m), 6.97–7.00 (2 H, m) for 4-benzhydrylphenol 34 [52]; ^13C-NMR (100 MHz, CDCl₃) δ 28.3, 37.7 for adamantane 18; δ 49.3, 35.5, 32.6 for 1-bromoadamantane 31; δ 82.2, 127.4, 128.0, 147.0 for triphenylmethanol 32; δ 56.1, 115.3, 144.3 for 4-benzhydrylphenol 34. These signals are consistent with the literature values and reference samples. This crude material was purified by column chromatography (0%–10% ethyl acetate in hexane) to give both benzophenon-one 33 [51] (7 mg, 4%) as a yellow oil (Found: (GCMS-EI) C_{19}H_{15}O (M)** 182.0); ν_{max} (film)/cm^{-1} 3057, 1655, 1597, 1445, 1275, 1175, 939, 918, 808, 762; ^1H-NMR (400 MHz, CDCl₃) δ 7.49 (4 H, t, J = 8.0 Hz, ArH), 7.60 (2 H, t, J = 8.0 Hz, ArH), 7.82 (4 H, d, J = 8.0 Hz, ArH); ^13C-NMR (100 MHz, CDCl₃) δ 128.2 (4 × CH), 130.2 (4 × CH), 132.6 (2 × CH), 137.5 (2 × C), 196.7 (C) and 4-benzhydrylphenol 34 [52] (18.9 mg, 7%) as a yellow oil (Found: (GCMS-EI) C_{19}H_{16}O (M)** 260.1); ν_{max} (film)/cm^{-1} 3366, 2361, 2336, 1595, 1508, 1491, 1449, 1238, 1173, 1103, 1030, 816, 800, 750, 735; ^1H-NMR (400 MHz, CDCl₃) δ 4.82 (1 H, br s, OH), 5.49 (1 H, s, CH), 6.73–6.77 (2 H, m, ArH), 6.97–7.00 (2 H, m, ArH), 7.11–7.13 (4 H, m, ArH), 7.19–7.32 (6 H, m, ArH); ^13C-NMR (100 MHz, CDCl₃) δ 56.1 (CH), 115.3 (2 × CH), 126.4 (2 × CH), 128.4 (4 × CH), 129.5 (4 × CH), 130.7 (2 × CH), 136.4 (C), 144.3 (2 × C), 154.1 (C). Triphenylmethanol 32 ^1H-NMR (400 MHz, CDCl₃) δ 2.79 (1 H, s, OH), 7.26–7.34 (15 H, m, ArH), 7.57 (2 H, d, J = 8.4 Hz, ArH); ^13C-NMR (100 MHz, CDCl₃) δ 82.2 (C), 127.4 (CH), 128.1 (6 × CH), 147.0 (9 × C). These signals are consistent with a commercial sample used as a reference.

3.9.2. Table 2, Entry 2

Potassium triphenylmethanolate 30 (597 mg, 2 mmol, 4.0 eq.), adamantane 18 (68 mg, 0.5 mmol) and dichloromethane (3.13 mL) were added to an oven-dried pressure tube and the reaction mixture was stirred at 40 °C for 90 h in the dark. The reaction mixture was cooled to RT and quenched with...
aqueous hydrochloric acid (1 M, 5 mL) and extracted with diethyl ether (4 × 10 mL). The organic phases were combined, dried over Na₂SO₄, filtered and concentrated in vacuo. The yield of adamantane 18 (87%), triphenylmethanol 32 (81%) and benzophenone 33 (1%) were determined by adding 1,3,5-trimethoxybenzene to the crude mixture as an internal standard for ¹H-NMR. The products were identified by the following characteristic signals; ¹H-NMR (400 MHz, CDCl₃) δ 1.75–1.78 (12 H, m), 1.88 (4 H, br s) for adamantane 18; δ 7.27–7.34 (15 H, m) for triphenylmethanol 32, δ 7.49 (4 H, d, J = 8.0 Hz, ArH), 7.60 (2 H, d, J = 8.0 Hz, ArH), 7.82 (4 H, d, J = 8.0 Hz, ArH) for benzophenone 33; ¹³C-NMR (100 MHz, CDCl₃) δ 28.3, 37.7 for adamantane 18; δ 82.2, 127.4, 128.0, 147.0 triphenylmethanol 32 [49]. These signals are consistent with the literature values and reference samples.

4. Conclusions

This study has led to a revision of earlier thoughts on the mechanism for the halogenation of adamantane 18 by using a combination of KO'Bu and CBr₄. It is proposed that the mechanism does not occur through SET, as was previously believed, but proceeds through hypobromite intermediates (Scheme 7). The alkoxide in the reaction mixture, 53, forms a hypobromite in the presence of CBr₄. The hypobromite 54 can undergo reaction along two pathways. The first option is an elimination reaction to form the alkene 57, which reacts with carbenes formed in the reaction to afford final product 58. The second pathway is the O–Br bond homolysis of the hypobromite 54. This forms the alkoxyl radical 55 and a bromine radical. These radical intermediates perform a hydrogen atom abstraction from adamantane 18 to form adamantyl radical 56 (alternatively, the hydrogen atom abstraction may occur at the C-2 position to ultimately give the 2-Br isomer). The radical 56 will abstract a bromine from a hypobromite molecule 54, or from CBr₄, to form 31 and an alkoxyl radical 55, or CBr₃ radical. The radical formed will propagate the chain pathway by hydrogen atom abstraction from adamantane 18, thus creating a radical chain mechanism. Thus, it appears that the search for reactions where ground-state KO'Bu behaves as an electron donor must continue. The outcomes of this project have led us to reexamine the remaining claims [3,4] of this phenomenon.

**Scheme 7.** The modified mechanism for halogenation of adamantane.

**Supplementary Materials:** The following are available online, (i)Additional computational analysis and xyz coordinates relating to all computed structures (ii) Table S1 “The reaction of tert-butyl hypochlorite 46 in dichloromethane or carbon tetrachloride as solvent” (iii) Table S2. tert-Butyl hypobromite 50 in bromination of adamantane 18; (iv) Experimental procedures and spectroscopic data in support of the experiments discussed in those Tables (v) NMR spectra of key products.

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**Sample Availability:** Samples of the compounds are not available.