

THERMOLYSIS OF SODIUM SALT OF FURFURAL TOSYLHYDRAZONE IN THE PRESENCE OF SILVER CHROMATE: FORMATION OF 2-FURYL(p-TOLUENESULFONYL)METHANE VIA 1,3 N→C MIGRATION OF TOSYL GROUP

Katsuhiro Saito\* and Hiraku Ishihara

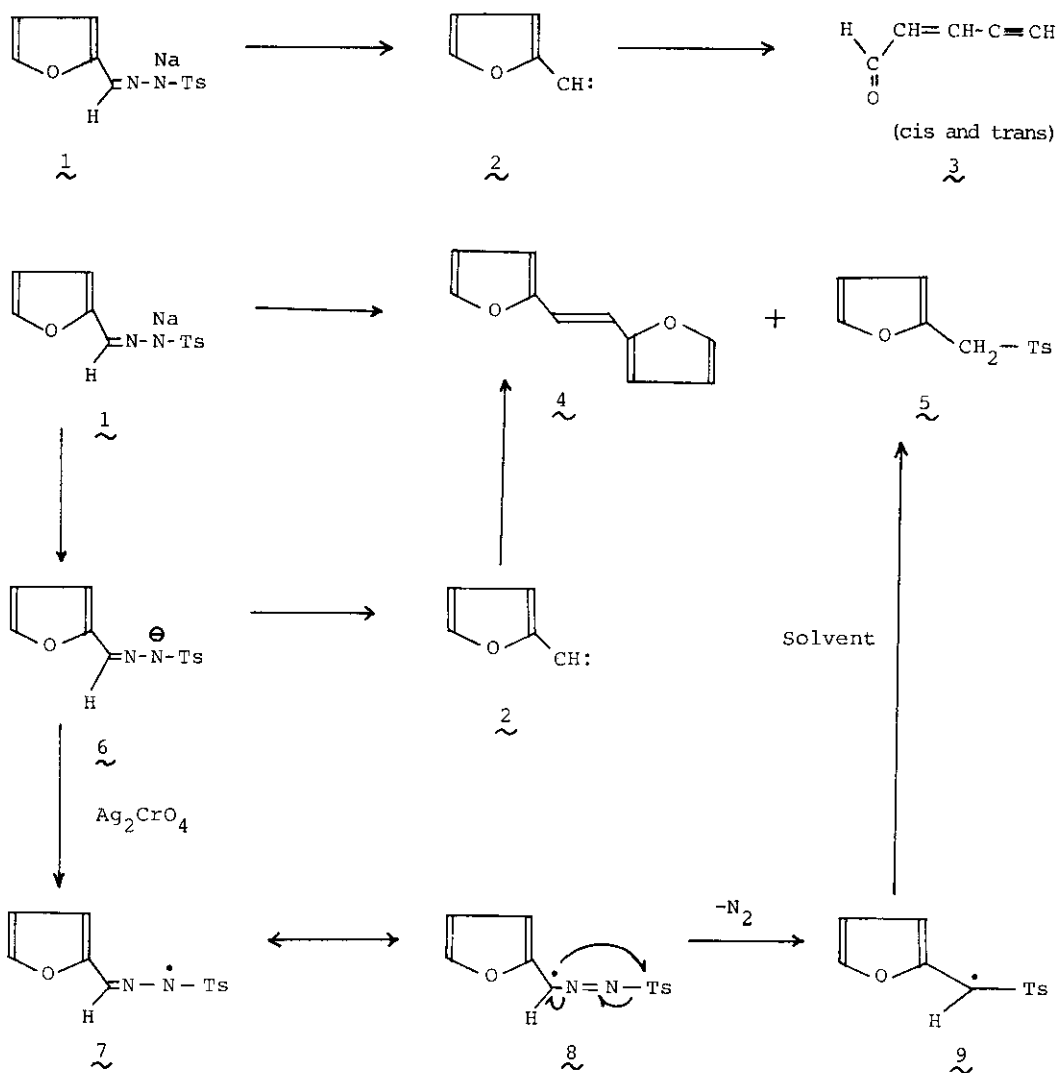
Department of Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Aichi 466, Japan

**Abstract**— The thermal decomposition of sodium salt of furfural tosylhydrazone in diglyme in the presence of silver chromate afforded trans-1,2-di(2-furyl)ethylene and 2-furyl(p-toluenesulfonyl)methane. The former product is formed via (2-furyl)methylene, while the latter product is considered to be derived via 1,3 N→C migration of tosyl group in furfural tosylhydrazyl radical, which is generated by one electron oxidation of furfural tosylhydrazone by silver chromate.

Much attention has been paid to the chemistry of tosylhydrazone derivatives from the viewpoint of synthetic utility and elucidation of the chemical reactivity because tosylhydrazones afford carbenes<sup>1</sup> or pyrazole derivatives<sup>2</sup> by heating or irradiations. The authors have investigated reactions of variable tosylhydrazones in the presence of silver chromate, and have reported that sodium salts of some kinds of conjugated tosylhydrazones generate tosylhydrazyl radicals<sup>3</sup> by one electron oxidation by silver chromate.<sup>4</sup>

The reactivity of sodium salt of furfural tosylhydrazone (1) is expected to be influenced by the conjugation of the tosylhydrazone moiety with the furan ring. Previously, Shechter et al. documented that gas phase pyrolysis of (1) gave cis- and trans-2-penten-4-ynals (3) via ring opening of the carbene, (2-furyl)methylene (2).<sup>5</sup> In order to investigate the influence of silver chromate to the reactivity of tosylhydrazones, which are conjugated with heterocyclic moiety, we have studied decomposition of (1) in the presence of silver chromate using diglyme as a solvent and found a 1,3 N→C migration of tosyl group.

A mixture of (1) and one molar equivalent of silver chromate in anhydrous diglyme



was heated at 115°C for 2 h to evolve 90% yield of nitrogen gas. The separation and purification of the reaction mixture by thin layer chromatography afforded trans-1,2-di(2-furyl)ethylene (4) and 2-furyl(p-toluenesulfonyl)methane (5) in 1 and 16% yields, respectively. The same reactions but without silver chromate gave (4) in the same yield as above (1%), however, the yield of (5) decreased to 1%. The physical properties of the products are as follows.

(4): mp 98-99°C. Mass m/z (rel intensity): 160 ( $\text{M}^+$ , 100), 131 (75), 104 (41). IR (KBr): 3030, 1480, 1240  $\text{cm}^{-1}$ . UV (EtOH): 318 nm (log  $\epsilon$ , 3.67). NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 6.35 (narrow m, 2H), 6.42 (narrow m, 2H), 6.82 (2, 2H), 7.40 (narrow m, 2H).  
 (5): mp 110-111°C. Mass m/z (rel intensity): 236 ( $\text{M}^+$ , 79), 158 (35), 129 (100).

IR (KBr): 3030, 2980, 1600, 1320, 1155  $\text{cm}^{-1}$ . UV (EtOH): 226 nm ( $\log \epsilon$ , 4.22).  
 NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 2.44 (s, 3H), 4.41 (s, 2H), 6.28 (narrow m, 1H), 6.34 (narrow m, 1H), 7.30 (d, 2H,  $J=8$  Hz), 7.33 (narrow m, 1H), 7.64 (d, 2H,  $J=8$  Hz).

The structures of (4) and (5) were deduced on the basis of their spectral properties and confirmed by comparison of the spectral properties with those of the analogous compounds such as trans-1,2-di(2-thienyl)ethylene<sup>5</sup> and 2-thienyl-(p-toluenesulfonyl)methane,<sup>6</sup> respectively.

The following explanation can be proposed for the reaction pathway. Decomposition of (1) generates the carbene (2), which then dimerizes to form (4).<sup>7</sup> On the other hand, one electron oxidation of the anion of the tosylhydrazone (6) by silver chromate<sup>4</sup> gives tosylhydrazyl radical intermediate (7).<sup>3</sup> The 1,3 N $\rightarrow$ C migration of the tosyl group<sup>8</sup> in the canonical formula (8)<sup>9</sup> of (7) leaves nitrogen gas to afford the radical intermediate (9), which then yields (5) via hydrogen abstraction from the solvent.

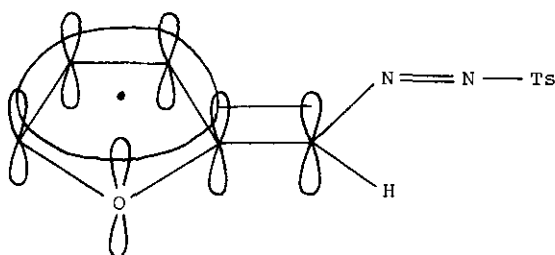
#### ACKNOWLEDGEMENT

The authors are indebted to Professor Toshio Mukai of Tohoku University and Professor Takashi Toda of Utsunomiya University for their fruitful suggestions.

#### REFERENCES

- 1) R. B. Bamford and T. S. Stevens, J. Chem. Soc., 1952, 4735; R. M. MacDonald and R. A. Klueger, J. Org. Chem., 31, 488 (1966); W. M. Jones and C. L. Ennis, J. Am. Chem. Soc., 89, 3069 (1967); S. Murahashi, I. Moritani, and M. Nishino, ibid., 89, 1257 (1967); Y. Yamamoto, I. Moritani, Y. Maeda, and S. Murahashi, Tetrahedron, 26, 251 (1970); K. Saito, Y. Omura, and T. Mukai, Chem. Lett., 1980, 349; K. Saito, ibid., 1983, 463; K. Saito, Y. Omura, and T. Mukai, Bull. Chem. Soc. Jpn., 58, 1663 (1985); K. Saito and H. Ishihara, ibid., 58, 2664 (1985).
- 2) C. D. Hurd and S. C. Lui, J. Am. Chem. Soc., 57, 2656 (1935); G. L. Closs, L. E. Closs, and W. A. Boll, ibid., 85, 3796 (1963); A. Ledwith and D. Parry, J. Chem. Soc., B, 1967, 41; H. Hart and J. L. Brewbaker, J. Am. Chem. Soc., 91, 706 (1969); J. L. Brewbaker and H. Hart, ibid., 91, 711 (1969).
- 3) K. Saito, T. Toda, and T. Mukai, Heterocycles, 3, 445 (1975); K. Saito, T. Toda, and T. Mukai, Bull. Chem. Soc. Jpn., 57, 1567 (1984).
- 4) H. Honer and J. Dehnert, Chem. Ber., 96, 786 (1963).

- 5) R. V. Hoffman and H. Shechter, J. Am. Chem. Soc., 93, 5940 (1971); R. V. Hoffman, G. G. Orphanides, and H. Shechter, ibid., 100, 7927 (1978); R. V. Hoffman and H. Shechter, ibid., 100, 7934 (1978).
  - 6) G. G. M. Janssen, P. M. van Lier, P. Scipper, L. H. J. G. Simmons, and E. F. Godefroi, J. Org. Chem., 45, 3159 (1980).
  - 7) Although Shechter et al. obtained the ethylene derivatives (cis- and trans-1,2-di(2-thienyl)ethylene) corresponding to (4) in the gas phase pyrolysis of 2-thiophenecarboxaldehyde tosylhydrazone, they did not detected (4) in the same type gas phase pyrolysis of (1).<sup>5</sup>
  - 8) S. Searles and S. Nukina, Chem. Rev., 59, 1077 (1959); H. Dorn and G. Higetag, Chem. Ber., 97, 695 (1964); R. P. Loven and W. N. Speckamp, Tetrahedron, 31, 1729 (1975).
  - 9) The delocalization of the radical electron in the 2p orbital of the methylene moiety of (8) through the conjugation with the furan moiety is considered to stabilize the radical as shown bellow.
- G. Vincow, H. J. Dauben, Jr., F. R. Hunter, and W. V. Volland, J. Am. Chem. Soc., 91, 2823 (1969); F. A. Bell, A. Ledwith, and D. C. Sherrington, J. Chem. Soc., C, 1969, 2719; K. Okamoto, K. Komatsu, O. Murai, O. Sakaguchi, and Y. Matsui, Bull. Chem. Soc. Jpn., 46, 1785 (1973); M. Pomerantz, G. L. Combs, Jr., and R. Fink, J. Org. Chem., 45, 143 (1980).



Received, 12th February, 1986