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$CHBr_3/TiCl_4/Mg$ as an Unusual Nucleophilic CBr_2 Carbenoid: Effective and Chemoselective Dibromomethylenation of Aldehydes and Ketones

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We report that instead of using CBr_4, $CHBr_3$ can serve as a highly nucleophilic dibromomethylene carbenoid in chemoselective carbonyl dibromomethylenation. Successful application of the dibromomethylenation to various carbonyl compounds such as enolizable and sterically hindered ketones by using the $CHBr_3/Mg/TiCl_4$ system highlights the weakly basic nature, extraordinary reactivity, and synthetic versatility of the approach.

Introduction

1,1-Dibromoalkenes can not only serve as important precursors in the preparation of alkynes[1] but are also valuable building blocks in molecular transformations such as (i) the construction of 1,3-diynes[2a] through the palladium-promoted direct coupling of 1,1-dibromoalkenes, (ii) the synthesis of conjugated 1,3-enynes and 1,3-dienes through the Pd-catalyzed cross-coupling of 1-bromoalkenes with alkenyl- or alkynylmetals,[2b–2d] and (iii) the preparation of (*E*)-[3a–3c] and (*Z*)-vinyl bromides.[2c,3d] The vast importance of dibromoalkenes in synthesis has stimulated much interest in the development of new, efficient methodologies for their construction. Whereas the CBr_2 transfer reaction of CBr_4 promoted by phosphorus reagents such as PPh_3,[4a–4c] $P(OiPr)_3$,[4d] or $(OEt)_2P(=O)CHClLi$[4e] involved direct dibromomethylenation of ketones and aldehydes, the basic character and the low nucleophilic nature of these phosphorus-derived dibromomethylene complexes[4] limit the general and practical utility of the Wittig method. On the other hand, the generation of these dibromomethane complexes suffers from one or more experimental drawbacks, such as the requirement for high reaction temperature conditions (≥80 °C) and the use of a large excess of PPh_3 and expensive CBr_4. The direct coupling of hydrazones derived from simple saturated aldehydes and ketones with CBr_4 promoted by CuCl constitutes an alternative two-stage dibromomethylenation process.[5] However, sterically more hindered ketones such as diisopropyl ketone and *tert*-butyl methyl ketone cannot be converted into the corresponding 1,1-dibromoalkenes.[5] To develop a new entry to these compounds using (1,1-dibromomethylene)metal complexes that are nucleophilic and available in bulk at a low price, we were attracted to the development of a $TiCl_4/Mg$-mediated carbonyl dibromomethylenation process. To the best of our knowledge, no metal-induced dibromomethylenation procedure, wherein $CHBr_3$ serves as a CBr_2 partner, has been recorded. Earlier work in our laboratories established that the $TiCl_4/Mg$-promoted CH_2 transfer reaction of CH_2Cl_2 represents an efficient carbonyl methylenation.[6a–6e] On the other hand, the $TiCl_4/Mg$-promoted direct coupling of $CHCl_3$ with ketones and aldehydes has so far been limited to CHCl transfer reactions.[6f] In this paper, we wish to report that, in contrast to cleavage of two C–Cl bonds in CH_2Cl_2 and $CHCl_3$, $CHBr_3$ can be directed to serve as in a CBr_2 transfer reaction by using $TiCl_4/Mg$-promoted cleavage of C–H and C–Br bonds. This $CHBr_3/TiCl_4/Mg$ system can serve as a highly nucleophilic and selective dibromomethylene complex in the dibromomethylenation of a variety of aldehydes and ketones, especially in enolizable or sterically hindered ketones.

Results and Discussion

The dibromomethylenation of 2-methylcyclohexanone (**1a**) with $CHBr_3$ was chosen to test the feasibility of the process (Table 1). Addition of a 1,2-dimethoxyethane (DME) (1.0 mL)/dichloromethane (CH_2Cl_2) solution of **1a** (1 mmol) to a mixture of $TiCl_4$ (1 equiv.), $CHBr_3$ (0.3 mL), and magnesium powder (5 mmol) in CH_2Cl_2 at 0 °C gave a 40% yield of the desired vinyl dibromide **2a**, with starting material remaining (Table 1, Entry 1). Increasing the amount of Mg and $TiCl_4$ led to an increase in the yield of **2a** (Table 1, Entries 2–6). Notably, reducing the amount of $CHBr_3$ or titanium chloride relative to Mg led to not only incomplete dibromomethylenation but also to reductive cleavage of vinyl dibromides. DME appeared to be a good choice as an electron-pair-donor (EPD) additive to effect

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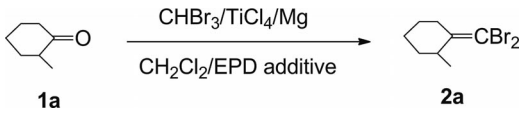
CBr_2 transfer reaction of $CHBr_3$ to the carbonyl group of **1a**. Other EPD additives including tetrahydrofuran (THF) and diethyl ether gave unsatisfactory results (Table 1, Entries 7 and 8). Notably, the reaction could be directly scaled up; thus, 1,1-dibromoalkene **2a** (Table 1, Entry 9) was obtained in 74% yield on a 10 mmol scale using $TiCl_4$ (8 mmol) and Mg (70 mmol).

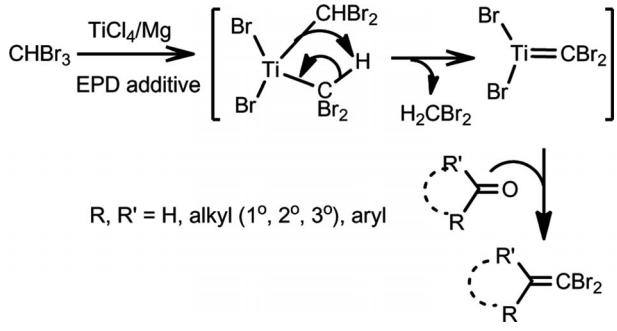
Table 1. Reaction conditions for dibromomethylenation of ketone **1a**.



Entry	EPD additive (mL)	$TiCl_4$/Mg[a] [mmol]	Yield [%][b] 1a	2a
1	DME (1.0)	1:5	ca. 55	40
2	DME (1.0)	1:8	ca. 30	60
3	DME (1.0)	2:8	ca. 20	65
4	DME (1.0)	3:8	ca. 15	72
5	DME (1.2)	3:8	0	80
6	DME (1.5)	3:8	0	75
7	THF (1.0–1.2)	3:8	0	ca. 60
8	Et_2O (1.0–1.2)	3:8	60	ca. 25
9	DME (8.0)	8:70	0	74[c]

[a] Reaction conditions (1 mmol scale): CH_2Cl_2/EPD additive/$CHBr_3$ (0.3 mL), 0 °C to r.t. [b] Isolated yield. [c] Reaction conditions (10 mmol scale): CH_2Cl_2 (30 mL), 0 °C to r.t.

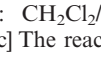
The reaction is best envisioned as involving interception of a presumed EPD–$TiCl_4$ complex by magnesium powder to give an active dimetallic [Ti-$MgCl_2$-$(EPD)_n$][7] complex, followed by dibromomethylene coordinated to both the titanium and magnesium to generate the presumed [Ti-CBr_2-$MgCl_2$-$(EPD)_n$] complex (Scheme 1).[8a]



Scheme 1. Mg-Ti dimetallic complex promoted CBr_2 transfer reaction of $CHBr_3$.

Having established the feasibility of the dibromomethylenation, we studied its generality with respect to the structure of the ketones. 2,6-Dimethylcyclohexanone (**1b**) also gave satisfactory results (85%) with the $CHBr_3$/Mg/$TiCl_4$ complex (Table 2, Entry 1). Variation of ring size was briefly explored. Dibromomethylenation onto cyclopentanone (**1c**) and cycloheptanone (**1d**) was equally effective (Table 2, Entries 2 and 3). Disopropyl ketone (**1e**) also reacted with $CHBr_3$-derived dibromomethylenation reagent to give the desired dibromide product **2e** (80%) (Table 2, Entry 4). Due to the weakly basic nature of the $CHBr_3$/$TiCl_4$/Mg system, enolizable ketones also proved to be satisfactory substrates. Thus, both 2-indanone (**1f**) and β-tetralone (**1g**) reacted with the $CHBr_3$-derived bromomethylenation reagent to give the desired dibromoalkene products **2f** (73%) and **2g** (68%), respectively (Table 2, Entries 5 and 6).[9] To further demonstrate the scope of this dibromomethylene-forming methodology, the utility of this protocol was examined in the dibromomethylenation of sterically demanding ketones. In contrast to CBr_4-derived phosphorus reagents[4] and Tebbe–Grubbs reagents,[8] the $CHBr_3$/Mg/$TiCl_4$ complex reacted with the 2,2-dimethylcyclohexanone (**1h**). Thus, using a 3:8 $TiCl_4$/Mg ratio, a 72% yield of **2h** was obtained (Table 2, Entry 7). This $TiCl_4$/Mg-mediated CBr_2 transfer reaction of $CHBr_3$ was also found to be suitable for the dibromomethylenation of unsaturated cyclohexenone **1i** and hindered unsaturated cyclohexenone **1j** (Table 2, Entries 8 and 9).

Table 2. $CHBr_3$/Mg/$TiCl_4$-promoted dibromomethylenation of ketones.[a]

Entry	Substrate	$TiCl_4$/Mg [mmol]	DME [mL]	Product	Yield [%][b]
1	 1b	3:8	1.2	 2b	85
2	 1c	3:8	1.2	 2c	71
3	 1d	3:8	1.2	 2d	77
4	 1e	3:8	1.2	 2e	77
5	 1f	3:8	1.2	 2f	73
6	 1g	3:8	1.2	 2g	68
7	 1h	3:8	1.2	 2h	72
8	 1i	3:8	1.2	 2i	78
9	 1j	3:8	1.2	 2j	66[c]
10	 1k	3:8	1.2	 2k	87
11	 1l	3:8	1.2	 2l	82
12	 1m	3:8	1.2	 2m	84
13	 1n Ar = *P*-MeO-Ph	3:8	1.2	 2n	90
14	 1o	3:8	1.2	 2o	85

[a] Reaction conditions (1 mmol scale): CH_2Cl_2/DME/$CHBr_3$ (0.3 mL) at 0 °C to r.t. [b] Isolated yield. [c] The reaction was performed in $ClCH_2CH_2Cl$ at 0 °C to r.t.

With an eye to extending the procedure to other less reactive carbonyl compounds, we explored the $TiCl_4$/Mg-promoted CBr_2 transfer to aromatic ketones. Fortunately, exposing α-tetralone (**1k**), acetophenone (**1l**), dimethylacetophenone (**1m**), and 4,4′-dimethoxychalcone (**1n**) to the

$CHBr_3$/Mg/$TiCl_4$/DME system led to dibromomethylenation to give the desired vinyl dibromides **2k** (87%), **2l** (82%), **2m** (84%), and **2n** (90%), respectively (Table 2, Entries 10–13). A dramatic illustration of the nucleophilic nature of the [Ti-CBr_2-Mg-Clx-$(EPD)_n$] complex was the dibromomethylenation of benzophenone (**1o**) (Table 2, Entry 14), which, by virtue of the low reactivity of the carbonyl group, demands very vigorous conditions. Performing the $TiCl_4$/Mg-promoted direct coupling of $CHBr_3$ with benzophenone at 0 °C to room temperature led to complete consumption of starting material within 3 h and formation of the desired vinyl dibromide **2o** in 85% yield.[10] The ability to effect such a dibromomethylenation at low temperatures highlights the reactivity of this new (dibromomethylene)titanium complex.

On the other hand, dibromomethylenation of *p*-tolualdehyde (**1p**) was equally effective (Table 3, Entry 1); in this case the olefination product **2p** was obtained in 80% yield. Changing the aromatic aldehyde to *p*-(dimethylamino)benzaldehyde (**1q**), piperonal (**1r**), and 2-furaldehyde (**1s**) provided equally satisfactory results with formation of 1,1-dibromoalkenes **2q**, **2r**, and **2s**, respectively (Table 3, Entries 2–4). Changing the aromatic aldehydes to aliphatic aldehydes **1t**, **1u**, **1v**, and **1w** also gave the expected dibromides in good yields (Table 3, Entries 5–8).

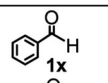
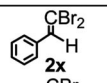
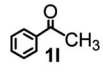
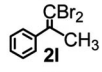
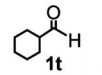
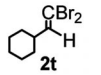
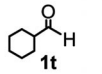
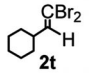
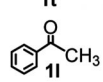
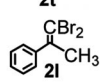
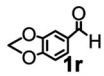
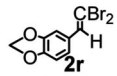
Table 3. $CHBr_3$/Mg/$TiCl_4$-promoted dibromomethylenation of aldehydes.[a]

Entry	Substrate	$TiCl_4$/Mg [equiv.]	DME [mL]	Product	Yield [%][b]
1	 **1p**	3:8	1.2	 **2p**	80
2	 **1q**	3:8	1.2	 **2q**	87
3	 **1r**	3:8	1.2	 **2r**	82
4	 **1s**	3:8	1.2	 **2s**	78
5	 **1t**	3:8	1.2	 **2t**	75
6	 **1u**	3:8	1.2	 **2u**	87
7	 **1v**	3:8	1.2	 **2v**	70
8	 **1w**	3:8	1.2	 **2w**	85

[a] Reaction conditions (1 mmol scale): bromoform (0.3 mL), 0 °C to r.t. [b] Isolated yield.

The chemoselectivity was briefly explored with a series of carbonyl compounds, as summarized in Table 4. As expected, exposure of a mixture of aldehyde (1 mmol) and ketone (1 mmol) to $CHBr_3$ (1–1.7 mmol) at –10 to –5 °C for ca. 0.5 h produced exclusively the aldehyde-derived vinyl dibromide (Table 4, Entries 1–3). A particularly interesting example illustrating the chemoselectivity of this process is the dibromomethylenation of a mixture of aliphatic and aromatic aldehydes (Table 4, Entry 4). The preference for methylenation of an aliphatic aldehyde highlights the chemoselectivity of the process.

Table 4. Selectivity in the dibromomethylenation of ketones and aldehydes mediated by the $CHBr_3$/Mg/$TiCl_4$/DME system.

Entry	Ester mixture	$TiCl_4$/Mg solvent	Product	Yield [%][a]
1	 **1x**	5:8[b] CH_2Cl_2	 **2x**	65
	 **1l**		 **2l**	0
2	 **1t**	3:8[c] $ClCH_2CH_2Cl$	 **2t**	57
	 **1a**		 **2a**	0
3	 **1t**	3:8[c] $ClCH_2CH_2Cl$	 **2t**	53
	 **1l**		 **2l**	0
4	 **1t**	3:8[d] $ClCH_2CH_2Cl$	 **2t**	56
	 **1r**		 **2r**	0

[a] Isolated yield. [b] Reaction conditions: bromoform (1.7 mmol), –5 °C, 25 min. [c] Reaction conditions: bromoform (1.0 mmol), –10 °C, 45 min. [d] Reaction conditions: bromoform (1.0 mmol), –5 °C, 25 min. Piperonyl alcohol (10%) was produced as byproduct.

Conclusions

This method constitutes the first report on the use of $CHBr_3$ as an effective dibromomethylene equivalent in chemoselective carbonyl dibromomethylenation. The nucleophilicity involved suggested several intriguing applications that are currently under active investigation.

Experimental Section

General: Dichloromethane was distilled from P_2O_5 prior to use. Commercially available ketones and aldehydes were used as received. Bromoform, titanium tetrachloride, and magnesium powder (ca. 50 mesh) were used as received. Flash chromatography was performed on silica gel 60 (230–400 mesh). All reactions were carried out under N_2. ^1H and ^{13}C NMR spectra were recorded with a Varian VXR 400 MHz spectrometer at ambient temperature. High-resolution mass spectra were determined with a Jeol JMS-HX 110 spectrometer.

Typical Procedure for the Dibromomethylenation of Carbonyl Compounds. 1-(Dibromomethylene)-2-methylcyclohexane (2a): To a suspension of Mg (194 mg, 8 mmol) and $TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 3 mL) at 0 °C was added over a 2.0 min period a solution

of 2-methylcyclohexanone (**1a**; 112 mg, 1 mmol) in CH_2Cl_2 (1 mL), $CHBr_3$ (0.3 mL), and DME (1.2 mL). The black slurry was stirred at 0–25 °C for 3 h, then recooled to 0 °C and carefully poured into ice-cold saturated potassium carbonate solution (10 mL). The resulting mixture was stirred with CH_2Cl_2 (20 mL), and the phases were separated. The procedure was repeated twice, and the combined extracts were dried, concentrated, and purified by chromatography on silica gel (elution with hexane) to give **2a** (213 mg, 80%) as a colorless oil. R_f = 0.89 (*n*-hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.04 (d, J = 7.2 Hz, 3 H), 1.21–1.25 (m, 1 H), 1.46–1.54 (m, 4 H), 1.74 (d, J = 8.0 Hz, 1 H), 1.91–1.98 (m, 1 H), 2.78 (d, J = 14.4 Hz, 1 H), 3.20 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 17.0, 19.8, 26.4, 30.1, 32.1, 36.3, 82.0, 147.9 ppm. HRMS: calcd. for $C_8H_{12}Br_2$ 265.9306; found 265.9315.

2-(Dibromomethylene)-1,3-dimethylcyclohexane (2b): Prepared as described above with **1b** (126 mg, 1 mmol) and Mg (8 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.2 mL). The black slurry was stirred at 0 °C → r.t. for 3 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2b** (239 mg, 85%) as a colorless oil. R_f = 0.90 (*n*-hexane). IR (neat): $\tilde{\nu}$ = 2963, 2930, 2867, 1608, 1578, 1459, 1376, 1240, 1146, 1112, 1049, 985, 898, 878, 835, 767, 675 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.12 (d, J = 7.6 Hz, 6 H), 1.52–1.63 (m, 6 H), 3.09 (t, J = 6.8 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 15.0, 19.6, 31.6, 35.3, 85.5, 150.4 ppm. HRMS: calcd. for $C_9H_{14}Br_2$ 279.9462; found 279.9471.

(Dibromomethylene)cyclopentane (2c):[5] Prepared as described above with **1c** (84 mg, 1 mmol) and Mg (8 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/ DME (1.2 mL). The black slurry was stirred at 0 °C → r.t. for 3 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2c** (169 mg, 71%) as a colorless oil. R_f = 0.96 (*n*-hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.78–1.82 (m, 4 H), 2.30–2.33 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 27.19, 36.6, 78.2, 151.0 ppm. HRMS: calcd. for $C_6H_8Br_2$ 237.8993; found 237.8997.

(Dibromomethylene)cycloheptane (2d):[5] Prepared as described above with **1d** (112 mg, 1 mmol) and Mg (8 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.2 mL). The black slurry was stirred at 0 °C → r.t. for 3 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2d** (205 mg, 77%) as a colorless oil. R_f = 0.88 (*n*-hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.50–1.64 (m, 8 H), 2.44 (t, J = 6.4 Hz, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 26.4, 28.8, 36.0, 84.8, 146.8 ppm. HRMS: calcd. for $C_8H_{12}Br_2$ 265.9306; found 265.9309.

3-(Dibromomethylene)-2,4-dimethylpentane (2e): Prepared as described above with **1e** (114 mg, 1 mmol) and Mg (8 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.2 mL). The black slurry was stirred at 0 °C → r.t. for 3 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2e** (197 mg, 73%) as a colorless oil. R_f = 0.97 (*n*-hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.13 (d, J = 6.8 Hz, 12 H), 2.94 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.4, 22.5, 82.9, 153.4 ppm. HRMS: calcd. for $C_8H_{14}Br_2$ 267.9462; found 267.9461.

2-(Dibromomethylene)-2,3-dihydro-1*H*-indene (2f): Prepared as described above with **1f** (132 mg, 1 mmol) and Mg (8 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.2 mL). The black slurry was stirred at 0 °C → r.t. for 3 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2f** (209 mg, 73%) as a colorless oil. R_f = 0.70 (*n*-hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.68 (s, 4 H), 7.20 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 42.2, 81.9, 124.6, 126.9, 140.4, 146.5 ppm. HRMS: calcd. for $C_{10}H_8Br_2$ 285.8993; found 285.9002.

2-(Dibromomethylene)-1,2,3,4-tetrahydronaphthalene (2g): Prepared as described above with **1g** (146 mg, 1 mmol) and Mg (8 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.2 mL). The black slurry was stirred at 0 °C → r.t. for 3 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2g** (205 mg, 68%) as a colorless oil. R_f = 0.62 (*n*-hexane). IR (neat): $\tilde{\nu}$ = 3064, 3021, 2931, 2844, 1678, 1626, 1572, 1492, 1453, 1423, 1283, 1220, 1105, 947, 866, 793, 745 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.59 (t, J = 6.8 Hz, 2 H), 2.80 (t, J = 6.0 Hz, 2 H), 3.60 (s, 2 H), 7.14 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 29.1, 32.7, 37.6, 83.9, 126.3, 126.5, 127.6, 127.9, 134.6, 137.5, 141.5 ppm. HRMS: calcd. for $C_{11}H_{10}Br_2$ 299.9149; found 299.9145.

2-(Dibromomethylene)-1,1-dimethylcyclohexane (2h): Prepared as described above with **1h** (126 mg, 1 mmol) and Mg (8 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.2 mL). The black slurry was stirred at 0 °C → r.t. for 3 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2h** (203 mg, 72%) as a colorless oil. R_f = 0.84 (*n*-hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.33 (s, 6 H), 1.46 (d, J = 4.8 Hz, 2 H), 1.56 (d, J = 13.2 Hz, 4 H), 2.46 (t, J = 5.2 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 18.7, 21.8, 26.8, 33.4, 39.2, 40.5, 80.9, 149.9 ppm. HRMS: calcd. for $C_9H_{14}Br_2$ 279.9462; found 294.9455.

3-(Dibromomethylene)cyclohex-1-ene (2i):[11a] Prepared as described above, **1i** (96 mg, 1 mmol) and Mg (194 mg, 8 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.2 mL). The black slurry was stirred at 0 °C → r.t. for 3 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2i** (194 mg, 78%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.71 (m, 2 H), 2.10–2.05 (m, 2 H), 2.47 (t, J = 6.4 Hz, 2 H), 6.06–6.02 (tt, J = 10.0, 4.0 Hz, 1 H), 6.47–6.43 (tt, J = 10.0, 6.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.9, 25.3, 31.2, 87.5, 126.2, 133.9, 138.6 ppm. HRMS: calcd. for $C_7H_8Br_2$ 249.8993; found 249.8986.

2-(Dibromomethylene)-4-methyl-1-(propan-2-ylidene)cyclohexane (2j): Prepared as described above with **1j** (152 mg, 1 mmol) and Mg (194 mg, 8 mmol)/$TiCl_4$ (1 M in $ClCH_2CH_2Cl$, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.2 mL). The black slurry was stirred at 0 °C → r.t. for 3 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2j** (203 mg, 66%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (d, J = 11.6 Hz, 3 H), 1.52–1.76 (m, 11 H), 2.62–2.67 (m, 1 H), 2.89–2.93 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3, 21.9, 22.0, 30.5, 34.7, 36.2, 44.9, 82.5, 125.9, 132.9, 147.1 ppm. HRMS: calcd. for $C_{11}H_{16}Br_2$ 305.9618; found 305.9622.

1-(Dibromomethylene)-1,2,3,4-tetrahydronaphthalene (2k): Prepared as described above with **1k** (146 mg, 1 mmol) and Mg (8 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.2 mL). The black slurry was stirred at 0 °C → r.t. for 2 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2k** (262 mg, 87%) as a colorless oil. R_f = 0.79 (*n*-hexane). IR (neat): $\tilde{\nu}$ = 3064, 3032, 2939, 2864, 2843, 1479, 1452, 1074, 1016, 917, 794, 747, 636, 503 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.81–1.85 (m, 2 H), 2.65–2.71 (m, 4 H), 7.16–7.29 (m, 3 H), 7.90 (d, J = 7.2 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.8, 30.0, 34.1, 86.5, 125.1, 127.5, 128.2,

128.9, 134.4, 140.3, 140.6 ppm. HRMS: calcd. for $C_{11}H_{10}Br_2$ 299.9149; found 299.9147.

(2,2-Dibromo-1-methylvinyl)benzene (2l):[11b] Prepared as described above with **1l** (120 mg, 1 mmol) and Mg (8 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.2 mL). The black slurry was stirred at 0 °C → r.t. for 2 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2l** (225 mg, 82%) as a colorless oil. R_f = 0.62 (*n*-hexane). IR (neat): $\tilde{\nu}$ = 3056, 3025, 29.16, 2848, 1600, 1489, 1441, 1371, 1074, 1028, 912, 750, 697, 582, 529 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.23 (s, 3 H), 7.21–7.36 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 26.1, 87.5, 127.3, 127.6, 128.3, 141.9, 143.0 ppm. HRMS: calcd. for $C_9H_8Br_2$ 273.8993; found 273.8992.

1-(1,1-Dibromo-3-methylbut-1-en-2-yl)benzene (2m):[11c] Prepared as described above with **1m** (148 mg, 1 mmol) and Mg (8 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.2 mL). The black slurry was stirred at 0 °C → r.t. for 2 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2m** (255 mg, 84%) as a colorless solid. R_f = 0.80 (*n*-hexane). ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.96 (d, J = 6.8 Hz, 6 H), 3.32 (sept, J = 6.8 Hz, 1 H), 7.02–7.05 (m, 2 H), 7.34–7.40 (m, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 26.3, 35.6, 88.2, 127.5, 128.1, 128.4, 138.7, 152.2 ppm. HRMS: calcd. for $C_{11}H_{12}Br_2$ 301.9306; found 301.9310.

(*E*)-1,1-Dibromo-2,4-bis(4-methoxyphenyl)buta-1,3-diene (2n): Prepared as described above with **1n** (268 mg, 1 mmol) and Mg (194 mg, 8 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.2 mL). The black slurry was stirred at 0 °C → r.t. for 3 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **10a** (382 mg, 90%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.80 (s, 3 H), 3.86 (s, 3 H), 6.11 (d, J = 15.6 Hz, 1 H), 6.84 (d, J = 8.8 Hz, 2 H), 6.97 (d, J = 8.4 Hz, 2 H), 7.12 (d, J = 8.4 Hz, 2 H), 7.29 (s, 1 H), 7.32 (d, J = 8.8, Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.23, 55.29, 91.9, 113.9, 114.1, 126.4, 128.2, 129.4, 130.5, 131.1, 136.0, 145.1, 159.2, 159.9 ppm. HRMS: calcd. for $C_{18}H_{16}Br_2O_2$ 421.9517; found 421.9513.

(2,2-Dibromoethene-1,1-diyl)dibenzene (2o):[11b] Prepared as described above with **1o** (182 mg, 1 mmol) and Mg (8 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.2 mL). The black slurry was stirred at 0 °C → r.t. for 2 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2o** (287 mg, 85%) as a colorless oil. R_f = 0.62 (*n*-hexane). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.24–7.32 (m, 10 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 90.2, 127.9, 128.3, 128.6, 141.3, 147.8 ppm. HRMS: calcd. for $C_{14}H_{10}Br_2$ 335.9149; found 335.9157.

1-(2,2-Dibromovinyl)-4-methylbenzene (2p):[12a] Prepared as described above with **1p** (120 mg, 1 mmol) and Mg (6 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 2 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.0 mL). The black slurry was stirred at 0 °C → r.t. for 2.5 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2p** (220 mg, 80%) as a colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.36 (s, 3 H), 7.14 (d, J = 8.0 Hz, 1 H), 7.24 (d, J = 15 Hz, 1 H), 7.31 (t, J = 7.3, 10.4 Hz, 2 H), 7.45 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.3, 89.2, 125.4, 128.2, 129.0, 129.3, 135.2, 137.0, 138.0 ppm. HRMS: calcd. for $C_9H_8Br_2$ 273.8993; found 273.8988.

4-(2,2-Dibromovinyl)-*N*,*N*-dimethylaniline (2q):[12b] Prepared as described above with **1q** (149 mg, 1 mmol) and Mg (6 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 2 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.0 mL). The black slurry was stirred at 0 °C → r.t. for 1.5 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2q** (265 mg, 87%) as a colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.97 (s, 6 H), 6.64 (d, J = 8.8 Hz, 2 H), 7.33 (s, 1 H), 7.47 (d, J = 8.8 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 40.1, 84.1, 111.5, 122.9, 129.6, 136.6, 150.2 ppm. HRMS: calcd. for $C_{10}H_{11}NBr_2$ 302.9258; found 302.9256.

5-(2,2-Dibromovinyl)benzo[*d*][1,3]dioxole (2r):[12c] Prepared as described above with **1r** (150 mg, 1 mmol) and Mg (6 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 2 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.0 mL). The black slurry was stirred at 0 °C → r.t. for 3.0 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2r** (207 mg, 68%) as a colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ = 5.98 (s, 2 H), 6.78 (d, J = 8.0 Hz, 1 H), 6.93 (d, J = 6.4 Hz, 1 H), 7.18 (s, 1 H), 7.36 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 87.8, 101.3, 108.0, 108.2, 123.3, 129.1, 136.2, 147.5, 147.7 ppm. HRMS: calcd. for $C_9H_6Br_2O_2$ 303.8735; found 303.8737.

2-(2,2-Dibromovinyl)furan (2s):[12b] Prepared as described above with **1s** (96 mg, 1 mmol) and Mg (6 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 2 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.0 mL). The black slurry was stirred at 0 °C → r.t. for 3.0 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2s** (195 mg, 78%) as a colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.46 (dd, J = 1.6 Hz,1 H), 6.95 (dd, J = 0.4, 3.2 Hz, 1 H), 7.40 (s, 1 H), 7.44 (t, J = 1.2 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 87.1, 111.4, 111.5, 126.4, 142.5, 150.0 ppm. HRMS: calcd. for $C_6H_4Br_2O$ 249.8629; found 249.8631.

(2,2-Dibromovinyl)cyclohexane (2t):[11b] Prepared as described above with **1t** (112 mg, 1 mmol) and Mg (8 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.2 mL). The black slurry was stirred at 0 °C → r.t. for 3.0 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2t** (199 mg, 75%) as a colorless oil. R_f = 0.87 (*n*-hexane). IR (neat): $\tilde{\nu}$ = 2926, 2851, 1610, 1448, 1349, 1311, 1273, 1257, 1217, 1139, 956, 893, 832, 814, 765 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.06–1.34 (m, 5 H), 1.61–1.73 (m, 5 H), 2.25 (m, 1 H), 6.21 (d, J = 9.2 Hz 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 25.4, 25.7, 31.2, 42.4, 86.9, 143.7 ppm. HRMS: calcd. for $C_8H_{12}Br_2$ 265.9306; found 265.9301.

1,1-Dibromo-4-methylpenta-1,3-diene (2u):[12b] Prepared as described above with **1u** (84 mg, 1 mmol) and Mg (194 mg, 8 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.2 mL). The black slurry was stirred at 0 °C → r.t. for 2.0 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2u** (207 mg, 87%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.73 (s, 3 H), 1.78 (s, 3 H), 5.84 (m, 1 H), 7.06 (d, J = 10.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 18.8, 25.9, 89.18, 122.6, 133.9, 140.6 ppm. HRMS: calcd. for $C_6H_8Br_2$ 237.8993; found 237.8998.

1-(2,2-Dibromovinyl)-2-chlorocyclohex-1-ene (2v): Prepared as described above with **1v** (144 mg, 1 mmol) and Mg (194 mg, 8 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.0 mL). The black slurry was stirred at 0 °C → r.t. for 2.0 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2v** (210 mg, 70%) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2937, 2881, 2860, 2837, 1655, 1570, 1447, 1434, 1336, 1261, 1097, 995, 905, 877, 850, 822, 809, 669, 601, 539 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.69–1.55 (m, 4 H), 2.31 (d, J = 6.0 Hz, 4 H), 7.17 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.9, 23.3, 28.7, 34.0, 90.0, 129.8, 132.7, 136.3 ppm. HRMS: calcd. for $C_8H_9ClBr_2$ 297.8759; found 297.8757.

1-(4,4-Dibromobut-3-en-2-yl)benzene (2w):[12d] Prepared as described above with **1w** (134 mg, 1 mmol) and Mg (8 mmol)/$TiCl_4$ (1 M in CH_2Cl_2, 3 mmol, 4 mL)/$CHBr_3$ (0.3 mL)/DME (1.2 mL). The black slurry was stirred at 0 °C → r.t. for 3.0 h to give a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded **2w** (245 mg, 85%) as a colorless oil. R_f = 0.80 (*n*-hexane). ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.38 (d, J = 7.2 Hz, 3 H), 3.72–3.80 (m, 1 H), 6.49 (d, J = 9.6 Hz, 6 H), 7.23–7.32 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.0, 43.3, 88.4, 126.7, 126.8, 128.6, 142.7, 142.9 ppm. HRMS: calcd. for $C_{10}H_{10}Br_2$ 287.9150; found 287.9157.

Supporting Information (see footnote on the first page of this article): Copies of NMR spectra.

Acknowledgments

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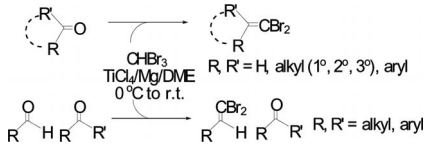
Dibromomethylenation

Bromoform can serve as a highly nucleophilic dibromomethylene carbenoid in chemoselective carbonyl dibromomethylenation reactions with various carbonyl compounds such as enolizable and sterically hindered ketones by using the $CHBr_3$/Mg/$TiCl_4$ system.



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