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Novel efficient synthesis of dibromoalkenes. A first example of catalytic olefination of aliphatic carbonyl compounds

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A new simple and efficient *one pot* transformation of various aliphatic carbonyl compounds to the corresponding dibromoalkenes is described. A wide range of hydrazones of aldehydes and ketones, prepared *in situ*, were easily converted into dibromoalkenes by treatment with carbon tetrabromide in the presence of CuCl. The reaction proceeds under mild conditions to give the target products in good to high yields.

Introduction

Olefination of carbonyl compounds, that is $R^1R^2C{=}O$ to $R^1R^2C{=}CXY$ transformation, is one of the most successful synthetic routes to a wide variety of substituted alkenes.[1] Recently, we reported a novel *catalytic olefination reaction* (COR) of aromatic aldehydes and ketones.[2] It was found that *N*-unsubstituted hydrazones of aromatic carbonyl compounds could be smoothly transformed into the corresponding substituted alkenes by treatment with polyhalogenated alkanes in the presence of catalytic amounts of CuCl. Based on COR we expanded this novel approach to the synthesis of dichloroalkenes, dibromoalkenes, vinylbromides, vinyliodides and fluoroalkenes from aromatic and heteroaromatic carbonyl precursors.[2] A possible mechanism of olefination was discussed and the catalytic cycle of COR was reported earlier.[2]

However, CORs of aliphatic aldehydes and ketones have not been investigated previously. In the present paper we investigate the olefination of a wide range of aliphatic carbonyl compounds by carbon tetrabromide (Fig. 1).

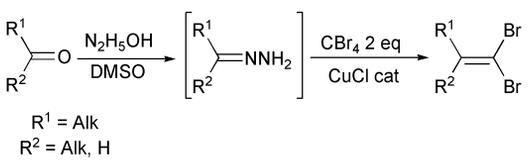

Fig. 1 Olefination of carbonyl compounds, *via* hydrazones prepared *in situ*, by treatment with CBr_4.

1,1-Dibromoolefins are important reagents in modern organic synthesis, being synthetic precursors of terminal and asymmetric acetylenes [3,4] and bromoacetylenes.[5] Some methods for the stereoselective reduction of dibromoalkenes into *E*- and *Z*-isomers of terminal vinyl bromides have been elaborated.[6] Recently, various cross-coupling reactions with dibromoalkenes were described.[7]

The same common carbonyl–dibromoalkene conversion, using a Wittig-type reaction with CBr_4 and triphenylphosphine, has been reported for aldehydes [3,8] and ketones.[9,10] The necessity of large amounts of PPh_3 is a significant disadvantage of this approach.

Results and discussion

In our approach to dibromoalkene synthesis, a wide range of aliphatic aldehydes and ketones were converted into hydrazones by reaction with equimolar amounts of hydrazine hydrate. It was found that full conversion of carbonyl compounds into hydrazones proceeded within 2–24 hours (TLC control). All reactions were carried out under an argon atmosphere to prevent oxidation of the unstable hydrazones by air (degassed DMSO was used as a solvent). After the formation of hydrazone the reaction mixture was treated with carbon tetrabromide in the presence of catalytic amounts of CuCl.

It was found that aliphatic carbonyl compounds can be converted into target dibromoalkenes **1**–**12** in good to excellent yield using a *one pot* procedure (Table 1).

Both aldehydes and ketones can be used as appropriate substrates for the preparation of alkenes. Olefination of aldehydes leads to trisubstituted alkenes **1**–**3**, whereas ketones are converted into tetrasubstituted alkenes **4**–**12**.

We found that steric hindrance and electronic factors strongly affected the yields of the target dibromoalkenes. For example, nonanone-2 was converted into alkene **4** in 97% yield, whereas isomeric nonanone-5 having a shielded carbonyl group gave the target alkene **5** in only 54% yield.

More sterically hindered ketones such as methyl *tert*-butyl ketone, diisopropyl ketone and dicyclohexyl ketone cannot be converted into the corresponding dibromoalkenes.

It should be noted that cyclopropyl methyl ketone undergoes this transformation without opening of the cyclopropane ring. The final product **6** contains a cyclopropyl dibromovinyl group, an important fragment of some pyrethroids.[11]

It should also be noted that cyclic and caged ketones can participate in the reaction. A number of cycloalkanones were transformed into 5-, 6-, 7- and 8-membered (dibromomethylene)cycloalkenes **7**–**10**. The yield of the target product increased with increasing ring size. The sterically hindered cyclic ketone, menthone, was also successfully converted into dibromoalkene **11**.

Caged ketone, adamantanone, can be introduced into the reaction to give the corresponding dibromoalkene **12** in relatively low yield.

The hydrazone of D(+)-camphor cannot be prepared and used *in situ* due to the low activity of camphor.[12] The starting hydrazone was therefore prepared separately and following treatment with CBr_4 gave dibromoalkene **13** in 60% yield.

The mechanism of COR was previously reported for the olefination of hydrazones of aromatic hydrazones and arylalkyl ketones.[2c–e] We believe that the proposed mechanism of olefination can be expanded to describe the reactions of aliphatic hydrazones. The catalytic cycle illustrating the reaction mechanism and formation of the dibromoalkenes is given in Fig. 2.

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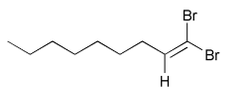
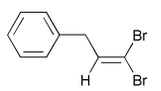
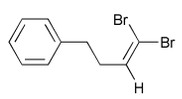
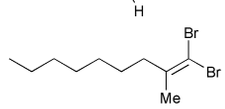
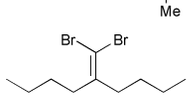
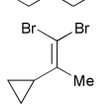
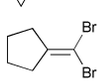
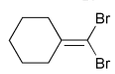
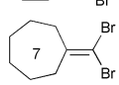
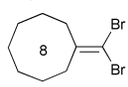
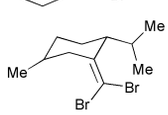
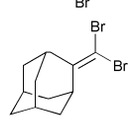
Table 1 Synthesis of dibromoalkenes from carbonyl compounds

Entry	Dibromoalkene	Yield (%)
1		83
2		43
3		70
4		97
5		54
6		71
7		52
8		68
9		73
10		78
11		53
12		43

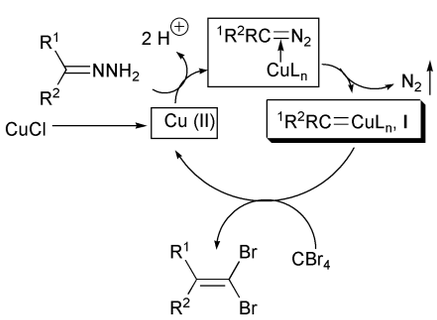


Fig. 2 Catalytic cycle of the olefination reaction.

At the initial step CuCl is oxidized into copper(II) by CBr_4. The formed copper(II) species oxidizes the hydrazone into the corresponding diazoalkane. Earlier we postulated the copper–carbene complex **I** as a key intermediate of the olefination reaction.[2c–e] This complex is formed in the copper-catalysed decomposition of diazoalkane. Further interaction of **I** and carbon tetrabromide leads to the target dibromoalkene.

Conclusion

In summary, we elaborated a novel general method for the preparation of *gem*-dibromoalkenes from aliphatic carbonyl precursors. The field of synthetic application of this novel catalytic two-stage olefination reaction was expanded to include aliphatic substrates. Mild conditions and simplicity of the reaction procedure are significant features of the method.

Experimental

General

^1H and ^{13}C NMR spectra were obtained using Varian VXR-400 and Bruker AM 400C spectrometers in CCl_4–$CDCl_3$ with TMS as an internal standard. Chemical shifts are reported in ppm. Column chromatography was performed on silica gel (63–200 mesh, Merck). Mass-spectra were recorded on a HP5890 mass spectrometer with a 5989x-G detector. All new compounds gave satisfactory 400 MHz ^1H- and 100 MHz ^{13}C-NMR spectral data. All chemical shifts (δ) are quoted in ppm downfield from TMS. *J* values are given in Hz. Known compounds **1**, **6**, **7**, **8**, **9**, **12** were characterized by comparison of their spectral and physical data with the literature.

General procedure for dibromoalkenes 1–12

All reactions were carried out under argon. A solution of carbonyl compound (10 mmol) in degassed DMSO (5 mL) was added dropwise to a solution of hydrazine hydrate (0.49 mL, 10 mmol) in degassed DMSO (5 mL). The reaction mixture was stirred until the carbonyl compound disappeared (TLC monitoring). Then freshly purified copper(I) chloride (1 mmol, 100 mg) and aqueous ammonia (1.4 mL) were added. Then a solution of carbon tetrabromide (6.64 g, 20 mmol) in degassed DMSO (20 mL) was added dropwise at 20 °C. The reaction mixture was stirred for 24 h, quenched with hydrochloric acid (5%) (300 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The extracts were dried over sodium sulfate, dichloromethane was evaporated *in vacuo* and the residue was purified by column chromatography (hexane).

The hydrazone of D(+)-camphor was prepared according to Kishner[12] and treated by CBr_4 in the presence of CuCl and aqueous ammonia as described for the *one pot* procedure to give the alkene **13**.

1,1-Dibromonon-1-ene (1). Prepared from octanal. Colourless oil, R_f (hexane) 0.90.[3]

(3,3-Dibromoprop-2-enyl)benzene (2). Prepared from phenyl acetaldehyde. Colourless oil, R_f (hexane) 0.65. Found: C, 39.43; H, 3.06. Calcd for $C_9H_8Br_2$: C, 39.17; H, 2.92%. ^1H NMR (CCl_4–$CDCl_3$) δ 3.37 (2 H, d, *J* 7.3, CH_2), 6.49 (1 H, t, *J* 7.3, –CH=), 7.07–7.24 (5 H, m, Ph). ^{13}C NMR (CCl_4–$CDCl_3$) δ 39.33 (CH_2), 90.29 (CBr_2), 126.83, 128.44, 128.82, 137.11 (–CH=), 137.44.

(4,4-Dibromobut-3-enyl)benzene (3). Prepared from 3-phenyl propionaldehyde. Colourless oil, R_f (hexane) 0.65. Found: C, 41.24; H, 3.28. Calcd for $C_{10}H_{10}Br_2$: C, 41.42; H, 3.48%. ^1H NMR (CCl_4–$CDCl_3$) δ 2.32 (2 H, dt, *J* 7.9, *J* 7.3, –CH_2), 2.64 (2 H, d, *J* 7.9, –CH_2–Ph), 6.30 (1 H, t, *J* 7.3, –CH=), 7.03–7.22 (5 H, m, Ar). ^{13}C NMR (CCl_4–$CDCl_3$) δ 34.02 (CH_2), 34.78 (CH_2), 89.84 (CBr_2), 126.34, 128.34, 128.57, 137.40 (–CH=), 140.33.

1,1-Dibromo-2-methylnon-1-ene (4). Prepared from nonanone-2. Colourless oil, R_f (hexane) 0.80. Found: C, 40.02; H, 5.84. Calcd for $C_{10}H_{18}Br_2$: C, 40.30; H, 6.09%. ^1H NMR (CCl_4–$CDCl_3$) δ 0.84 (3 H, t, *J* 6.9, *Me*–CH_2), 1.18–1.32 (2 H, m, CH_2), 1.32–1.43 (10 H, m, CH_2), 1.82 (3 H, s, Me–C=C), 2.20 (2 H, d, *J* = 7.8, CH_2–C=C). ^{13}C NMR (CCl_4–$CDCl_3$) δ 14.08, 22.64, 22.70, 26.95, 29.07, 29.19, 31.76, 38.14, 84.62 (CBr_2), 142.27 (–C=).

1,1-Dibromo-2-butylhex-1-ene (5). Prepared from nonanone-5. Colourless oil, R_f (hexane) 0.90. Found: C, 40.11; H, 6.24. Calcd for $C_{10}H_{18}Br_2$: C, 40.30; H, 6.09%. ^1H NMR (CCl_4–

$CDCl_3$) δ 0.88 (6 H, t, J 7.2, Me), 1.23–1.42 (8 H, m, CH_2), 2.18 (4 H, t, J 7.8, CH_2–C=C). ^{13}C NMR (CCl_4–$CDCl_3$) δ 14.08, 22.74, 29.51, 36.04, 85.62 (CBr_2), 146.19 (–C=).

(2,2-Dibromo-1-methylvinyl)cyclopropane (6). Prepared from methyl cyclopropyl ketone. Colourless oil, R_f (hexane) 0.80.[13]

(Dibromomethylene)cyclopentane (7). Prepared from cyclopentanone. Colourless oil, R_f (hexane) 0.80.[14]

(Dibromomethylene)cyclohexane (8). Prepared from cyclohexanone. Colourless oil, R_f (hexane) 0.75.[14]

(Dibromomethylene)cycloheptane (9). Prepared from cycloheptanone. Colourless oil, R_f (hexane) 0.80.[15]

(Dibromomethylene)cyclooctane (10). Prepared from cyclooctanone. Colourless oil, R_f (hexane) 0.80. Found: C, 38.15; H, 4.77. Calcd for $C_9H_{14}Br_2$: C, 38.33; H, 5.00%. ^{1}H NMR (CCl_4–$CDCl_3$) δ 1.37–1.49 (6 H, m, CH_2), 1.65–1.72 (4 H, m, CH_2), 2.32 (t, J 6.2, 4 H, CH_2–C=C). ^{13}C NMR (CCl_4–$CDCl_3$) δ 25.22, 25.61, 27.05, 35.47, 84.41 (CBr_2), 147.05 (–C=).

2-(Dibromomethylene)-1-isopropyl-4-methyl cyclohexane (11). Prepared from menthone. Was obtained as a mixture of diastereomers in a 6 : 1 ratio. Colourless oil, R_f (hexane) 0.80. Found: C, 42.32; H, 5.86. Calcd for $C_{11}H_{18}Br_2$: C, 42.61; H, 5.85%. ^{1}H NMR (CCl_4–$CDCl_3$), Major isomer: δ 0.78 (3 H, d, J 6.7), 0.89 (6 H, m), 1.10–1.17 (1 H, m), 1.55–1.92 (4 H, m), 2.02–2.09 (2 H, m), 2.52–2.65 (2 H, m). Minor isomer: δ 2.42–2.52 (2 H, m), 3.01 (1 H, hept, J 6.9). Other signals of the minor isomer were overlapped by signals of the major isomer. ^{13}C NMR (CCl_4–$CDCl_3$) δ 17.60, 19.71, 20.09, 20.48, 20.95, 21.33, 22.97, 25.08, 26.40, 27.48, 30.30, 30.88, 31.18, 33.80, 36.61, 45.29, 49.61, 83.93 (CBr_2), 139.37 (–C=), 145.43 (–C=). MS (EI, 70 eV); *m*/*z* (%): major isomer: 310 (M^+, 29), 267 (87, $M^+ - C_3H_7$), 229 (5, $M^+ - Br$), 187 (45, $M^+ - Br - C_3H_7$), 149 (50, $M^+ - 2Br - H$), 106 (100, $M^+ - 2Br - C_3H_8$), 91 (63, C_7H_7). Minor isomer: 310 (12, M^+), 267 (57, $M^+ - C_3H_7$), 229 (6, $M^+ - Br$), 187 (50, $M^+ - Br - C_3H_7$), 149 (51, $M^+ - 2Br - H$), 106 (100, $M^+ - 2Br - C_3H_8$), 91 (64, C_7H_7).

2-(Dibromomethylene)adamantane (12). Prepared from adamantanone. R_f (hexane) 0.80.[16]

2-(Dibromomethylene)-1,7,7-trimethylbicyclo[2.2.1]heptane (13). Prepared from the hydrazone of D(+)-camphor. R_f (hexane) 0.75. Found: C, 42.61; H, 5.34. Calcd for $C_{11}H_{16}Br_2$: C, 42.89; H, 5.24%. ^{1}H NMR (CCl_4–$CDCl_3$) δ 0.80 (3 H, s, 7-Me), 0.84 (3 H, s, 7-Me), 1.06 (1H, d, J 8.5), 1.24 (3 H, s, 1-Me), 1.47–1.53 (2 H, m), 1.71–1.74 (2 H, m), 1.87 (1 H, d, J 16.7), 2.32–2.42 (1 H, m). ^{13}C NMR (CCl_4–$CDCl_3$) δ 14.76 (Me), 19.15 (Me), 19.98 (Me), 27.60, 33.56, 44.26, 44.72, 50.64 (C-1 or C-7), 56.50 (C-1 or C-7), 76.64 (CBr_2), 152.82 (–C=). MS (EI, 70 eV); *m*/*z* (%): 308 (M^+, 29), 265 (21, $C_8H_9Br_2$), 252 (61, $C_7H_8Br_2$), 227 (15, $M^+ - Br$), 185 (18, C_8H_9Br), 171 (30, C_7H_8Br), 158 (19, C_6H_6Br), 148 (100, $M^+ - 2Br$), 105 (52, C_8H_9), 91 (51, C_7H_7).

Acknowledgments

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