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A FACILE METHOD FOR DEBROMINATION OF vic-DIBROMIDES

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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. ¹H NMR (CDCl₃): 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 C₂₃H₃₃N₅O₇: C, 56.20; H, 6.77; N, 14.25. Found: C, 56.12; H, 6.75; N, 14.20

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A FACILE METHOD FOR DEBROMINATION OF *vic*-DIBROMIDES

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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

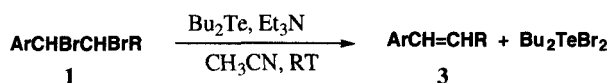
been reported. The fact that α -bromocarbonyl compounds are easily debrominated by dibutyl telluride⁶ to give carbonyl compounds led us to investigate its reaction with *vic*-dibromides.

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-1-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

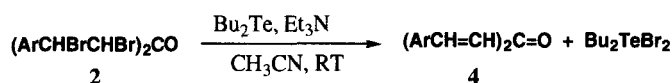
TABLE 1. Reaction Time, Yields and mp.

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: Bu₂Te: Et₃N = 1:1:1 (molar ratio); 2a-c: Bu₂Te: Et₃N = 1:2:2 (molar ratio)

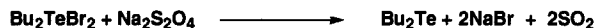


- a) Ar = R = C₆H₅ b) Ar = C₆H₅, R = *p*-O₂NC₆H₄ c) Ar = C₆H₅, R = *p*-ClC₆H₄
d) Ar = C₆H₅, R = *p*-CH₃OC₆H₄ e) Ar = C₆H₅, R = *m*-O₂NC₆H₄CO
f) Ar = *p*-BrC₆H₄, R = C₆H₅CO g) Ar = *p*-CH₃C₆H₄, R = *m*-O₂NC₆H₄CO
h) Ar = C₆H₅, R = CO₂H i) Ar = C₆H₅, R = C₆H₅CO
j) Ar = *p*-ClC₆H₄, R = C₆H₅CO k) Ar = *m*-O₂NC₆H₄, R = C₆H₅CO



- a) Ar = C₆H₅ b) Ar = *p*-ClC₆H₄ c) Ar = *p*-CH₃C₆H₄ d) Ar = *m*-ClC₆H₄

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.



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. ¹H NMR spectra were run on a BRUKER QC-P200 spectrometer in CDCl₃ 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 ¹H 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 ¹H 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)

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