# Reaction of Tosylhydrazones with Phenyltrimethylammonium Perbromide. Synthesis of Tosylazoalkenes[1]

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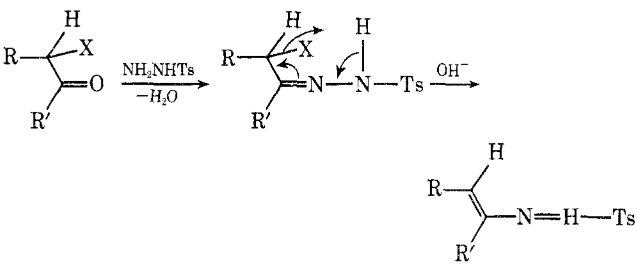
Tosylhydrazones 1-6 undergo oxidation to tosylazoalkenes in mild conditions using phenyltrimethylammonium perbromide followed by basic treatment effected *in situ*. A mechanistic pathway of the reaction is proposed. The procedure appears to be a convenient method for preparing tosylazoalkenes.

Tosylazoalkenes are a new class of unstable compounds that have been the subject of considerable study[2-10] and have been proposed as intermediates in a number of organic reactions.[11-16]

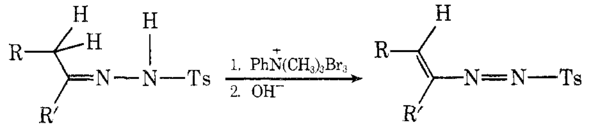
The preparation of tosylazoalkenes by treatment with alkali of tosylhydrazones of the corresponding ketones and aldehydes containing a leaving group on the α carbon is an established preparative reaction.[2,5-8,10]



X = Cl, Br, F, OAc, epoxy, $OSO_2CH_3$

However, using some α-halo carbonyl compounds, substitution and/or dehydrohalogenation has been observed as reported for α-halo ketones upon treatment with ammonia or primary or secondary amines.[17,18]

Herein we wish to report that aldehyde and ketone tosylhydrazones can be directly converted into tosylazoalkenes in fair to good yields in mild conditions using phenyltrimethylammonium perbromide (PTAB) followed by basic treatment effected *in situ*.



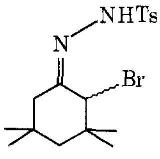
Some results given by our process are shown in Table I where the yields refer to analytically pure products obtained by crystallization from reactions in tetrahydrofuran.

Phenyltrimethylammonium perbromide (PTAB) is a mild and extremely efficient reagent for the α-bromination of ketones and cyclic ketals.[19-25]

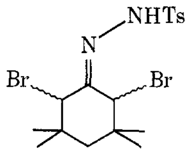
However, all attempts to oxidize tosylhydrazones to tosylazoalkenes performed with molecular bromine, dioxane dibromide, and *N*-bromosuccinimide in a range of solvents failed.

Tosylhydrazones of nonenolizable ketones such as benzophenone did not react with PTAB. When 1,3-diphenylpropanone tosylhydrazone (**2**) was treated with 2 mol of PTAB, it was possible to isolate bromotosylazoalkene **2b** after basic treatment of the reaction mixture. Tosylazoalkene **6a** was prepared by reaction of 3,3,5,5-tetramethylcyclohexanone tosylhydrazone (**6**) with 1 mol of PTAB at −20°. At room temperature, **6** gave bromotosylazoalkene **6b** also using only 1 mol of PTAB; the yield of **6b** was increased when 2 mol of PTAB was used.

All attempts to isolate brominated intermediates from the reactions performed between tosylhydrazones **1-5** and PTBA were unsuccessful. However, when the reaction of **6** with 1 mol of PTAB was performed at −20°, the corresponding α-bromo ketone tosylhydrazone **7** was isolated in 55% yield. The reactions performed with 2 mol of PTAB at room temperature gave the α,α′-dibromo ketone tosylhydrazone **8** in 83% yield (see Experimental Section).



7

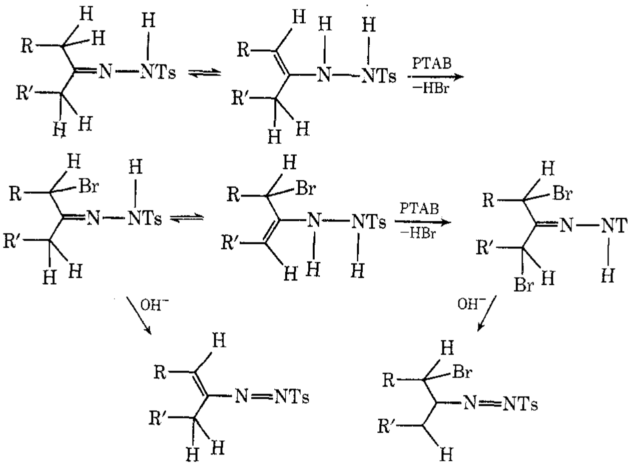


8

Compound **7** dissolved in tetrahydrofuran and added with another mole of PTAB gave dibromo derivative **8** in 87% yield. Compounds **7** and **8** underwent 1,4-dehydrobromination by treatment with an aqueous solution of sodium carbonate to afford tosylazoalkenes **6a** and **6b**.

The detailed mechanism of the oxidation of enolizable ketone and aldehyde tosylhydrazones with PTAB and basic treatment has not been established; however, in order to explain the above results and observations, the following reaction sequence is proposed for this new reaction of tosylhydrazones (Scheme I).

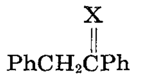
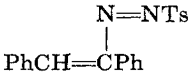
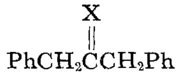
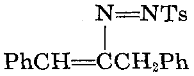
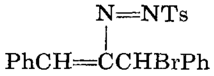
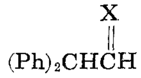
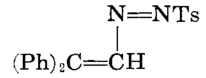
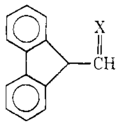
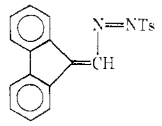
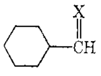
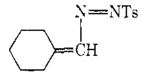
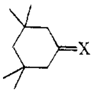
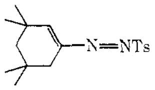
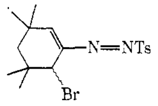
**Scheme I**



This reaction of tosylhydrazones with PTAB appears similar to the acid-catalyzed bromination of enolizable ketones.[26] The isomerization of tosylhydrazones to ene hydrazine tautomers can be considered the key step of the reaction and the formation of α,α′-dibromo derivatives can be rationalized assuming a further acid-catalyzed bromination on the other side of the keto imino group.[27]

The basic treatment performed after addition of 1 or 2 mol of PTAB to tosylhydrazone dissolved in tetrahydrofu-

**Table I**

| No. | Tosylhydrazones (NNHTs)=X | No. | Tosylazoalkenes | PTAB, mol | Mp, °C, dec | Yield, % |
|---|---|---|---|---|---|---|
| 1 |  $\mathrm{PhCH_2\overset{\overset{X}{\|}}{C}Ph}$ | 1a |  $\mathrm{PhCH{=}\overset{\overset{N=NTs}{\vert}}{C}Ph}$ | 1 | 84–85 | 65 |
| 2 |  $\mathrm{PhCH_2\overset{\overset{X}{\|}}{C}CH_2Ph}$ | 2a |  $\mathrm{PhCH{=}\overset{\overset{N=NTs}{\vert}}{C}CH_2Ph}$ | 1 | 84–85 | 60 |
|  |  | 2b |  $\mathrm{PhCH{=}\overset{\overset{N=NTs}{\vert}}{C}CHBrPh}$ | 2 | 90–92 | 72 |
| 3 |  $\mathrm{(Ph)_2CH\overset{\overset{X}{\|}}{C}H}$ | 3a |  $\mathrm{(Ph)_2C{=}\overset{\overset{N=NTs}{\vert}}{C}H}$ | 1 | 82 | 72 |
| 4 |  | 4a |  | 1 | 138 | 75 |
| 5 |  | 5a |  | 1 | 54–55 | 64 |
| 6 |  | 6a |  | 1[a] | 87 | 82 |
|  |  | 6b |  | 2 | 85–86 | 74 |

[a] Reaction performed at −20°.

ran induces a 1,4 elimination of hydrogen bromide to give tosylazoalkene or bromotosylazoalkene.

This new route to tosylazoalkenes is remarkable for its simplicity. Easily accessible starting materials such as tosylhydrazones and PTAB are used. The reactions are performed under mild conditions and generally are free from reaction by-products which might interfere with easy isolation of the tosylazoalkenes.

## Experimental Section

All melting points are uncorrected. Spectra were recorded on Perkin-Elmer 257, Unicam SP-800, and Joel C 60 HL spectrometers. Nmr spectra were recorded using TMS as internal standard. Microanalyses were performed using the C, H, N, Analyzer Model 185 of the Hewlett-Packard Co. Deoxybenzoin, 1,3-diphenylpropanone, diphenylacetaldehyde, cyclohexanecarboxaldehyde, 3,3,5,5-tetramethylcyclohexanone, and tosylhydrazine are commercial materials. 9-Formylfluorene[28] and phenyltrimethylammonium perbromide (PTAB)[19,20] were prepared as previously reported. Analytical grade tetrahydrofuran was purified by the standard method.[29]

**Preparation of Tosylhydrazones. General Procedure.** The tosylhydrazones 1–6 were readily prepared in good yields from the carbonyl compounds by addition of equimolar quantities of tosylhydrazine in methanol or ethanol at temperatures not exceeding 50° (1–2 hr). The corresponding tosylhydrazone, which crystallized from the solution after cooling, was isolated by filtration, dried *in vacuo,* and used in the next step without further purification. An analytical sample was prepared by recrystallization from methanol or ethanol. These derivatives all showed ir absorption (KBr) at approximately 3200, 1600, 1360, 1170, and 820 cm$^{-1}$.

**Deoxybenzoin Tosylhydrazone (1).** Deoxybenzoin gave 1 in 87% yield, mp 141–142°.

*Anal.* Calcd for $C_{21}H_{20}N_2O_2S$: C, 69.21; H, 5.53; N, 7.69. Found: C, 69.30; H, 5.85; N, 7.31.

**1,3-Diphenylpropanone Tosylhydrazone (2).** 1,3-Diphenylpropanone gave 2 in 85% yield, mp 183–184°.

*Anal.* Calcd for $C_{22}H_{22}N_2O_2S$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.90; H, 5.85; N, 7.31.

**Diphenylacetaldehyde Tosylhydrazone (3).** Diphenylacetaldehyde gave 3 in 87% yield, mp 143–145°.

*Anal.* Calcd for $C_{21}H_{20}N_2O_2S$: C, 69.21; H, 5.53; N, 7.69. Found: C, 69.12; H, 5.46; N, 7.83.

**9-Formylfluorene Tosylhydrazone (4).** 9-Formylfluorene[28] gave 4 in 94% yield, mp 169–170°.

*Anal.* Calcd for $C_{21}H_{18}N_2O_2S$: C, 69.60; H, 4.85; N, 7.73. Found: C, 69.58; H, 4.81; N, 7.79.

**Cyclohexanecarboxaldehyde Tosylhydrazone (5).** Cyclohexanecarboxaldehyde gave 5 in 95% yield, mp 99–100°.

*Anal.* Calcd for $C_{14}H_{20}N_2O_2S$: C, 59.98; H, 7.19; N, 9.99. Found: C, 59.81; H, 7.05; N, 9.88.

**3,3,5,5-Tetramethylcyclohexanone Tosylhydrazone (6).** 3,3,5,5-Tetramethylcyclohexanone gave 6 in 87% yield, mp 160–162°.

*Anal.* Calcd for $C_{17}H_{26}N_2O_2S$: C, 63.33; H, 8.13; N, 8.69. Found: C, 63.39; H, 8.17; N, 8.56.

**Preparation of Tosylazoalkenes. General Procedure.** A solution containing 1.0 × 10$^{-2}$ mol of tosylhydrazone in anhydrous tetrahydrofuran (100 ml) was stirred at room temperature under nitrogen and PTAB (1 or 2 equiv) was slowly added. The orange color of PTAB rapidly disappeared and phenyltrimethylammonium salt precipitated. After another 10 min, diethyl ether was added and the mixture was shaken with a saturated aqueous solution of sodium carbonate. A yellow color rapidly appeared. The layers were separated and the resulting ethereal solution was dried ($Na_2SO_4$) and concentrated under reduced pressure at a temperature not exceeding 40°. Generally the crystallization of tosylazoalkenes was accomplished by addition of *n*-hexane.

**Tosylazostilbene (1a).** Tosylhydrazone 1 (3.64 g, 1.0 × 10$^{-2}$ mol) by reaction with PTAB (3.79 g, 1.0 × 10$^{-2}$ mol) gave **1a** (2.3 g, 65% yield), mp 95° dec; spectroscopic data are in agreement with those recorded on a sample independently prepared.[8]

*Anal.* Calcd for $C_{21}H_{18}N_2O_2S$: C, 69.60; H, 5.0; N, 7.73. Found: C, 69.85; H, 4.95; N, 7.83.

**2-Tosylazo-1,3-diphenylpropene (2a).** Tosylhydrazone 2 (3.78 g, 1 × 10$^{-2}$ mol) with PTAB (3.79 g, 1.0 × 10$^{-2}$ mol) gave **2a** (2.25 g, 65% yield), mp 84–85° dec; spectroscopic data are in agreement with those recorded on a sample independently prepared.[8]

*Anal.* Calcd for $C_{22}H_{20}N_2O_2S$: C, 70.2; H, 5.36; N, 7.44. Found: C, 69.86; H, 5.05; N, 7.68.

**3-Bromo-1,3-diphenyl-2-tosylazoprop-1-ene (2b).** 1,3-Diphenylpropanone tosylhydrazone (2) (3.78 g, 1.0 × 10$^{-2}$ mol) was dissolved in anhydrous tetrahydrofuran (100 ml) and stirred at room temperature. PTAB (7.58 g, 2 × 10$^{-2}$ mol) was added during a period of 30 min. After another 10 min, the mixture was treated as reported above and an orange product was isolated (3.30 g, 72% yield): mp 90–92° dec; uv max ($C_6H_6$) 363 mμ (ε 13,100); nmr ($CDCl_3$) δ 7.85–7.00 (m, 15 H, aromatic and 1 vinylic protons), 6.27 (s, 1 H, –CHBr), 2.47 (s, 3 H, p-$CH_3C_6H_4$).

*Anal.* Calcd for $C_{22}H_{19}BrN_2O_2S$: C, 58.02; H, 4.16; N, 6.29: Found: C, 58.18; H, 4.25; N, 6.21.

**2,2-Diphenyl-1-tosylazoethylene (3a).** Tosylhydrazone 3 (3.64 g, 1.0 × $10^{-1}$ mol) with PTAB (3.79 g, 1.0 × $10^{-2}$ mol) gave **3a** (2.60 g, 72% yield), mp 82° dec; spectroscopic data are in agreement with those recorded on a sample independently prepared.[9]

*Anal.* Calcd for $C_{21}H_{18}N_2O_2S$: C, 69.61; H, 4.97; N, 7.73. Found: C, 69.56; H, 5.05; N, 7.78.

**9-Tosylazomethylenefluorene (4a).** Tosylhydrazone 4 (3.62 g, 1.0 × $10^{-2}$ mol) with PTAB (3.79 g, 1.0 × $10^{-2}$ mol) gave **4a** (2.79 g, 75% yield): mp 138° dec; uv max ($CHCl_3$) 227 mμ (ε 22,100); nmr ($CDCl_3$) δ 7.9–7.1 (m, 13 H, aromatic and 1 vinylic protons), 2.5 (s, 3 H, p-$CH_3C_6H_4$).

*Anal.* Calcd for $C_{21}H_{16}N_2O_2S$: C, 69.99; H, 4.48; N, 7.77. Found: C, 69.73; H, 4.52; N, 7.81.

**Tosylazomethylenecyclohexane (5a).** Tosylhydrazone 5 (2.8 g, 1.0 × $10^{-2}$ mol) with PTAB (3.79 g, 1.0 × $10^{-2}$ mol) gave **5a** (1.8 g, 64% yield): mp 53–54° dec; uv max (n-hexane) 280 mμ (ε 15,000) and 420 (80); nmr ($CDCl_3$) δ 7.55 (AA′BB′ pattern, 4 H, $J$ = 8 Hz, p-$C_6H_4$), 3.5 (s, 1 H, vinylic proton), 2.45 (s, 3 H, p-$CH_3C_6H_4$), 2.00–1.00 (m, 10 H, other aliphatic protons).

*Anal.* Calcd for $C_{14}H_{18}N_2O_2S$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.36; H, 6.60; N, 10.12.

**2-Bromo-3,3,5,5-tetramethylcyclohexanone Tosylhydrazone (7).** 3,3,5,5-Tetramethylcyclohexanone tosylhydrazone (3.22 g, 1.0 × $10^{-2}$ mol) was dissolved in anhydrous tetrahydrofuran (100 ml) and stirred at −20°. PTAB (3.79 g, 1.0 × $10^{-2}$ mol) was added during a period of 15 min. After another 10 min, the precipitate was collected by filtration and the resulting solution was evaporated under reduced pressure at a temperature not exceeding 40°. The residue was dissolved with diethyl ether, and methanol was added until precipitation of a white product occurred. The crystals of 7 were collected and dried (2.20 g, 55% yield): mp 122–123° dec; nmr ($CDCl_3$) δ 8.18 (broad s, 1 H, –$SO_2NH$–), 7.50 (AA′BB′ pattern, 4 H, $J$ = 8 Hz, p-$C_6H_4$), 4.35 (s, 1 H, –CHBr), 2.40 (s, 3 H, p-$CH_3C_6H_4$), 2.42–2.17 (AB systems, q, 2 H, $|J_{AB}|$ = 14 Hz, $C_6$ $H_2$, partially overlapped with singlet of $CH_3C_6H_4$), 1.72–1.12 (AB system, q, 2 H, $|J_{AB}|$ = 14 Hz, $C_4H_2$, partially overlapped with signals of methyl protons), 1.1–0.7 (m, 12 H, methyl protons).

*Anal.* Calcd for $C_{17}H_{24}N_2O_2S$: C, 63.16; H, 7.50; N, 8.75. Found: Found: C, 50.98; H, 6.52; N, 6.99.

**3,3,5,5-Tetramethyl-1-tosylazocyclohexene (6a).** The ethereal solution of 7 (4.0 g, 1.0 × $10^{-2}$ mol) was shaken with a saturated aqueous solution of sodium carbonate and then washed several times with water, dried ($Na_2SO_4$), and filtered. The ether was evaporated and a yellow compound, **6a**, was obtained by addition of n-hexane (2.62 g, yield 82%): mp 87° dec; uv max (n-hexane) 275 mμ (ε 20,000); nmr ($CCl_4$) δ 7.40 (AA′BB′ pattern, 4 H, $J$ = 7.5 Hz, p-$C_6H_4$), 6.60 (s, 1 H, vinylic proton), 2.45 (s, 3 H, p-$CH_3C_6H_4$), 2.00 (s, 2 H, $C_6$ $H_2$) 1.40 (s, 2 H, $C_4$ $H_2$), 1.15 [s, 6 H, $C_3$ $(CH_3)_2$], 1.00 [s, 6 H, $C_5$ $(CH_3)_2$].

*Anal.* Calcd for $C_{17}H_{24}N_2O_2S$: C, 63.16; H, 7.50; N, 8.75. Found: C, 63.22; H, 7.38; N, 8.87.

**6-Bromo-3,3,5-5-tetramethyltosylazocyclohex-1-ene (6b).** Tosylhydrazone 6 (3.22 g, 1.0 × $10^{-2}$ mol) with PTAB (7.58 g, 2.0 × $10^{-2}$ mol) gave **6b** (2.86 g, 74% yield): mp 85–86° dec; uv max (n-hexane) 2.79 mμ (ε 17,300) and 420 (125); nmr ($CCl_4$) δ 7.5 (AA′BB′ pattern, 4 H, $J$ = 8 Hz, p-$C_6H_4$), 6.7 (s, 1 H, vinylic proton), 4.5 (m, 1 H, –CHBr), 2.5 (s, 3 H, p-$CH_3C_6H_4$), 1.98–1.32 (AB system, q, 2 H, $|J_{AB}|$ = 14 Hz: $C_4$ $H_2$, partially overlapped with other aliphatic protons), 1.3–1.0 (m, 18 H, other aliphatic protons).

*Anal.* Calcd for $C_{17}H_{23}BrN_2O_2S$: C, 51.13; H, 5.77; N, 7.01. Found: C, 51.43; H, 5.82; N, 7.14.

The same reaction performed at room temperature using 1 equiv of PTAB gave a 30% yield of **6b.**

**2,6-Dibromo-3,3,5,5-tetramethylcyclohexanone Tosylhydrazone (8).** 3,3,5,5-Tetramethylcyclohexanone tosylhydrazone (3.22 g, 1.0 × $10^{-2}$ mol) was dissolved in anhydrous tetrahydrofuran (100 ml) and stirred at room temperature. PTAB (7.58 g, 2.0 × $10^{-2}$ mol) was added during a period of 15 min. After another 10 min, the precipitate was collected and the solution was evaporated under reduced pressure at a temperature not exceeding 40°. The residue was dissolved with diethyl ether and allowed to stand in a refrigerator until precipitation of a white product occurred. The crystals of 8 were collected and dried (4.08 g, yield 85%): mp 112–113° dec; nmr ($CDCl_3$) δ 7.50 (AA′BB′ pattern, 4 H. $J$ = 8 Hz, p-$C_6H_4$), 7.67 (broad a partially covered by AA′BB′ pattern, 1 H, –$SO_2NH$–), 5.05 (s, 1 H, $C_6$ HBr), 4.7 (m, 1 H, $C_2$ HBr), 2.40 (s, 3 H, p-$CH_3C_6H_4$), 1.42 (AB system, q, 2 H, $|J_{AB}|$ = 15 Hz, $C_4$ $H_2$), 1.3–0.2 (m, 12 H, other aliphatic protons).

*Anal.* Calcd for $C_{17}H_{24}Br_2N_2O_2S$: C, 42.50; H, 5.00; N, 5.84. Found: C, 42.63; H, 4.91; N, 5.91.

The same reaction performed on compound 6 using 1 mol of PTAB at room temperature gave a 35% yield of 8.

**Dehydrobromination of 8.** The ethereal solution of 8 was shaken with a saturated aqueous solution of sodium carbonate, washed several times with water, dried ($Na_2SO_4$), and filtered, and after evaporation of the solvent, afforded compound **6b** (83% yield).

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**Registry No.**—**1,** 19816-85-4; **1a,** 29127-96-6; **2,** 19816-88-7; **2a,** 29127-97-7; **2b,** 42449-02-5; **3,** 42449-03-6; **3a,** 34220-14-9; **4,** 35432-46-3; **4a,** 42449-06-9; **5,** 34266-29-0; **5a,** 42449-08-1; **6,** 42449-09-2; **6a,** 42449-10-5; **6b,** 42449-11-6; **7,** 42449-12-7; **8,** 42407-03-4; PTAB, 4207-56-1.

## References and Notes

(1) This work was done with financial support of the Italian National Research Council (C. N. R.).

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