

THERMOLYSIS OF SODIUM SALTS OF TOSYLHYDRAZONES OF SOME HETEROCYCLIC ALDEHYDES IN THE PRESENCE OF SILVER CHROMATE:

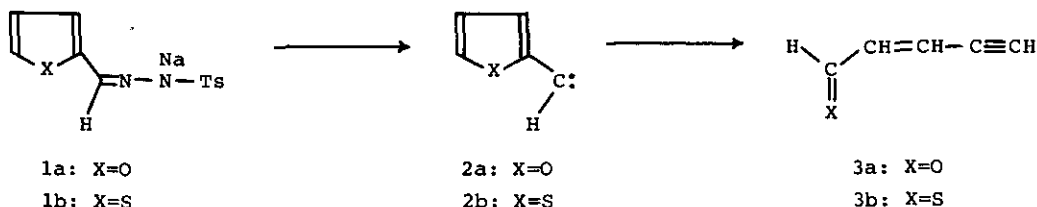
1,3 N→C MIGRATION OF TOSYL GROUP

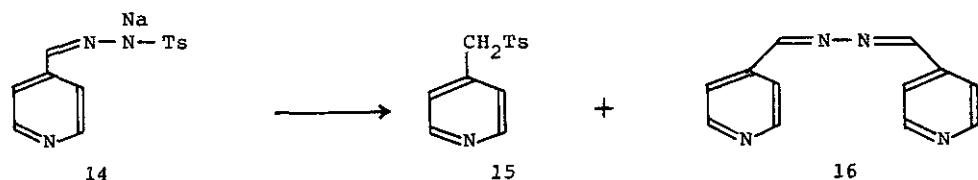
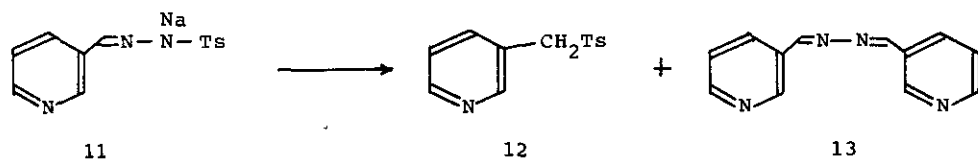
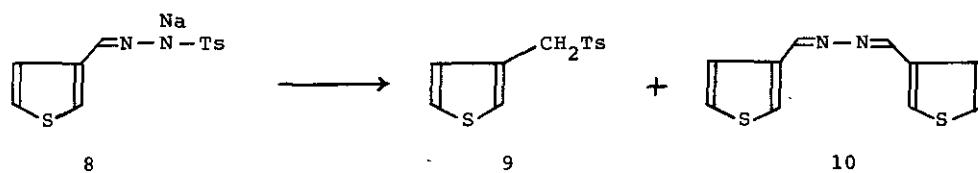
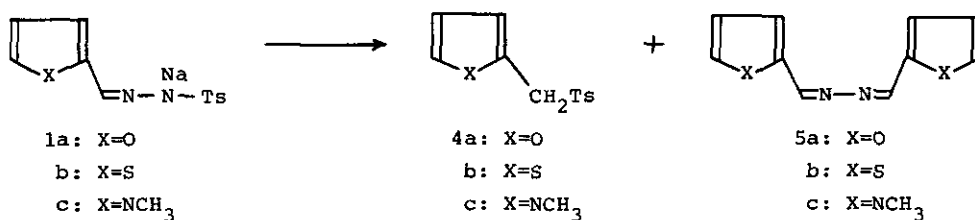
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Abstract—The thermal decompositions of sodium salts of tosylhydrazones of furfural, thiophene-2-aldehyde, 1-methylpyrrole-2-aldehyde, and pyridine-2-aldehyde in the presence of silver chromate gave 2-furyl(p-toluenesulfonyl)methane, thiophene-2-(p-toluenesulfonyl)methane, 1-methylpyrrole-2-(p-toluenesulfonyl)methane, and pyridine-2-(p-toluenesulfonyl)methane, respectively, via 1,3 N→C migration of tosyl group. The same type of reactions with sodium salts of tosylhydrazones of thiophene-3-aldehyde, pyridine-3-aldehyde, and pyridine-4-aldehyde also afforded the corresponding p-toluenesulfonylmethanes but the yields were slightly lower comparing to the above cases.

It is known that thermolysis of sodium salts of tosylhydrazones of furfural (1a) and thiophene-2-aldehyde (1b) give the corresponding carbenes (2a, b), which afford insertion products via reactions with suitable alkanes.¹ In the absence of the suitable alkanes, the carbenes (2a, b) rearrange to acetylene derivatives (3a, b), which are very unstable and degrade rapidly upon even storage at room temperature.¹ We have reported that thermolysis of 1a in the presence of silver chromate afforded 2-furyl(p-toluenesulfonyl)methane (4a) via 1,3 N→C migration of





tosyl group in furfural tosylhydrazone radical, which was generated by one electron oxidation of 1a by silver chromate.² In order to obtain additional examples of this type of reaction we investigated the 1,3 N→C migration reaction of tosyl group using various tosylhydrazones conjugated with heterocyclic moieties. Here the result will be reported.

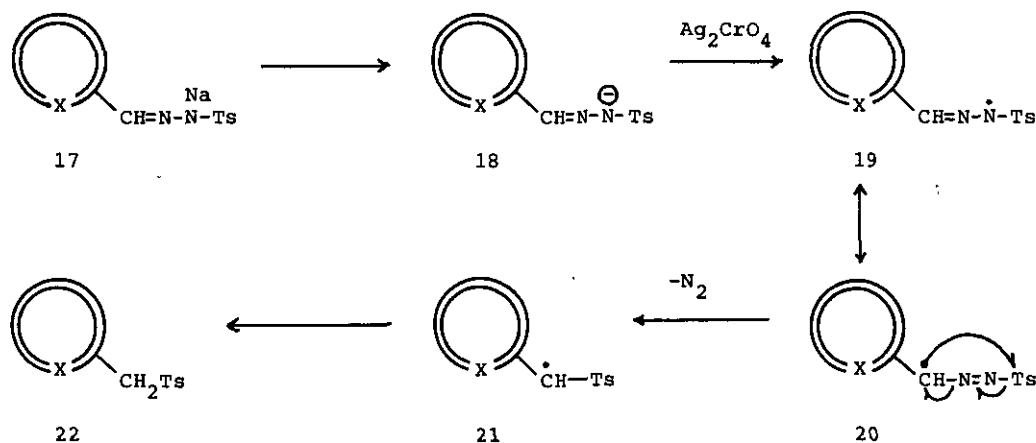
Sodium salt of furfural tosylhydrazone (1a) was heated at 130°C for 10 min in anhydrous diglyme in the presence of silver chromate. After evolution of a 90% yield of nitrogen gas had ceased the reaction mixture was extracted with ether and chromatographed on silica gel to give 2-furyl(p-toluenesulfonyl)methane (4a) and a ketazine derivative (5a) in the yields of 6.5 and 3.5%, respectively. The same type of reactions with sodium salts of thiophene-2-aldehyde tosylhydrazone

(1b), 1-methylpyrrole-2-aldehyde tosylhydrazone (1c), and pyridine-2-aldehyde tosylhydrazone (6)³ gave the corresponding p-toluenesulfonylmethanes (4b,⁴ 7.1%; 4c, 13.1%; and 7, 9.4%) and the corresponding ketazine derivatives 5b (2.1%) and 5c (6.3%), respectively.⁵

In order to investigate the influence of the positions of the hetero-atoms in the heterocyclic moieties, the same type of reactions with isomers of 1 and 6 were carried out. Reactions of sodium salts of tosylhydrazones of thiophene-3-aldehyde (8), pyridine-3-aldehyde (11), and pyridine-4-aldehyde (14) under the same conditions as above gave the corresponding p-toluenesulfonylmethanes (9, 2.1%; 12 1.1%; and 15, 1.0%) and the corresponding ketazine derivatives (10, 3.5%; 13, 2.1%; and 16, 2.7%), respectively.⁶

The structure of 4b was deduced on the basis of its spectral properties and confirmed by comparison of the spectral properties and the melting point to those of the authentic sample.⁴ The structures of the another p-toluenesulfonylmethanes were deduced on the basis of their spectral properties and confirmed by comparison of the spectral properties to those of the analogous compounds⁴ containing 4b. The structures of the ketazine derivatives were also deduced on the basis of their spectral properties and confirmed by comparison of the spectral properties to those of the analogous compounds.⁷

The reaction can be explained as follows.² One electron oxidation of the anion (18) of the tosylhydrazone (17) by silver chromate gives tosylhydrazyl radical (19) of the tosylhydrazone (17) by silver chromate gives tosylhydrazyl radical



intermediate (19).⁸ The 1,3 N C migration of the tosyl group⁹ in the canonical formula (20) of 19 leaves nitrogen gas to form the radical intermediate (21). Hydrogen abstraction of 21 from the solvent can afford the p-toluenesulfonyl-methane derivative 22.¹⁰

EXPERIMENTAL

Melting points were recorded on Yanagimoto micro melting point apparatus and are uncorrected. Nmr spectra were measured with Varian XL 200 or Hitachi R-20B spectrometers with tetramethylsilane as an internal standard. Uv and ir spectra were measured with Hitachi 220A and DS-701G spectrometers, respectively. Mass spectra were measured with Hitachi M-52 or JMS-DX300 spectrometers. Wako gel C 200 and Wako gel B5F were used for column and thin-layer chromatography, respectively. Diglyme was dried over Molecular Sieves 3A 1/16.

Reaction of 1a with Silver Chromate. To a solution of furfural tosylhydrazone (2.50 g, 9.5 mmol) in anhydrous diglyme (30 ml) was added sodium hydride (230 mg, 10 mmol). After the evolution of hydrogen gas had ceased silver chromate (4.73 g, 14.3 mmol) was added and the mixture was heated at 130°C for 10 min to evolve nitrogen gas (190 ml, 90%). The reaction mixture was poured into water, extracted with ether, and the extract was washed with water and brine, and dried over anhydrous sodium sulfate. After evaporation of the solvent on a rotary evaporator the residue was chromatographed on silica gel to give crystals 4a (145 mg, 6.5%) and an oil 5a (63 mg, 3.5%) by the use of benzene-ether 9:1 and benzene-ether 4:1, respectively. The crystals 4a were recrystallized from ethyl acetate. The oil 5a was purified with thin-layer chromatography on silica gel using pet. ether-ether 1:1 as a developing solvent ($R_f=0.66$).

4a: mp 110-111°C. Anal. Calcd for $C_{12}H_{12}O_3S$: C, 61.01; H, 5.08. Found: C, 60.72; H, 5.09. Ms m/z (rel intensity): 236 (M^+ , 79), 158 (35), 129 (100); ir (KBr): 3100, 2980, 1600, 1320, 1155 cm^{-1} ; uv (EtOH): 226 nm (log ϵ , 4.22). 1H -nmr ($CDCl_3$): δ 2.44 (s, 3H), 4.41 (s, 2H), 6.28 (m, 1H), 6.34 (m, 1H), 7.30 (d, 2H, J=8 Hz), 7.33 (m, 1H), 7.64 (d, 2H, J=8 Hz).

5a: HRMS: 188.0598. Calcd for $C_{10}H_8O_2N_2$: 188.0610. Ms m/z (rel intensity): 188 (M^+ , 100), 160 (20), 131 (54); ir (oil): 3100, 1640, 1470 cm^{-1} ; uv (EtOH): 295 nm (log ϵ , 4.11); 1H -nmr ($CDCl_3$): δ 6.50 (dd, 2H, J=4 and 2 Hz), 6.80 (d, 2H, J=4 Hz), 7.60 (d, 2H, J=2 Hz), 8.51 (s, 2H).

Reaction of 1b with Silver Chromate. A mixture of thiophene-2-aldehyde tosyl-

hydrazone (2.50 g, 9 mmol), sodium hydride (230 mg, 9 mmol), and silver chromate (4.65 g, 14 mmol) in anhydrous diglyme (30 ml) was reacted as above at 130°C for 10 min to evolve nitrogen gas (210 ml, 100%). After the same treatment as above the resulting oily material was chromatographed on silica gel to give crystals 4b (161 mg, 7.1%) and 5b (40 mg, 2.1%) by the use of pet. ether-benzene 3:7 and benzene, respectively. The crystals 4b and 5b were recrystallized from benzene and ethyl acetate, respectively.

4b: mp 137-138°C. Anal. Calcd for $C_{12}H_{12}O_2S_2$: C, 57.14; H, 4.76. Found: C, 57.12; H, 4.55. Ms m/z (rel intensity): 252 (M^+ , 100), 187 (36), 173 (21); ir (KBr): 3100, 2980, 1592, 1310, 1145 cm^{-1} ; uv (EtOH): 225 nm (log ϵ , 4.22). 1H -nmr ($CDCl_3$): δ 2.38 (s, 3H), 4.44 (s, 2H), 6.7-7.6 (m, 7H).

5b: mp 159-160°C. Anal. Calcd. for $C_{10}H_8N_2S_2$: C, 54.55; H, 3.64. Found: C, 54.78; H, 3.54. Ms m/z (rel intensity): 220 (M^+ , 100), 192 (61), 148 (26); ir (KBr): 3100, 1610, 1420 cm^{-1} ; uv (EtOH): 333 nm (log ϵ , 4.17). 1H -nmr ($CDCl_3$): δ 7.07 (m, 2H), 7.37 (m, 4H), 8.72 (s, 2H).

Reaction of 1c with Silver Chromate. A mixture of 1-methylpyrrole-2-aldehyde tosylhydrazone (2.50 g, 9.5 mmol), sodium hydride (240 mg, 10 mmol), and silver chromate (4.65 g, 14 mmol) in anhydrous diglyme (30 ml) was reacted as usual at 130°F for 10 min to evolve nitrogen gas (210 ml, 100%). The reaction mixture was treated as usual and the resulting oily material was thin-layer chromatographed on silica gel using benzene as a developing solvent to give crystals 4c (309 mg, 13.1%, $R_f=0.41$) and 5c (130 mg, 6.3%, $R_f=0.32$). The crystals 4c and 5c were recrystallized from ethyl acetate.

4c: mp 168-169°C. Anal. Calcd. for $C_{13}H_{15}NO_2S$: C, 62.65; H, 6.02. Found: C, 62.71; H, 6.03. Ms m/z (rel intensity): 249 (M^+ , 100), 184 (33), 139 (17); ir (KBr): 3100, 2980, 1595, 1295, 1130 cm^{-1} , uv (EtOH): 223 nm (log ϵ , 4.32); 1H -nmr ($CDCl_3$): δ 2.40 (s, 3H), 3.47 (s, 3H), 4.29 (s, 2H), 5.71 (m, 1H), 5.94 (m, 1H), 6.67 (m, 1H), 7.20 (d, 2H, $J=8$ Hz), 7.50 (d, 2H, $J=8$ Hz).

5c: mp 123-124°C. HRMS: 214.1228. Calcd. for $C_{12}H_{14}N_4$: 214.1238. Ms m/z (rel intensity): 214 (M^+ , 100), 186 (10), 149 (12); ir (KBr): 3100, 2970, 1630, 1420 cm^{-1} ; uv (EtOH): 353 nm (log ϵ , 4.49). 1H -nmr ($CDCl_3$): δ 3.88 (s, 6H), 6.03 (m, 2H), 6.50 (m, 2H), 6.64 (m, 2H), 8.34 (s, 2H).

Reaction of 6 with Silver Chromate. A mixture of pyridine-2-aldehyde tosylhydrazone (2.50 g, 9 mmol), sodium hydride (230 mg, 9 mmol), and silver chromate (4.65 g, 14 mmol) in anhydrous diglyme (30 ml) was reacted as usual at 160°C for

40 min to evolve nitrogen gas (170 ml, 84%). Treatment of the reaction mixture was carried out as usual and the resulting oily material was thin layer chromatographed on silica gel using ethyl acetate-chloroform 1:1 as a developing solvent to give crystals 7 (212 mg, 9.4%, $R_f=0.45$). The crystals 7 were recrystallized from ethyl acetate.

7: mp 154-155°C. Anal. Calcd. for $C_{13}H_{13}NO_2S$: C, 63.16; H, 5.26. Found: C, 63.40; H, 5.33. Ms m/z (rel intensity): 183 (100), 168 (8), 114 (10); ir (KBr): 3040, 2990, 1586, 1435 cm^{-1} ; uv (EtOH): 261 nm (log ϵ , 3.61); 1H -nmr ($CDCl_3$): δ 2.33 (s, 3H), 4.46 (s, 2H), 7.0-8.5 (m, 8H).

Reaction of 8 with Silver Chromate. A mixture of thiophene-3-aldehyde tosylhydrazone (2.50 g, 9 mmol), sodium hydride (230 mg, 9 mmol), and silver chromate (4.65 g, 14 mmol) in anhydrous diglyme (30 ml) was reacted as usual at 130°C for 10 min to evolve nitrogen gas (210 ml, 100%). The reaction mixture was treated as usual and the resulting oily material was thin-layer chromatographed on silica gel using chloroform as a developing solvent to give an oil 9 (48 mg, 2.1%, $R_f=0.40$) and crystals 10 (69 mg, 3.5%, $R_f=0.45$). The crystals 10 were recrystallized from ethyl acetate.

9: HRMS: 252.0267. Calcd. for $C_{12}H_{12}O_2S_2$: 252.0279. Ms m/z (rel intensity): 252 (M^+ , 100), 188 (70), 139 (66); ir (oil): 3100, 2960, 1595, 1300, 1150 cm^{-1} ; uv (EtOH): 225 nm (log ϵ , 4.71); 1H -nmr ($CDCl_3$): δ 2.32 (s, 3H), 4.21 (s, 2H), 6.8-7.7 (m, 7H).

10: mp 150-151°C. HRMS: 220.0107. Calcd. for $C_{10}H_8N_2S_2$: 220.0129. Ms m/z (rel intensity): 220 (M^+ , 100), 193 (30), 148 (16); ir (KBr): 3075, 3030, 1620 cm^{-1} ; uv (EtOH): 298 nm (log ϵ , 4.20); 1H -nmr ($CDCl_3$): δ 7.3-7.7 (m, 8H), 8.55 (s, 2H).

Reaction of 11 with Silver Chromate. A mixture of pyridine-3-aldehyde tosylhydrazone (2.50 g, 9 mmol), sodium hydride (230 mg, 9 mmol), and silver chromate (4.65 g, 14 mmol) in anhydrous diglyme (30 ml) was reacted as usual at 130°C for 10 min to evolve nitrogen gas (210 ml, 100%). After the usual treatment the resulting oily material was thin-layer chromatographed on silica gel using ethyl acetate as a developing solvent to give an oil 12 (25 mg, 1.1%, $R_f=0.30$) and crystals 13 (25 mg, 2.1%, $R_f=0.17$). The crystals 13 were recrystallized from ethyl acetate.

12: HRMS: 247.0680. Calcd. for $C_{13}H_{13}NO_2S$: 247.0667. Ms m/z (rel intensity): 247 (M^+ , 100), 205 (55), 181 (30); ir (oil): 3030, 2980, 1595, 1310, 1155 cm^{-1} ; uv (EtOH): 261 nm (log ϵ , 3.61); 1H -nmr ($CDCl_3$): δ 2.46 (s, 3H), 4.21 (s, 2H),

7.1-8.4 (m, 8H).

13: mp 144-145°C. Anal. Calcd. for $C_{12}H_{10}N_4$: C, 68.57; H, 4.76. Found: C, 68.77; H, 4.75. Ms m/z (rel intensity): 210 (M^+ , 16), 182 (9), 132 (100); ir (KBr): 3030, 1630, 1422 cm^{-1} ; uv (EtOH): 296 nm (log ϵ , 4.46), 1H -nmr ($CDCl_3$): δ 7.3-8.2 (m, 8H), 8.48 (s, 2H).

Reaction of 14 with Silver Chromate. A mixture of pyridine-4-aldehyde tosyl-hydrazone (2.50 g, 9 mmol), sodium hydride (230 mg, 9 mmol), and silver chromate (4.65 g, 14 mmol) in anhydrous diglyme (30 ml) was reacted as usual at 130°C for 10 min to evolve nitrogen gas (210 ml, 100%). After the usual treatment the resulting oily material was thin-layer chromatographed on silica gel using ethyl acetate as a developing solvent to give crystals 15 (21 mg, 1.0%, $R_f=0.25$) and 16 (51 mg, 2.7%, $R_f=0.11$). The crystals were recrystallized from ethyl acetate.

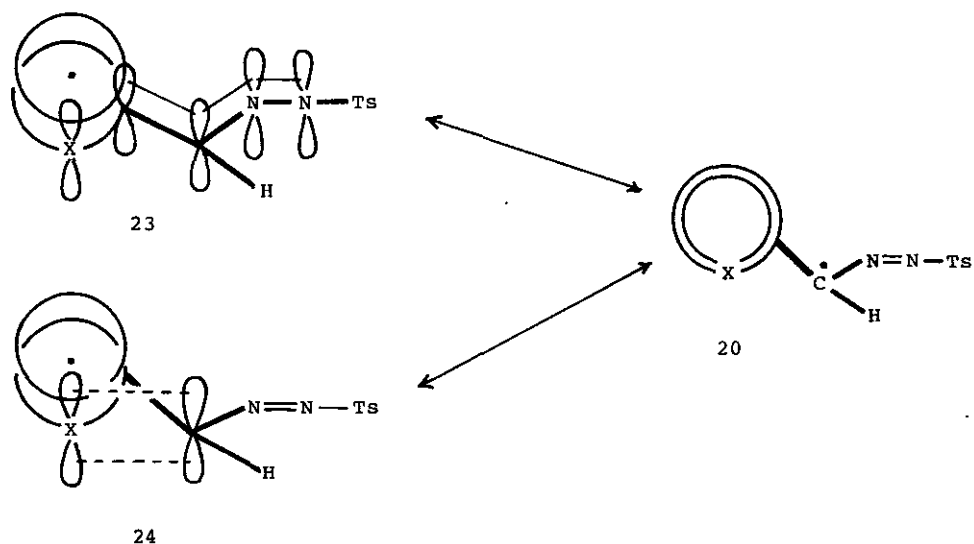
15: mp 184-185°C. Anal. Calcd. for $C_{13}H_{13}NO_2S$: C, 63.16; H, 5.26. Found: C, 63.12; H, 5.36. Ms m/z (rel intensity): 247 (M^+ , 100), 183 (5), 155 (47); ir (KBr): 3030, 2950, 1600, 1315, 1150 cm^{-1} ; uv (EtOH): 261 nm (log ϵ , 3.42); 1H -nmr ($CDCl_3$): δ 2.37 (s, 3H), 4.20 (s, 2H), 6.9-8.4 (m, 8H).

16: mp 91-92°C. Anal. Calcd. for $C_{12}H_{10}N_4$: C, 68.57; H, 4.76. Found: C, 68.08; H, 4.63. Ms m/z (rel intensity): 210 (M^+ , 93), 183 (15), 133 (100); ir (KBr): 3030, 1630, 1595 cm^{-1} ; uv (EtOH): 314 nm (sh. log ϵ , 4.00); 1H -nmr ($CDCl_3$): δ 7.52 (d, 4H, $J=6$ Hz), 8.38 (s, 2H), 8.56 (d, 4H, $J=6$ Hz).

REFERENCES

- The low product yields of the present reactions may be explained by the partial formation of these types of acetylene derivatives.
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- It is known that the carbenes which are thought to be generated by decompositions of 6, 11, and 14 are interconvertible each other under photolytic conditions.
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5. The yield of 4a increased to 16% when 1a was reacted at 115°C for 2h.²
6. In addition to these products, the dimers of the corresponding carbenes were obtained in some cases (1a, 1%; 1b, 9%; 6, 1%; 8, 38%).
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10. The effect of the positions of the hetero-atoms is not so obvious but the slight influence on the yields of the p-toluenesulfonylmethanes is considered to be explained by the through-space interaction (24) of the 2p-orbital on the hetero-atoms with the 2p-orbital on the carbon atom. In the cases of 1 and 6, the distances between both 2p-orbitals are short enough to interact each other by the through-space interactions. On the other hand, in the cases of 8, 11, and 14, no such through-space interaction can be expected because of the long distances between both 2p-orbitals. In every cases the intermediate 20 is considered to be stabilized by the conjugation of the type 23.
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