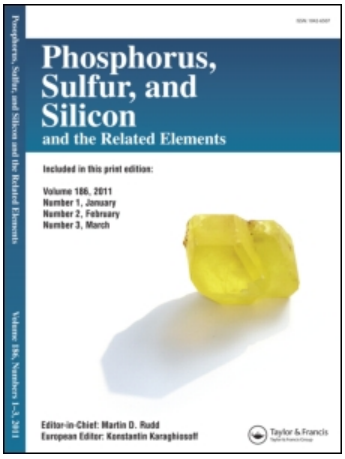

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Chemoselective Bromination in a Two-Step Substitution Under the Influence of Tetrachlorosilane and *N*-Bromosuccinimide

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Chemoselective Bromination in a Two-Step Substitution Under the Influence of Tetrachlorosilane and *N*-Bromosuccinimide

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The synthesis of gem dibromide carbonyl compounds via a cheep and readily available combined reagent from tetrachlorosilane and N-bromosuccinimide (TCS-NBS).

N-bromosuccinimide has been used as a source of bromine atoms for the monosubstitution of an allylic position, aromatic side chains,[1,2] or an addition to a double bond.[3] Also, it has been used for the oxidation[4–7] and halogenation of 9-methylanthracene, which occurs slowly in the absence of iodine to afford solely 9-(bromomethyl)anthracene. The bromo product reacted more slowly with NBS in the presence of iodine to give 9-bromo-10-methylanthracene (67%) together with 9-(bromomethyl)anthracene[8] (31%). Iodine is known to retard free radical brominations.[9] Also, an aromatic nuclei reacted with NBS in the presence of stoichiometric amounts or catalytic amounts of Lewis acids or concentrated H_2SO_4,[10–12] TsOH,[13] silica gel,[14] and the zeolite HZSM-5.[15]

Recently, gem-dibromoalkenes have been prepared either via the reaction of appropriate carbonyl compounds with diethyl dibromomethyl phosphonate[16] or by the dibromomethylenation reaction[17] of the corresponding ketones in the presence of CBr_4 and Ph_3P.

We set for ourselves the goal of inventing a new type of bromination reaction that involves the ordered reassembly of ketone and a reagent for a maximum influence. Then we examined the reaction of various

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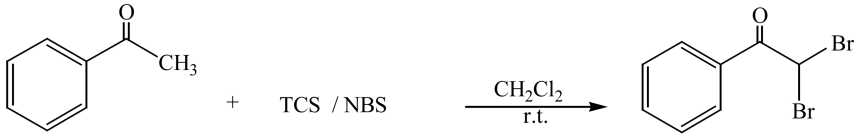
methylene ketones with TCS-NBS in the presence of CH_2Cl_2 as a solvent at ambient temperature; the corresponding 2,2-dibromoethanones were obtained in good yields. In the case of the reaction of TCS-NBS with acetophenone, the bromination took place selectively at the methyl group of the ethanone chain giving a gem dibromide. The highest yield (95%) of 2,2-dibromo-1-phenylethanone (1) was obtained with a twofold equimolecular amount of TCS-NBS reagent as on mechanism. The use of three or four moles of a brominating reagent led to a more complex mixture with a diminished yield of the required compound (1) (Scheme 1).



(1)

SCHEME 1

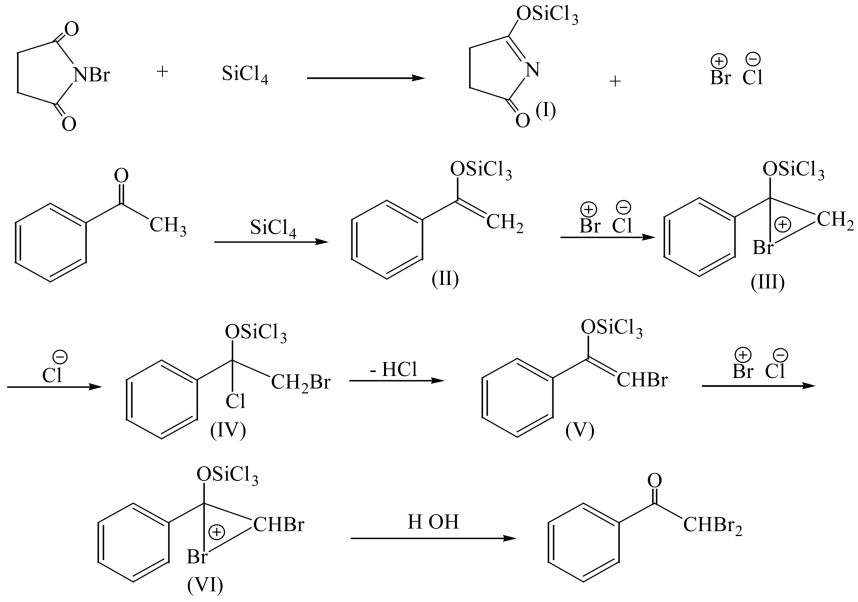
This procedure was applied to a number of useful selected substituted aromatic ethanones and aliphatic methyl carbonyl compounds. The bromination of some ethanones with TCS-NBS took place to give gem-dibromoethanone derivatives, as can be judged from the results compiled in Table I.

The use of a halogenated solvent, such as CH_2Cl_2, enhanced the reactivity of TCS-NBS for bromination. The halogenation media, which favored the propose mechanism, improved the use of TCS-NBS as a halogenated system. In accordance with this work, the use of TCS-NBS

TABLE I Using TCS/$ZnCl_2$. as a Binary Reagent in a Gem Dibromination Reaction

Exp. no.	Substrate	Time (h)	Product	Yield (%)
1	Acetophenone	5	2,2-dibromo-1-phenylethanone (1)	95
2	4-Chloroacetophenone	4	2,2-dibromo-1-(4′-chlorophenyl)ethanone (2)	91
3	4-Nitroacetophenone	6	2,2-dibromo-1-(4′-nitrophenyl)ethanone (3)	90
4	4-Methylacetophenone	3	2,2-dibromo-1-(*p*-tolyl)ethanone (4)	96
5	4-Acetylbiphenyl	3.5	2,2-dibromo-1-(4′-biphenyl)ethanone (5)	92
6	2-Acetylnaphthalene	4.5	2,2-dibromo-1-(2′-naphthyl)ethanone (6)	92
7	4-Acetylpyridine	5	2,2-dibromo-1-(4′-pyridyl)ethanone (7)	82
8	Acetanilide	1.5	2′,4′-dibromo acetanilide (8)	95

for bromination, an addition mechanism to vinyl silyl ether, may be operated in these processes.



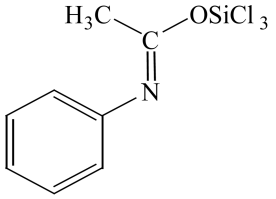
SCHEME 2

In the proposed mechanism, mixture of tetrachlorosilane and N-bromosuccinimide affords a siloxy imine (I) and bromonium chloride, which is considered a source of positive bromine. The addition of a positive bromine to an olefinic bond is believed to proceed via a bridged bromonium ion[18] (intermediate III) if the corresponding open β-bromocarbocation is less stable. The bromonium ion (III) may be interconverted by way of a strong nucleophile. The opening of the bromonium ion by a nucleophile (Cl^-) followed by the elimination of HCl would lead to intermediate (V) as illustrated in Scheme 2. The favored reaction of the monobromo-ethanone derivative by a second bromination, rather than the ring bromination, probably is due to the conformation of the monobromo-ethanone substituents, which preclude alignment of the methylene hydrogens with the formation of vinyl silyl enols. The second bromination proceeds the same way, and the product was obtained after hydrolysis.

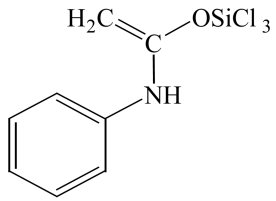
As indicated in Scheme 2, the electron density around the nitrogen atom in NBS is decreased on the coordination of $SiCl_4$, and the N—Br bond becomes weaker.[19] Subsequently, the electrophilic character, and therefore the hydride ion abstracting capacity of NBS, is increased after

complexation with TCS, resulting in an interaction with the protons of methylene groups.

The combination of stoichiometric quantities of NBS with TCS is quite efficient for a reaction of acetanilide. The isolated product was identified as 2′,4′-dibromoacetanilide (8). In this reaction, a mixture of tetrachlorosilane and acetanilide may be afforded the corresponding trichlorosiloxy imine (i) and not the trichlorosilyl vinyl ether (ii), which was not so sufficiently nucleophilic to react with the brominating reagent. The positive bromine may be interconverted by way of the activated aromatic nucleus of acetanilide as a strong nucleophile to form the corresponding 2′,4′-dibromo compound.



(i)



(ii)

SCHEME 3

EXPERIMENTAL

All reactions were carried out under atmospheric conditions at r.t. in the closed system with a condenser to abstract any HCl produced and avoid moisture. TCS and NBS were obtained in pure from a fluka bottle.

The solvents were distilled and dried over $CaCl_2$ before use. Reactions were monitored by TLC on 0.25 mm Merk Silica gel sheets (60 GF 354) (4 × 2 cm) developed with U.V. light or I_2 vapor.

General Procedure

A mixture of tetrachlorosilane (4.8 mL, 40 mmole) N-bromosuccinimide (3.6 g, 20 mmole), in CH_2Cl_2(20 ml) as solvent, was allowed to stir 5 min with an exclusion of moisture at an ambient temperature, 25°C. Ketones with α-two hydrogen atoms (10 mmole) were, added and the reaction mixtures were allowed to stir again for the time specified in Table I. It was poured into ice-cold (100 mL) water neutralized with a Na_2CO_3 solution and extracted with $CHCl_3$ (2 × 50 mL). The extract was dried over anhydrous Na_2SO_4, and the solvent was removed by

distillation. The residue was purified by column chromatography using pet. ether (60:80):ethyl acetate (6:1) as an eluant for isolated pure products.

2,2-Dibromo-1-phenylethanone (1)

The general procedure yielded the title compound (1)(2.94 g, 95%) from acetophenone (1.17 mL. 10 mmole), which was isolated using pet. ether (60:80): ethyl acetate (6:1) as an eluent system for column chromatography, $R_f = 0.65$ using an eluent (10:1), m.p. = 73–75°C.(Lit.[20]) IR ν = 3034–3000 (CH, Ar); 2935 (CH); 1698 (CO); 1600 (C=C); 600 (C—Br) cm $^{-1}$. ^{1}H NMR($CDCl_3$) δ = 7.86–7.80 (d, 2H, ArH), 7.37, 7.32 (m, 3H, Ar); 6.75 (s, 1H, CH); ppm. M.S.: (m/z, %) 278 (M^+, 1.16); 149 (M^+ - $CHBr_2$, 12.46); 105 (M^+ - $CHBr_2$, 100).

2,2-Dibromo-1-(4′-chlorophenyl)ethanone (2)

The general procedure yielded the title compound (2) (2.83 g, 91%) from p-chloroacetophenone (1.29 mL, 10 mmole), which was isolated using pet. ether (60:80):ethyl acetate (6:1) as an eluent system for column chromatography, m.p. = 99°C (Lit.[1] m.p. = 101°C), $R_f = 0.6$ using an eluent (10:1).

IR (KBr plate): ν = 3024–2953 (CH, Ar); 2890 (CH); 1693 (CO); 1600, 1575 (C=C); 630 (C—Br)cm $^{-1}$.

^{1}H NMR($CDCl_3$) δ = 8.11–8.08 (d, 2H, ArH), 7.58, 7.48 (d, 2H, Ar); 6.63 (s, 1H, CH); ppm.

M.S.: (m/z,%) 312 (M^+, 0.7); 232 (M^+ - Br, 0.2); 139 (M^+- $CHBr_2$, 100); 105 (M^+,-[$CHBr_2$, Cl], 0.2).

2,2-Dibromo-1-(4′-nitrophenyl)ethanone (3)

A mixture of tetrachlorosilane (8.2 mL, 70 mmole) N-bromosuccinimide (3.6 gm, 20 mmole) and p-nitroacetophenone (1.65 mL, 10 mmole) yielded the title compound (3) (2.90 g, 90%), which was isolated using pet. ether (60:80):ethyl acetate (6:1) as an eluent system for column chromatography, m.p. = 110°C, $R_f = 0.52$ using an eluent (10:1) (Lit.[2] m.p. = 111°C).

IR (KBr plate): ν = 3074–3047 (CH, Ar); 2934 (CH); 1704 (CO); 1599 (C=C); 600 (C—Br) cm $^{-1}$.

^{1}H NMR($CDCl_3$) δ = 8.3–8.1 (d, 2H, ArH), 8.12–8.10 (d, 2H, Ar); 6.91 (s, 1H, CH); ppm.

2,2-Dibromo-1-(*p*-tolyl)ethanone (4)

The general procedure yielded the title compound (4) (2.80 gm, 96%) from p-methylacetophenone (1.34 mL, 10 mmole), which was isolated using pet. ether (60:80):ethyl acetate (6:1) as an eluent system for column chromatography, m.p. = 89°C (Lit.[1] m.p. = 89°C), $R_f = 0.62$ using an eluent (10:1).

IR (KBr plate): ν = 3023–3007 (CH, Ar); 2955–2939 (CH); 1695 (CO); 1607, 1572 (C=C); 600 (C—Br) cm $^{-1}$.

^{1}*H NMR(CDCl$_3$)* δ = 7.74–7.7 (d, 2H, ArH), 7.17 (d, 2H, Ar); 2.2(s, 3H, Ar); 6.61(s, 1H, CH); ppm.

2,2-Dibromo-1-(4′-biphenyl)ethanone (5)

The general procedure] yielded the title compound (5) (3.15 gm, 92%) from 4-acetylbiphenyl (1.85 mL, 10 mmole), which was isolated using pet. ether (60:80):ethyl acetate (6:1) as an eluent system for column chromatography, m.p. = 126°C (Lit.[3] m.p. = 128°C), $R_f = 0.7$ using an eluent (10:1).

IR (KBr plate): ν = 3049–2957-(CH, Ar); 2851(CH); 1675 (CO); 1620, 1595 (C=C); 630 (C—Br) cm $^{-1}$.

^{1}*HNMR(CDCl$_3$)* δ = 7.92–7.88 (d, 2H, ArH), 7.59 (d, 2H, ArH), 7.48–7.42 (d, 2H, ArH), 7.37 7.22 (m, 3H, Ar); 6.88 (s,1H,CH); ppm.

2,2 -Dibromo-1-(2′-naphthyl)ethanone (6)

The general procedure yielded the title compound (6) (3.00 gm, 92%) from 2′-acetyl aphthalene (1.28 mL, 10 mmole), which was isolated using pet. ether (60:80):ethyl acetate (6:1) as an eluent system for column chromatography, m.p. = 108°C (Lit.[4] m.p. = 109°C), R_f = 0.63 using an eluent (10:1).

IR (KBr plate): ν = 3058–2992-(CH, Ar); 2851(CH); 1672 (CO); 1620, 1598 (C=C); 620 (C—Br) cm $^{-1}$.

^{1}*H NMR(CDCl$_3$)* δ = 8.67 (s, 1H, ArH), 8.15–8.14 (d, 1H, ArH), 8.00–8.09 (d, 1H, ArH), 7.99–7.92 (d, d, 2H, Ar); 7.79–7.59 (m, 2H, Ar) 6.90 (s, 1H, CH); ppm.

M.S.: (m/z, %) 328 (M^+, 1.4); 155 (M^+-CH Br_2 , 100); 174 ($CHBr_2$, 8.1) 139 (M^+-[$CHBr_2$, O], 11.9); 127 (naphthylion, 56).

2,2 -Dibromo-1-(4′-pyridyl)ethanone (7)

The general procedure yielded the title compound (7) (2.37 g, 85%) from 4′-acetyl pyridine (1.1 mL, 10 mmole), which was isolated using pet.

ether (60:80):ethyl acetate (6:1) as an eluent system for column chromatography, m.p. = 166°C, $R_f = 0.48$ using an eluent (10:1).

IR (KBr plate): $\nu = 3016, 2986$ (CH, Ar); 2914 (CH); 1693 (CO); 1620, 1591 (C=N, C=C); 680 (C–Br) cm^{-1}.

^1H *NMR(*$CDCl_3$*)* $\delta = 7.99$ (d, 2H, ArH), 7.96 (d, 2H, ArH); 6.24 (s, 1H, CH); ppm.

M.S.: (m/z,%) 279 (M^+, 2.1); 106 (M^+-CH Br_2 , 100); 78 (pyridylion, 36).

2′,4′-Dibromo acetanilide (8)

The general procedure yielded the title compound (8) (2.78 gm, 95%) from acetanilide (1.35 g, 10 mmole), which was isolated using pet. ether (60:80): ethyl acetate (6:1) as an eluent system for column chromatography, m.p. = 149°C, (Lit.[5] m.p. = 150°C). $R_f = 0.2$ using an eluent (10:1).

IR (KBr plate): $\nu = 3294$ (NH); 3194–3026 (CH, Ar); 2850 (CH); 1661 (CO); 1600 (C=C); 550 (C–Br) cm^{-1}.

^1H *NMR(DMSO)* $\delta = 9.53$ (s, 1H, NH); 7.90 (s, 1H, ArH); 7.58 (s, 2H, ArH); 2.09 (s, 3H, CH_3); ppm.

M.S.: (m/z,%) 293 (M^+, 15.22); 251 (M^+-1-acetyl, 95.39); 223 (dibromo cyclopentadienyl cation, 11.25); 214 (M^+-1-acetyl-Br, 28.31); 171 (M^+-acetyl-2Br, 22.17); 63 (C_5H_3 cation, 100).

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