Russian Journal of Organic Chemistry, Vol. 37, No. 1, 2001, pp. 52–55. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 1, 2001, pp. 63–66.

Synthesis of Bromoalkenes and Alkylidene Dibromides by Reactions of Carbonyl Compounds with 2,4,4,6-Tetrabromo-2,5-cyclohexadienone in the Presence of Triphenylphosphine

E. D. Matveeva, D. B. Feshin, and N. S. Zefirov

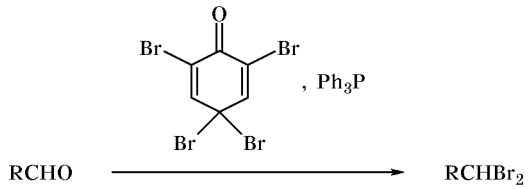
Faculty of Chemistry, Moscow State University, Vorob'evy gory, Moscow, 119899 Russia

Received June 2, 2000

Abstract—Reactions of aliphatic and aromatic aldehydes with the 2,4,4,6-tetrabromo-2,5-cyclohexadienone–triphenylphosphine complex result in formation of the corresponding geminal dibromides. Ketones react with the same complex to give vinyl bromides.

We previously showed that 2,4,4,6-tetrabromo-2,5-cyclohexadienone in the presence of triphenylphosphine is an efficient and mild reagent replacing the hydroxy group by bromine in alcohols [1, 2] and carboxylic acids [2]. The goal of the present work was to examine reactions of the system 2,4,4,6-tetrabromo-2,5-cyclohexadienone–triphenylphosphine (**I**) with aliphatic and aromatic carbonyl compounds. As model reaction we chose that between complex **I** and octanal. In order to optimize the reaction conditions we varied the solvent, the reactant ratio, and the order of their mixing.

Taking into account that only one bromine atom in the molecule of 2,4,4,6-tetrabromo-2,5-cyclohexadienone (**II**) is active, the stoichiometric reactant ratio carbonyl compound–tetrabromide **II**–triphenylphosphine (**III**) should be 1:2:2. Just this ratio was used in the present study. It should be noted that application of excess reagent (ratio 1:3:3) did not increase the yield of the target products.



The major product of the reaction of **I** with octanal was 1,1-dibromooctane (**IV**); also, 2,4,6-tribromophenol and triphenylphosphine oxide were formed. As solvents we tried acetonitrile, methylene chloride, and benzene. The best yields were obtained in boiling benzene. The order of mixing of the reactants also affects the product yield. When tetrabromocyclohexadienone **II** and phosphine **III** were mixed before addition of an aldehyde, the yield was lower. The optimal yield of 1,1-dibromooctane (**IV**) (83%) was obtained when reagent **II** was added to a solution of triphenylphosphine and octanal in benzene (Table 1).

The procedure is general, and it can also be used to synthesize other geminal dibromides of the aliphatic series. We thus converted dodecanal and heptadecanal into 1,1-dibromododecane and 1,1-dibromoheptadecane, respectively, in 95 and 78% yield. We also tried to involve in this process aromatic aldehydes. By reaction of benzaldehyde with complex **I** we obtained benzylidene dibromide in 90% yield. The yield of *p*-bromobenzylidene dibromide from *p*-bromobenzaldehyde was 62%. *p*- and *m*-Nitrobenzaldehydes reacted with complex **I** to afford 43 and 35% of *p*- and *m*-nitrobenzylidene bromides, respectively (Table 2).

Table 1 Reaction of octanal with the complex 2,4,4,6-tetrabromo-2,5-cyclohexadienone–triphenylphosphine

Solvent	Yield of 1,1-dibromooctane, %	
	method *a*[a]	method *b*[b]
Acetonitrile	30	55
Methylene chloride	30	57
Benzene	70	83

[a] Preliminary preparation of complex **I**.

[b] 2,4,4,6-Tetrabromo-2,5-cyclohexadienone was added last.

1070-4280/01/3701-0052 $25.00 © 2001 MAIK "Nauka / Interperiodica"

The purity of the products was checked by GLC. Their structure was confirmed by ^1H and ^{13}C NMR spectra. The ^1H NMR spectra of 1,1-dibromoalkanes contain a triplet at δ 5.7 ppm from the terminal CH proton and a multiplet at δ 2.4 ppm from the neighboring methylene group. The corresponding carbon signals appear in the ^{13}C NMR spectra at δ_C 46.3 and 45.4 ppm, respectively, in keeping with published data [3–6].

In the reaction of complex **I** with cyclohexanone the only product was 1-bromocyclohexene. Its highest yield (75%) was obtained in methylene chloride. By reactions of **I** with acetophenone and 1,3-cyclohexanedione we obtained, respectively, α-bromostyrene (52%) and 3-bromo-2-cyclohexenone (88%) (Table 3). Benzophenone failed to react with complex **I**. The structure of the resulting bromoalkenes was confirmed by the ^1H and ^{13}C NMR spectra which were consistent with published data (see Experimental).

To conclude we can state that we have developed a procedure for preparation of terminal geminal dibromoalkanes from aliphatic and aromatic aldehydes. Ketones react with complex **I** to give exclusively the corresponding bromoalkenes, and an additional study is to be performed in order to elucidate how the ketone structure affects the reaction direction.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a VXR-400 instrument (400 MHz for ^1H) using tetramethylsilane as internal reference. GLC analysis was performed on a Chrom-5 chromatograph equipped with a flame-ionization detector (SE-30 quartz capillary column, 25 m × 0.25 mm; carrier gas helium). The progress of reactions was monitored by TLC on Silufol plates; the chromatograms were developed first with iodine vapor and second with aqueous potassium permanganate. Preparative column chromatography was performed on silica gel (Merck 60, 70–230 mesh, and Chemapol, 5/40 and 40/100 μm).

Acetonitrile was refluxed over P_2O_5, distilled, and stored over calcium hydride. Methylene chloride was refluxed over P_2O_5 and distilled. Benzene was refluxed over metallic sodium and distilled. Triphenylphosphine (**III**) was recrystallized from 2-propanol and dried in a vacuum.

2,4,4,6-Tetrabromo-2,5-cyclohexadienone (II). A mixture of 15 g (0.086 mol) of *p*-bromophenol, 45 ml of ethyl alcohol, and 45 ml of acetic acid was cooled in an ice bath, and 13 ml (0.255 mol) of bromine was added from a dropping funnel over a period of 20 min. The mixture was stirred for 1 h and poured into a solution of 21 g of $NaHCO_3$ in 180 ml of water. When gaseous products no longer evolved, the precipitate was filtered off, washed with hexane, dried in air, and recrystallized from chloroform. Yield 31 g (87%), mp 142°C [7].

Table 2. Reactions of the 2,4,4,6-tetraboromo-2,5-cyclohexadienone–triphenylphosphine complex with aldehydes; temperature 79°C

Product	Time, h	Yield, %
1,1-Dibromooctane	72	83
1,1-Dibromododecane	72	95
1,1-Dibromoheptadecane	72	75
Benzylidene dibromide	18	90
p-Bromobenzylidene dibromide	36	62
p-Nitrobenzylidene dibromide	36	43
m-Nitrobenzylidene dibromide	36	35

Benzylidene dibromide. To a solution of 3.24 g (0.0123 mol) of triphenylphosphine in 15 ml of dry benzene we added with stirring under argon 0.525 g (0.00495 mol) of benzaldehyde in 2 ml of benzene. 2,4,4,6-Tetrabromo-2,5-cyclohexadienone, 5.07 g (0.0123 mol), was then added, and the mixture was refluxed for 18 h. The mixture was filtered through a layer of silica gel and evaporated, and the residue was subjected to column chromatography using a 5% solution of ether in hexane as eluent. Yield 1.115 g (90%). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.65 s (1H, $CHBr_2$), 7.3–7.4 m (5H, H_{arom}) (cf. [4, 8]); ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 41.11, 126.44, 128.65, 129.85, 141.86 (cf. [4]).

4-Bromobenzylidene dibromide. Following the above procedure, from 0.733 g (0.00283 mol) of triphenylphosphine, 0.25 g (0.00135 mol) of *p*-bromobenzaldehyde, and 1.163 g (0.0283 mol) of 2,4,4,6-tetrabromo-2,5-cyclohexadienone we obtained (after chromatographic purification using 1:4 toluene–hexane as eluent) 275 mg (62%) of 4-bromobenzylidene dibromide. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.59 s (1H, $CHBr_2$), 7.4–7.55 m (4H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 39.61, 123.82, 128.09, 131.79, 140.87.

3-Nitrobenzylidene dibromide was synthesized in a similar way from 1.82 g (0.00695 mol) of triphenylphosphine, 0.5 g (0.0033 mol) of *m*-nitrobenzaldehyde, and 2.85 g (0.00695 mol) of 2,4,4,6-tetrabromo-2,5-cyclohexadiene. Chromatographic purifica-

Table 3. Reactions of complex **I** with ketones[a]

Initial ketone	Product	Solvent	Temperature, °C	Time, h	Yield, %
Cyclohexanone	1-Bromocyclohexene	Acetonitrile	81	24	30
		Methylene chloride	40	24	75
		Benzene	79	24	20
1,3-Cyclohexanedione	3-Bromo-2-cyclohexenone	Methylene chloride	40	24	88 70[b]
Acetophenone	α-Bromostyrene	*o*-Dichlorobenzene	180	72	15

[a] Ratio ketone–2,4,4,6-tetrabromo-2,5-cyclohexadienone–triphenylphosphine 1:2:2.
[b] Ratio ketone–2,4,4,6-tetrabromo-2,5-cyclohexadienone–triphenylphosphine 1:4:4.

tion using 1:4 toluene–hexane as eluent gave 335 mg (35%) of 3-nitrobenzylidene dibromide. ^{1}H NMR spectrum (acetone-d_6, HMDS), δ, ppm: 7.29 s (1H, $CHBr_2$), 7.72 t (1H, H_{arom}), 8.06–8.1 m (1H, H_{arom}), 8.18– 8.22 m (1H, H_{arom}), 8.44 t (1H, H_{arom}). ^{13}C NMR spectrum, (acetone-d_6), δ_C, ppm: 38.74, 120.05, 123.3, 129.43, 129.98, 131.82, 143.11.

4-Nitrobenzylidene dibromide was synthesized in a similar way from 0.91 g (0.0034 mol) of triphenylphosphine, 0.25 g (0.00165 mol) of *p*-nitrobenzaldehyde, and 1.425 g (0.0034 mol) of 2,4,4,6-tetrabromo-2,5-cyclohexadienone. Chromatographic purification with 1:4 toluene–hexane as eluent gave 220 mg (43%) of 4-nitrobenzylidene dibromide. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.58 s (1H, $CHBr_2$), 7.73–7.77 d (2H, H_{arom}), 8.23–8.27 d (2H, H_{arom}) (cf. [9]). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 38.13, 124.03, 127.71, 134.89, 147.82.

1,1-Dibromooctane (IV) was obtained in a similar way from 2.56 g (0.00976 mol) of triphenylphosphine, 0.5 g (0.0039 mol) of octanal, and 4.0 g (0.00976 mol) of 2,4,4,6-tetrabromo-2,5-cyclohexadienone, followed by chromatographic purification with a 5% solution of ethyl acetate in hexane. Yield 835 mg (83%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.91 t (3H, CH_3), 1.2–1.4 m [10H, $(CH_2)_5CH_3$], 1.5–1.6 m (2H, $CH_2CH_2CHBr_2$), 2.39 m (2H, CH_2CHBr_2), 5.7 t (1H, $CHBr_2$) (cf. [3, 5]). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.06, 22.59, 28.08, 28.21, 28.99, 31.65, 45.45, 46.31.

1,1-Dibromododecane was obtained in a similar way from 1.78 g (0.00679 mol) of triphenylphosphine, 0.5 g (0.00272 mol) of dodecanal, and 2.784 g (0.00679 mol) of 2,4,4,6-tetrabromo-2,5-cyclohexadienone. Chromatographic purification using a 5% solution of ethyl acetate in hexane gave 840 mg (95%) of 1,1-dibromododecane. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.91 t (3H, CH_3), 1.2–1.4 m [16H, $(CH_2)_8CH_3$], 1.5–1.6 m (2H, $CH_2CH_2CHBr_2$), 2.39 m (2H, CH_2CHBr_2), 5.7 t (1H, $CHBr_2$). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.12, 22.69, 28.08, 28.25, 29.33 (2C), 29.45, 29.57 (2C), 31.89, 45.44, 46.18.

1,1-Dibromoheptadecane was synthesized in a similar way from 1.29 g (0.00492 mol) of triphenylphosphine, 0.5 g (0.00196 mol) of heptadecanal, and 2.015 g (0.00492 mol) of 2,4,4,6-tetrabromo-2,5-cyclohexadienone. The product was purified by chromatography using a 5% solution of ethyl acetate in hexane. Yield 580 mg (75%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.91 t (3H, CH_3), 1.22–1.4 m [26H, $(CH_2)_{13}CH_3$], 1.5–1.6 m (2H, $CH_2CH_2CHBr_2$), 2.39 m (2H, CH_2CHBr_2), 5.7 t (1H, $CHBr_2$). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.13, 22.09, 22.71, 28.27, 29.35, 29.38, 29.47, 29.59, 29.65, 29.68 (3C), 29.72 (2C), 31.93, 45.46, 46.29.

1-Bromocyclohexene was synthesized in a similar way from 3.16 g (0.012 mol) of triphenylphosphine, 0.5 g (0.00483 mol) of cyclohexanone, and 4.95 g (0.012 mol) of 2,4,4,6-tetrabromo-2,5-cyclohexadienone in dry methylne chloride. The product was purified by chromatography using a 5% solution of ethyl acetate in hexane. Yield 525 mg (75%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.5–1.9 m (4H), 2.0–2.2 m (2H), 2.35–2.45 m (2H), 6.0–6.05 m (1H) (cf. [10]). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.04, 24.43, 27.35, 35.10, 122.25, 128.77.

3-Bromo-2-cyclohexenone was synthesized in a similar way from 1.23 g (0.0468 mol) of triphenylphosphine, 0.25 g (0.00223 mol) of 1,3-cyclohexanedione, and 1.92 g (0.0468 mol) of 2,4,4,6-tetrabromo-2,5-cyclohexadienone in dry methylene chloride. The product was purified by chromatography using 1:1 hexane–chloroform as eluent. Yield 345 mg (88%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.9–2.05 m

(2H), 2.2–2.35 m (2H), 2.65–2.8 m (2H), 6.4 t (1H) (cf. [11]). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 22.83, 36.13, 36.26, 132.46, 149.91, 196.08 (cf. [12]).

α-Bromostyrene was synthesized in a similar way from 1.14 g (0.0024 mol) of triphenylphosphine, 0.25 g (0.002 mol) of acetophenone, and 1.79 g (0.0042 mol) of 2,4,4,6-tetrabromo-2,5-cyclohexadienone in *o*-dichlorobenzene. Subsequent chromatographic separation (using petroleum ether as eluent) gave 450 mg of a mixture of *o*-dichlorobenzene and α-bromostyrene at a ratio of 7:1 (according to the ^1H NMR data). The yield of α-bromostyrene was 15%. It was identified by the signals of the methylene [δ, ppm: 5.76 d (1H), 6.10 d (1H)] and aromatic protons [δ, ppm: 7.42 (5H)] (cf. [13]).

Reaction of complex I with benzophenone. A mixture of 0.863 g (0.00329 mol) of triphenylphosphine, 0.2 g (0.0011 mol) of benzophenone, and 1.348 g of 2,4,4,6-tetrabromo-2,5-cyclohexadienone in dry methylene chloride, anhydrous acetone, or anhydrous toluene was refluxed for 3 days. Chromatographic separation using 1:1 hexane–benzene gave 99% of initial benzophenone (retention time 3.72 min; oven temperature 220°C, injector temperature 270°C).

REFERENCES

1. Matveeva, E.D., Podrugina, T.A., and Zefirov, N.S., *Mendeleev Commun.,* 1998, no. 1, pp. 21–23.
2. Matveeva, E.D., Podrugina, T.A., Sandakova, N.G., and Zefirov, N.S., *Sbornik trudov konferentsii "Peterburgskie vstrechi-98"* (Proc. Conf. "St. Petersburg Meetings-98"), St. Petersburg, 1998, p. 175.
3. Villieras, J., Tarhouni, R., Kirscheger, B., and Rambaund, M., *Bull. Soc. Chim. Fr.,* 1985, no. 5, p. 825.
4. Hoffmann, R.W. and Bovicelli, P., *Synthesis,* 1990, p. 657.
5. Martinez, A.G., Fernandez, A.H., Alvarez, M.R., Fraile, A.G., Calderon, J.B., and Barcina, J.O., *Synthesis,* 1986, no. 12, pp. 1076–1078.
6. Kuchin, V.A., Markova, S.A., and Tolstikov, G.A., *Zh. Obshch. Khim.,* 1988, vol. 58, no. 4, p. 934.
7. Tsubota, M., Iso, M., and Suzuki, K., *Bull. Chem. Soc. Jpn.,* 1972, vol. 45, no. 4, p. 1252.
8. *The Aldrich Library of NMR Spectra,* 1974, vol. IV, p. 38.
9. Mironov, V.F., Ofitserov, E.N., Sinyashina, T.N., and Konovalova, I.V., *Zh. Org. Khim.,* 1990, vol. 26, no. 12, p. 2570.
10. Newnan, H. and Seebah, D., *Chem. Ber.,* 1978, vol. 111, no. 8, pp. 2785–2812.
11. Piers, E., Grierson, J.R., Lan, Ch.K., and Nikagura, I., *Can. J. Chem.,* vol. 60, no. 2, p. 210.
12. Hofle, G., *Tetrahedron,* 1976, vol. 32, no. 12, p. 1431.
13. Soderquist, J.A. and Hassner, A., *J. Org. Chem.,* 1983, vol. 48, no. 11, p. 1801.