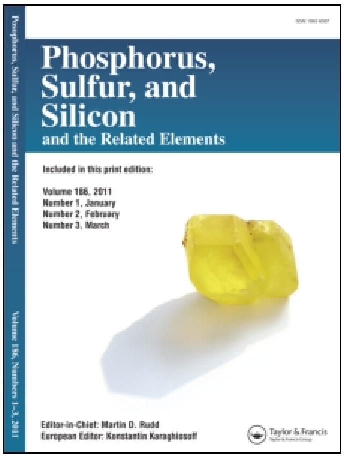

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N,N-DIBROMOBENZENESULFONAMIDE: A USEFUL REGENRABLE REAGENT FOR BROMINATION OF VARIOUS CARBANIONIC SUBSTRATES

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N,N-Dibromobenzenesulfonamide(dibromoamine-B), which is prepared easily in high yield, has been employed as effective brominating agent for carbanionic substrates under mild conditions. β-Diketones and β-ketoesters were brominated by this reagent without using any bases. The reagent can be recovered, rebrominated, and reused several times.

Keywords: β-Dicarbonyl compounds; bromination; dibromoamine-B

Since α-bromo carbonyl componds and 1-bromo-1-alkynes are useful synthetic intermediates in a number of widely different organic transformations, numerous methods are available for bromination of the α-position of carbonyl compounds, alkynes, and other organic compounds using various brominating reagents. These include: $KMnO_4/HBr/CH_3CN$[1] and $KBrO_3/KBr$/Dowex[2] for bromination of 1,3-dicarbonyl substrates, N-bromosuccinimide for bromination of carboxylic acids,[3] carbonyl-conjucated alkynes,[4] nitro compounds,[5] N-bromosaccharin for brominating of the benzylic and α-carbonylic positions,[6] triphenyl phosphine and CBr_4 for bromination of primary alkynes,[7] benzyl trimethylammonium tribromide,[8] tetra butylammonium tribromide,[9] trimethylamine-boron bromide,[10] carbon tetrabromide,[11] 1,2-dibromoethane,[12] quinolinium bromochromate

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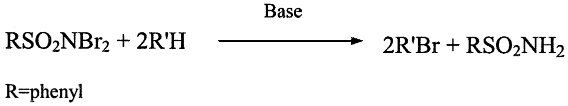
(QBC),[13] sodium hypobromite-sodium bisulfite ($NaBrO_3/NaHSO_3$),[14] and others[15] also were applied for brominating organic compounds. All these reagents have some disadvantages such as instability, low yield, toxic reagents, nonselectivity, and tedious work-up.

RESULTS AND DISCUSSION

The N,N-dibromobenzenesulfonamide is a stable crystalline compound easily prepared[16] by brominating directly a sodium carbonate or bicarbonate solution of the benzenesulfonamide, which gives an almost quantitative yield of the pure product. The reaction seems to proceed in two steps, $C_6H_5SO_2NBrNa$ first dissolving to give a yellow solution; then the second step occurs, and the yellow dibromide precipiates (Scheme 1).



$$RSO_2NBr_2 + 2R'H \xrightarrow{\text{Base}} 2R'Br + RSO_2NH_2$$

R=phenyl

SCHEME 1

Treatment of carbanions with N,N-dibromobenzenesulfonamide results in the transfer of bromine from nitrogen to carbon. A broad variety of anions, including β-diketones, β-ketoesters, malonates, nitroalkanes, and alkynes can be brominated in high yield (Table I). It should be mentioned that β-diketones and β-ketoesters are brominated at room temperatures and 60°C, respectively, without using any base.

The sulfonamide formed in this reaction is easily recovered, rebrominated, and reused several times.

EXPERIMENTAL

The chemicals were obtained from Aldrich Chemical Co. and were used as received without further purification. Fluka silica gel plates (F_{254}) were used for TLC. Elemental analyses (CHN) were performed on a Perkin-Elmer 2400 CHN analyzer. The IR spectra were recorded on a Perkin-Elmer 130 spectrophotometer and ^1H NMR spectra were recorded in CCl_4 on a Varian (60 and 90 MHz) spectrometer using TMS as an internal standard.

TABLE I Bromination of Carbanions with N,N-Dibromobenzenesulfonamide

Entry	Substrate	Product	Base	Temp. (°C)	Time (min)	Yield[a] (%)
1	$CH_3COCH_2COCH_3$	$CH_3COCBr_2COCH_3$	—	r.t.	30	85
2	$CH_3COCH_2CO_2C_2H_5$	$CH_3COCBr_2CO_2C_2H_5$	—	60	240	92
3	$PhCOCH_2COPh$	$PhCOCBr_2COPh$	—	60	120	85
4	$CH_2(CO_2C_2H_5)_2$	$CBr_2(CO_2C_2H_5)_2$	NaH	0	60	87
5	$CH_3CH(CO_2C_2H_5)_2$	$CH_3CBr(CO_2C_2H_5)_2$	NaH	0	60	88
6	$PhCH(CO_2C_2H_5)_2$	$PhCBr(CO_2C_2H_5)_2$	NaH	0	60	88
7	$NCCH_2CO_2C_2H_5$	$NCCBr_2CO_2C_2H_5$	NaH	0	60	90
8	$CH_3CHNO_2CH_3$	$CH_3CBrNO_2CH_3$	NaH	0	60	91
9	$PhC{\equiv}CH$	$PhC{\equiv}CBr$	NaH	0	60	95
10	$C_4H_9C{\equiv}CH$	$C_4H_9C{\equiv}CBr$	NaH	0	60	78

[a] Yield refers to the isolated productsv that exhibited physical and spectral properties in accordance with the assigned structure.

Preparation of N,N-Dibromobenzenesulfonamide

In a 250 ml three-necked flask were placed 5 g of benzenesulfonamide, 3.6 g of KOH and 25 ml of water; then 10 g of bromine were added with vigorous stirring. The resulting precipitate of N,N-dibromobenzenesulfonamide was filtered, washed in water and dried. The yield was 9.8 (98%).

a) Bromination of Acidic Organic Compound in the Presence of a Base

A solution of carbanion in anhydrous tetrahydrofuran [prepared in conventional fashion by adding an 80% dispersion of NaH (20 mmol) in oil to the substrate (10 mmol) in THF (10 ml)] was added under dry nitrogen to a stirred slurry of the reagent (10 mmol) in CH_2Cl_2 (15 ml) at 0°C. The reaction mixture was allowed to warm to room temperature and treated with diethyl ether (50 ml). The mixture was then washed with 0.5 M oxalic acid (30 ml), 10% aqueous potassium hydrogen carbonate (30 ml), and saturated brine (30 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was washed with n-hexane and filtered. The filtrate was evaporated to give the pure product in high yield (Table I). The solid phase was removed by filtration and recrystallized with ethanol and water to give the recovered sulfonamide in 80% yield.

b) Bromination of β-Diketones and β-Ketoesters without Base

To a solution of β-diketone or β-ketoester (9 mmol) in carbon tetrachloride or cyclohexane (20 ml) was added the reagent (9 mmol), and the mixture was stirred at room temperature and 60°C, 5 h for β-ketoeseters and 1/2 h for β-diketones. The progress of the reaction was monitored by TLC (eluent: hexane/EtoAc 5:1). The reaction mixture was filtered. The filtrate was evaporated to yield the α,α-dibromo β-diketones as pale yellow oils. All products were characterized by physical and spectral methods (M.P. IR, NMR, and CHN analysis).

3,3-Dibromo-2,4-pentandione: ^{1}H NMR(CCl_4)$\delta = 2.57$ (s, 6H, $2CH_3$). Anal. Calc. for $C_5H_6Br_2O_2$: C, 23.32; H, 2.21. Found: C, 23.21; H, 2.29.

Ethyl 2,2-dibromo acetoacetate: ^{1}H NMR(CCl_4)$\delta = 1.15$(t, 3H, CH_3—CH_2); 2.59 (s, 3H, CH_3); 4.37(q, 2H, CH_3—CH_2)/Anal. Calc. for $C_6H_8Br_2O_3$: C, 25.00; H, 2.78. Found: C, 25, 10; H, 2.80.

2-Bromo-2-nitropropane: ^{1}H NMR(CCl_4)$\delta = 2.28$ (s, 6H, $2CH_3$). Anal. Calc. for $C_5H_6BrNO_2$: C, 21.43; H, 3.57; N, 8.33. Found: C, 21.68; H, 3.90; N, 8.50.

Diethyl-2,2-dibromo malonate: ^{1}H NMR(CCl_4)$\delta = 1.25$ (t, 6H, $2CH_2$—CH_3); 4 (q, 4H, $2CH_3$—CH_2). Anal. Calc. for $C_7H_{10}Br_2O_4$: C, 26.41; H, 3.14. Found: C, 26.10; H, 3.00.

Diethyl 2-bromo-2-methylmalonate: ^{1}H NMR(CCl_4)$\delta = 1.3$(t, 6H, $2CH_2$—CH_3); 2(s, 3H, CH_3); 4.2(q, 4H, $2CH_3$—CH_2). Anal. Calc. for $C_8H_{13}BrO_4$: C, 37.94; H, 5.14. Found: C, 37.61; H, 4.98.

Diethyl 2-bromo-2-phenylmalonate: ^{1}H NMR(CCl_4)$\delta = 1.2$(t, 6H, $2CH_2$—CH_3); 4(q, 4H, $2CH_3$—CH_2), 7(s, 5H, aromatic H). Anal. Calc. for $C_{13}H_{15}BrO_4$: C, 49.52; H, 4.76. Found: C, 49.27; H, 4.71.

1-Bromo-2-phenylacetylene: ^{1}H NMR(CCl_4)$\delta = 6.8$(s, 5H, aromatic H). Anal. Calc. for C_8H_5Br: C, 53.04; H, 2.76. Found: C, 52.97; H, 2.71.

Ethyl 2,2-dibromo cyanoaceteate: ^{1}H NMR(CCl_4)$\delta = 1.25$(t, 3H, CH_2—CH_3); 4(q, 2H, CH_3—CH_2). Anal. Calc. for $C_5H_5Br_2NO_2$: C, 22.14; H, 1.84. N. 5.17, Found: C, 22.52; H, 1.99; N, 5.26.

3,3-Dibromo-1.3-diphenyl-1,3-propanedione: ^{1}H NMR(CCl_4)$\delta =$ 7.2(d, 10H, Aromatic H). Anal. Calc. for $C_{15}H_{15}Br_2O_2$: C, 47.12; H, 2.62. Found: C, 47.34; H, 2.51.

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