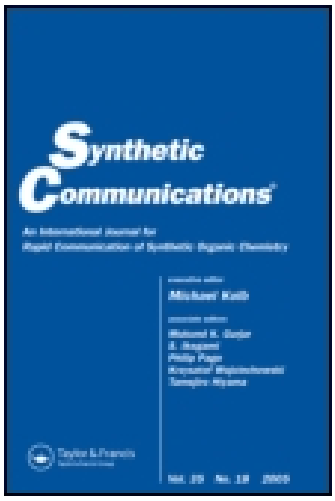

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BROMINATION OF ORGANIC ALLYLIC COMPOUNDS BY USING N,N′-DIBROMO-N,N′-1,2-ETHANE DIYL BIS(2,5-DIMETHYL BENZENE SULPHONYL)AMINE

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BROMINATION OF ORGANIC ALLYLIC COMPOUNDS BY USING *N*,*N*′-DIBROMO-*N*,*N*′-1,2-ETHANE DIYL *BIS*(2,5-DIMETHYL BENZENE SULPHONYL)AMINE

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ABSTRACT

N,*N*′-Dibromo-*N*,*N*′-1,2-ethane diyl *bis*(2,5-dimethyl benzene sulphonyl)amine is an efficient brominating agent for bromination of allylic positions of different organic compounds. This reagent in presence of benzoyl peroxide can brominates the allylic positions of organic compounds in ambient conditions in carbon tetrachloride.

Selective bromination of allylic compounds in organic chemistry is very important and can be achieved by many reagents.[1] One of the classic reagents is *N*-bromosuccinimide which is used for bromination of allylic positions.[2,3] Reaction mechanism is shown by McCoy and Douben,[4]

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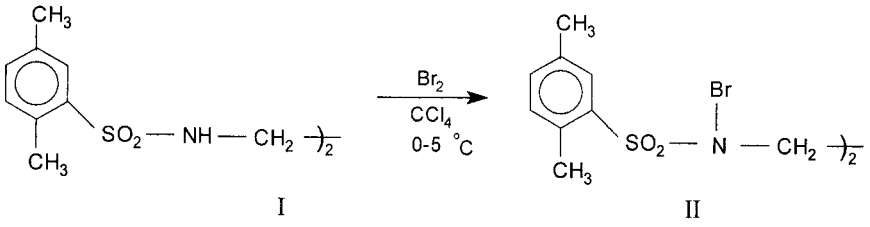
and further reaction mechanism is shown that a trace of bromine molecule is present with NBS.[5]

In these procedures, the bromination of allylic positions were not occurred without using of peroxide and also the yield of bromination product were not excellent.

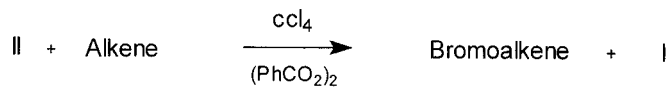
For this reason we attempted to work with our previous reagent to compare the ability of it with NBS[6] (Scheme 1).



I II

Scheme 1.

Here, we report a simple procedure for the bromination of allylic positions of different types of alkenes (Scheme 2). Bromination can be readily carried out by placing of II, alkene (1) in CCl_4 as the solvent in a reaction vessel and stirring the resulting mixture for 1–1.5 h under reflux conditions. The brominated alkenes were obtained by filtration and evaporation of the solvent. The results are shown in the Table1.



Scheme 2.

In order to show the capability of our reagent, the results are compared with NBS (Table 2).

The advantages of *N*-bromosulfonamide (II) are as follows:

1. The preparation of *N*-bromosulfonamide is very easy.
2. *N*-bromosulfonamide is stable for time in atmospheric condition.
3. After reaction of *N*-bromosulfonamide with substrate, the sulfonamide is recovered and can be reused many times without decreasing the yield.

Table 1. Bromination of Allylic Position of Alkenes with: *N*,*N*′-Dibromo-*N*,*N*′-1,2-ethane Diyl *bis*(2,5-Dimethyl Benzene sulphonyl)amine(II) in CCl_4 Under Reflux Condition

Entry	Substrate	Product	Reagent/Subst.	Time (h)	Yields (%)
1	Cyclohexene	3-Bromocyclohexene	0.516	1	60
2	1,5-Cyclooctadiene	3,5-Dibromo-1,5-cyclooctadiene	0.516	1	65
3	Methyl but-2-enolate	Methyl-4-bromobut-2-enolate	0.516	10	88
4	Ethyl but-2-enolate	Ethyl-4-bromobut-2-enolate	0.516	10	89
5	2-Heptene	4-Bromo-2-heptene	0.516	1	73
6	1-Phenyl-1-propene	3-Bromo-1-Phenyl-1-propene	0.516	1	76
7	Methyl-2-methyl acrylate	Methyl-2-(bromomethyl) acrylate	0.516	1	72
8	4-Methyl ethyl pant-2-enolate	4-Methyl ethyl 3-bromopant-2-enolate	0.516	6	82
9	2-Methyl methyl but-2-enolate	2-Methyl methyl-4-bromobut-2-enolate	0.516	5	51
10	2-Methyl acrylic acid	2-(Bromomethyl)acrylic acid	0.516	6	74

Table 2. Comparison of the Results Obtained by Our Method with Those Reported by NBS

	Yields	
Substrate	II	NBS
Cyclohexene	60	45[7]
Methyl but-2-enolate	88	86[7]
2-Heptene	73	58–64[8]
4-Methyl ethyl pant-2-enolate	82	81[9]
2-Methyl methyl but-2-enolate	51	45[10]

EXPERIMENTAL SECTION

IR and NMR spectra were recorded using a Shimadzu 435-U-04 spectrophotometer (KBr pellets) and a 90 MHz Geol FT-NMR spectrometer, respectively. NMR chemical shifts were measured relative to TMS (int; 1H). Reagent was prepared by our previously reported procedure.[6]

Bromination of Cyclohexene with *N*,*N*′-Dibromo-*N*,*N*′-1,2-ethylene *bis*(2,5-Dimethyl Benzenesulfonamide). A Typical Procedure

In a 50 mL round-bottomed flask 5.41 g (0.0098 mol) of *N*-bromosulfonamide, 30 mL of carbon tetrachloride, 1.61 g (0.0196 mol) of redistilled cyclohexene and 0.05 g of benzoyl peroxide is placed. The flask is equipped with a condenser and the reaction mixture allowed to stand at room temperature. After a short induction period the reaction mixture becomes warm and light, colourless sulfonamide(crystals) begin to precipitate. The flask was cold in ice-water. After the reaction the sulfonamide was filtered under suction and washed with 10 mL of cold carbon tetrachloride. Distil the filterate on a boiling water bath, first of all the carbon tetrachloride was removed (b.p. 77°C), then, unreacted cyclohexene (b.p. 83°C). The residue was distilled (b.p. 66–67°C/20 mm) with 60% yield. This compound was identified by T.L.C, IR, NMR spectroscopies and elemental analysis. IR (KBr pellets) 3050, 2950, 1650, 1170, 650 cm^{-1}; ^{1}H-NMR ($CDCl_3$): $\delta = 5.634$ (s, 2H), $\delta = 3.415$ (q. 1H), $\delta = 1.996$ (brd, 2H), $\delta = 1.196$ (t, 2H), ^{13}C-NMR : $\delta = 11.426$, 14.340, 16.886, 30.018, 120.878, 127.204. Found: C, 54.73; H, 6.90%. Calcd. for C_6H_9 Br: C, 54.92; H, 6.92%.

3,7-Dibromo-1,5-cyclooctadiene

The residue was distilled (b.p. 134–136°C/20 mm) with 65% yield. This compound was identified by T.L.C, IR, NMR spectroscopies and elemental analysis. IR (KBr pellets) 3100, 2970, 1690, 1200, 645 cm^{-1}; ^{1}H-NMR ($CDCl_3$): $\delta = 5.624$ (brd, 4H), $\delta = 3.419$ (q, 2H), $\delta = 1.197$ (t, 4H), ^{13}C-NMR: $\delta = 15.266$, 30.286, 122.657, 128.119. Found: C, 36.22; H, 3.55%. Calcd. for $C_8H_{10}Br_2$: C, 36.12; H, 3.80%.

Methyl 4-Bromobut-2-enoate

The residue was distilled (b.p. 77–78°C/8 mm) with 87% yield. This compound was identified by T.L.C, IR, NMR spectroscopies and elemental analysis. IR (KBr pellets) 3050, 2950, 1720, 1450, 1220 cm^{-1}; ^{1}H-NMR ($CDCl_3$): $\delta = 3.8$ (s, 3H), $\delta = 4.1$ (d, 2H), $\delta = 6$ (d, 1H), $\delta = 7$ (shul., 1H), ^{13}C-NMR: $\delta = 165.341$, 127.482, 120.542, 65.324, 31.15. Found: C, 33.62, H, 3.81%. Calcd. for $C_5H_7BrO_2$: C, 33.54; H, 3.94%.

Ethyl 4-Bromobut-2-enoate

The residue was distilled (b.p. 94–95°C/12 mm) with 89% yield. This compound was identified by T.L.C, IR, NMR spectroscopies and elemental analysis. IR (KBr pellets) 3050, 2950, 1750, 1430, 1280, 1100, 1000, 900, 850 cm^{-1}; ^{1}H-NMR ($CDCl_3$): $\delta = 1.3$ (t, 3H), $\delta = 4.1$ (m, 4H), $\delta = 6$ (d, 1H), $\delta = 7$ (m, 1H); ^{13}C-NMR: $\delta = 164.351$, 128.483, 119.315, 64.232, 30.16. Found: C, 31.21; H, 4.61%. Calcd. for $C_6H_9BrO_2$: C, 31.11; H, 4.70%.

4-Bromo-2-heptene

The residue was distilled (b.p. 70–71°C/32 mm) with 73% yield. This compound was identified by T.L.C, IR, NMR spectroscopies and elemental analysis. IR (KBr pellets) 3050, 2970, 1425, 670 cm^{-1}; ^{1}H-NMR ($CDCl_3$): $\delta = 1.3$ (d, 3H), $\delta = 1.2$ (m, 7H), $\delta = 4.1$ (m, 2H), $\delta = 6.1$ (m, 1H), $\delta = 7.2$ (m, 1H); ^{13}C-NMR: $\delta = 125.419$, 121.316, 60.182, 31.513. Found: C, 42.21; H, 7.92%. Calcd. for $C_7H_{14}Br$: C, 47.10; H, 7.81%.

3-Bromo-1-phenyl-1-propene

The residue (m.p. 27–29°C) with 76% yield. This compound was identified by T.L.C, IR, NMR spectroscopies and elemental analysis. IR (KBr pellets) 3040, 2980, 1440, 680 cm^{-1}; ^{1}H-NMR ($CDCl_3$): $\delta = 7.9$ (d, 3H), $\delta = 7.1$ (d, 2H), $\delta = 8$ (d, 1H), $\delta = 6.5$ (t, 1H), δ=3.8 (d, 2H); ^{13}C-NMR: $\delta = 125.310$, 121.140, 62.650. Found: C, 51.92; H, 4.90%. Calcd for C_9H_9Br: C, 51.90; H, 4.95%.

2-(Bromomethyl)acrylic Acid

The residue (m.p. 70–73°C) with 74% yield. This compound was identified by T.L.C, IR, NMR spectroscopies and elemental analysis. IR (KBr pellets) 3046, 2980, 1420, 670 cm^{-1}; ^{1}H-NMR ($CDCl_3$): $\delta = 1.3$ (m, 7H), $\delta = 4$ (m, 2H), $\delta = 6.2$ (m, 1H), $\delta = 7.1$ (m, 2H); ^{13}C-NMR: $\delta = 123.320$, 120.432, 62.270, 30.151. Found: C, 43.92; H, 7.39%. Calcd. for $C_6H_{12}Br$: C, 43.60; H, 7.42%.

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