Organic Preparations and Procedures International: The New Journal for Organic Synthesis
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uopp20

A FACILE METHOD FOR DEBROMINATION OF vic-DIBROMIDES

Ming Zheng [a] , Mei-Hua Zhang [a] , Jian-Guo Shao [a] & Qi Zhong [a]
[a] Department of Chemistry, Yangzhou University Yangzhou, Jiangsu, P. R. CHINA

To cite this article: Ming Zheng , Mei-Hua Zhang , Jian-Guo Shao & Qi Zhong (1996): A FACILE METHOD FOR DEBROMINATION OF vic-DIBROMIDES, Organic Preparations and Procedures International: The New Journal for Organic Synthesis, 28:1, 117-120

To link to this article: http://dx.doi.org/10.1080/00304949609355916

ethyl acetate (250 mL). The resulting mixture was heated to reflux for 10 minutes. After cooling to room temperature, the white solid was collected, washed with ethyl acetate (3 x 50 mL) and dried to give 13.7 g (93%) of buspirone N-oxide oxalic acid salt (**3**), mp 114-116°C. ^{1}H NMR ($CDCl_3$): δ 8.37 (d, J = 4.2Hz, 2H), 6.62 (t, J = 4.2Hz, 1H), 4.79 (m, 2H), 3.98 (m, 2H), 3.80 (m, 6H), 3.23 (m, 2H), 2.59 (s, 4H), 1.90 (m, 2H), 1.65 (m, 6H), 1.47 (m, 4H).

Anal. Calcd. for $C_{23}H_{33}N_5O_7$: C, 56.20; H, 6.77; N, 14.25. Found: C, 56.12; H, 6.75; N, 14.20

REFERENCES

† Current address: Chemical Process Technology, Bristol-Myers Squibb Pharmaceutical Research Institute, One Squibb Drive, New Brunswick, NJ 08903-0191.

1. K. L. Goa and A. Ward, *Drugs*, **32**, 114 (1986). A. S. Eison and D. L. Temple, *Am. J. Med.*, **80(3B)**, 1 (1986).
2. D. P. Taylor, *FASEB J.*, **2**, 2445 (1988), and references cited therein.
3. M. Hudlicky, in *Oxidations in Organic Chemistry*, pp 236-239, Am. Chem. Soc., Washington, DC, 1990.
4. For a review, see W. B. Cowden, in *Heterocyclic Compounds,* Vol. 16, Suppl. II, pp 353-356, D. J. Brown, Ed., John Wiley & Sons, 1985.
5. W. W. Zajac, Jr., T. R. Walters and M. G. Darcy, *J. Org. Chem.*, **53**, 5856 (1988).
6. For a review, see F. A. Davis and A. C. Sheppard, *Tetrahedron*, **45**, 5703 (1989).
7. F. A. Davis, S. Chattopadhyay, J. C. Towson, S. Lal and T. Reddy, *J. Org. Chem.*, **53**, 2087 (1988).

****

A FACILE METHOD FOR DEBROMINATION OF *vic*-DIBROMIDES

Submitted by (07/14/95)

Ming Zheng, Mei-Hua Zhang, Jian-Guo Shao and Qi Zhong*

Department of Chemistry, Yangzhou University
Yangzhou, Jiangsu, P. R. CHINA

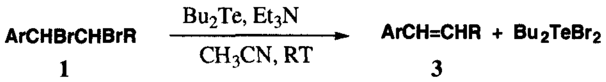
Dehalogenation of organic halides is an important and widely utilized reaction in organic chemistry.[1] Although there have been reports on the application of organotellurium reagents to the dehalogenation of *vic*-dihalides,[2,5] the debromination of *vic*-dibromides by dibutyl telluride has never been reported. The fact that α-bromocarbonyl compounds are easily debrominated by dibutyl telluride[6] to give carbonyl compounds led us to investigate its reaction with *vic*-dibromides.

We found that *vic*-dibromides could be debrominated by dibutyl telluride to give the corresponding olefins; the reaction is greatly accelerated by triethylamine. For example, the reaction of 1,2-dibromo-l-phenyl-2-(4-chlorophenyl)ethane and dibutyl telluride in acetonitrile at room temperature was complete in 3 hrs in the presence of an equimolar amount of triethylamine; in the absence of the amine, the reaction required 12 hrs. Similar results were obtained in the debromination of other *vic*-dibromides (1 and 2). Optimum conditions and results for all reactions are given in Table 1. The

TABLE 1. Reaction Time, Yields and mp.

Cmpd	Time[a] (hrs)	Yield (%)	mp (°C)	lit. mp (°C)
3a	3	94.4	123-124	124[9]
3b	2	97.8	151-152	155[9]
3c	3	97.7	125-126	129[9]
3d	3	95.2	130-131	136[9]
3e	2	94.1	125-126	131[9]
3f	3	94.7	121-123	123.5[9]
3g	3	94.3	140-141	142-143.5[7]
3h	2	86.0	131-132	135[9]
4a	4	91.3	109-110	112-113[9]
4b	3	94.1	189-190	193[9]
4c	6	92.3	170-171	175[9]

a) **1a-h**: Bu_2Te: Et_2N = 1:1:1 (molar ratio); **2a-c**: Bu_2Te: Et_2N = 1:2:2 (molar ratio)



$$\underset{\mathbf{1}}{\text{ArCHBrCHBrR}} \xrightarrow[\text{CH}_3\text{CN, RT}]{\text{Bu}_2\text{Te, Et}_3\text{N}} \underset{\mathbf{3}}{\text{ArCH=CHR}} + \text{Bu}_2\text{TeBr}_2$$

a) Ar = R = C_6H_5 b) Ar = C_6H_5, R = *p*-$O_2NC_6H_4$ c) Ar = C_6H_5, R = *p*-ClC_6H_4
d) Ar = C_6H_5, R = *p*-$CH_3OC_6H_4$ e) Ar = C_6H_5, R = *m*-$O_2NC_6H_4CO$
f) Ar = *p*-BrC_6H_4, R = C_6H_5CO g) Ar = *p*-$CH_3C_6H_4$, R = *m*-$O_2NC_6H_4CO$
h) Ar = C_6H_5, R = CO_2H i) Ar = C_6H_5, R = C_6H_5CO
j) Ar = *p*-ClC_6H_4, R = C_6H_5CO k) Ar = *m*-$O_2NC_6H_4$, R = C_6H_5CO

$$\underset{\mathbf{2}}{\text{(ArCHBrCHBr)}_2\text{CO}} \xrightarrow[\text{CH}_3\text{CN, RT}]{\text{Bu}_2\text{Te, Et}_3\text{N}} \underset{\mathbf{4}}{\text{(ArCH=CH)}_2\text{C=O}} + \text{Bu}_2\text{TeBr}_2$$

a) Ar = C_6H_5 b) Ar = *p*-ClC_6H_4 c) Ar = *p*-$CH_3C_6H_4$ d) Ar = *m*-ClC_6H_4

simplicity of manipulation and mild reaction conditions characterize this facile method for debromination of *vic*-dibromides. In addition, we found that the dibutyl dibromotelluride generated during the reaction can be reduced by sodium hydrosulfite to regenerate dibutyl telluride. Thus, only catalytic amounts of dibutyl telluride is required for the debromination reaction.

$$Bu_2TeBr_2 + Na_2S_2O_4 \longrightarrow Bu_2Te + 2NaBr + 2SO_2$$

The debromination of **1f, g, i, j, k, 2a** and **2d** by this convenient method (B) produced the olefins listed in Table 2.

EXPERIMENTAL SECTION

Melting point are uncorrected and were taken on a Buchi 535 apparatus. Elemental analyses were performed on a Carlo Erba 1106 apparatus. IR spectra were recorded on a Nicolet DX spectrophotometer. ^{1}H NMR spectra were run on a BRUKER QC-P200 spectrometer in $CDCl_3$ using TMS as internal standard.

General Procedures for the Debromination of *vic*-Dibromides. Method A.- A mixture of *vic*-dibromides (1 mmol), dibutyl telluride (1 mmol)[8] and triethylamine (1 mmol) in acetonitrile (8 mL) were stirred at room temperature. The reaction was monitored with HPLC. After completion of the reaction, water was added and the crystalline product was collected. The products (**3a-h, 4a-c**) were recrystallized from 95% ethanol.

Method B.- A mixture of vic-dibromides (1 mmol), dibutyl telluride (0.1 mmol) and sodium hydrosulfite (10 mmol) in benzene (7 mL) and water (5 mL) was stirred at reflux temperature under nitrogen. The progress of the reaction was monitored with TLC (1:1 petroleum ether- chloroform). Upon completion of the reaction, the organic phase was separated, and washed twice with water.

The aqueous phase was then extracted twice with benzene. The organic extracts were combined and dried over anhydrous sodium sulfate. Removal of benzene gave products **3f, g, i, j, k, 4a, 4d**, which were recrystallized from 95% ethanol (See Table 2). The structure of the products was confirmed by elemental analyses and by IR and ^{1}H NMR spectroscopy. The results are listed in Table 3.

TABLE 2. Mps, Yield, Reaction Time and Elemental Analyses

Cmpd	mp (°C)	Yield (%)	Time (hrs)	Analyses (Found) C	H	N
3f	121-123	80	14	62.68 (62.74)	3.83 (3.86)	
3g	140-141	77	2	71.79 (71.90)	4.68 (4.90)	4.97 (5.24)
3i	54-55	52	12	86.40 (86.51)	5.76 (5.81)	
3j	109-110	89	8	74.30 (74.23)	4.66 (4.57)	
3k	141-142	82	6	71.08 (71.14)	4.36 (4.38)	5.50 (5.53)
4a	109-110	85	10	86.98 (87.15)	5.99 (6.02)	
4d	120-121	99	7	67.51 (67.35)	3.79 (3.99)	

TABLE 3. IR and ^{1}H NMR Spectra

Cmpd	IR (cm^{-1})	^{1}H NMR (δ, ppm)
3f	1656	7.48 (1H, d, J = 15.8Hz), 7.50-7.60 (7H, m), 7.70 (1H, d, J = 15.8Hz), 7.99 (2H, d-d, J = 8.0Hz)
3g	1656	2.41 (3H, S), 7.24 (1H, d, J = 8.0Hz), 7.45 (4H, d-d), 7.67 (1H, d, J = 15.8Hz) 7.84 (1H, d, J = 15.2Hz), 8.33 (2H, m) , 8.82 (1H, S)
3i	1667	7.41-7.66 (8H, m), 7.50 (1H, d, J = 15.6Hz) 7.79 (1H, d, J = 15.8Hz), 8.01 (2H, d-d, J = 8.4Hz)
3j	1657	7.37 (2H, d, J = 8.4Hz), 7.47 (2H, d, J = 8.4Hz) 7.54 (1H, d, J = 15.7Hz), 7.73 (1H, d, J = 15.7Hz) 7.56 (3H, m), 7.99 (2H, d-d, J = 9.4Hz)
3k	1663	7.49-7.66 (3H, m), 7.53 (1H, d, J = 7.8Hz) 7.62 (1H, d, J = 15.2Hz), 7.80 (1H, d, J = 15.8Hz) 7.91 (1H, d, J = 7.8Hz), 8.03 (2H, d-d, J = 8.2Hz) 8.24 (1H, d-d, J = 8.2Hz), 8.06 (1H, S)
4a	1652	7.05 (2H, d, J = 16.0Hz), 7.40 (6H, m), 7.60 (4H, m) 7.71 (2H, d, J = 16.0Hz)
4d	1670	7.01 (2H, d, J = 16..0Hz), 7.35-7.50 (8H, m), 7.63 (2H, d, J = 16.0Hz)

REFERENCES

1. A. R. Pinder, *Synthesis*, 429 (**1980**).
2. M. M. Campos and N. Petragnan, Tetrahedron Lett., **15**, 5 (1960).
3. L. Engman, *ibid.*, **23**, 3601 (1982).
4. L. Engman and S. E. Bystron, *J. Org. Chem.*, **50**, 3170 (1985).
5. X. Huang and Y. Hou, *Synth. Commun.*, **17**, 2201 (1988).
6. Q. Zhong, F. Ma, C. Q. Liu and J. G. Shao, *Youji Huaxue,* **11**, 209 (1991); *Chem. Abs.*, **115**, 91764j (1991).
7. *Chem. Abs.*, 72, 66551Y (1970).
8. M. P. Balfe, C.A. Chaplin and H. Phillips, *J. Chem. Soc.*, 341 (**1938**).
9. *Bellstein's Handbuch der Org. Chem.*, H 5, 631; EI 5, 305; H 5, 633; H 6, 693; EII 7, 429; EIII 7,427; EIII 9,2672; EII 7,452; H 7,505; H 7,508.

****