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REACTIONS OF 2- AND 3-THIOPHENECARBALDEHYDE TOSYLHYDRAZONE SODIUM SALT WITH ACRYLONITRILE: CONCENTRATION DEPENDENCE OF REACTION SPECIES GENERATED FROM 2- AND 3-THIOPHENECARBALDEHYDE TOSYLHYDRAZONE SODIUM SALT

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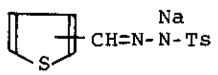
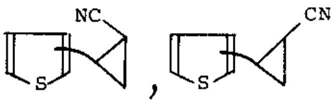
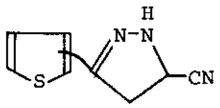
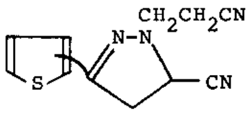
Abstract — The reactions of 2- and 3-thiophenecarbaldehyde tosylhydrazone sodium salt with an equimolar amount of acrylonitrile afforded the corresponding cyclopropane derivatives via 1,2-additions of 2- or 3-thienylmethylene to acrylonitrile. On the other hand, when the sodium salts were reacted with ten-molar requivalents of acrylonitrile, pyrazoline derivatives were formed via 1,3-dipolar additions of 2- or 3-thienyldiazomethane.

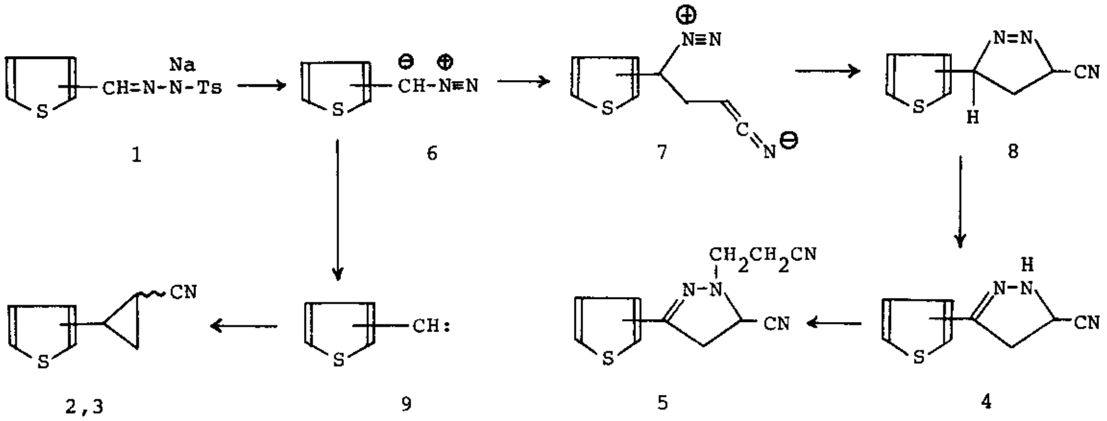
It is well known that sodium salts of tosylhydrazones generate carbenes by thermolysis or photolysis.[1] While many reports have been published on the reactivities of various kinds of tosylhydrazones, only a few researches have been undergone on the chemistry of tosylhydrazones conjugated with heterocyclic moieties. Shechter have published that tosylhydrazones of thiophenecarbaldehyde or furfural gave the corresponding carbenes, which rearrange to acetylene derivatives or insert into C-H bonds of alkanes.[2] Recently, we documented that the above tosylhydrazones gave p-toluenesulfonylmethanes via 1,3 N-C migration of tosyl group by thermolysis in the presence of silver chromate.[3] It was also reported that 2- and 3-thiophenecarbaldehyde tosylhydrazone gave cyclopropane derivatives via nucleophilic additions of singlet carbenes, 2- and 3-thienylmethylene, to olefins.[4] In order to obtain an additional information upon the chemistry of these tosylhydrazones, we investigated the reactions of 2- and 3-thiophenecarbaldehyde tosylhydrazone with acrylonitrile and found that the reaction species are dependent on the concentration of acrylonitrile. Here, we wish to report the results.

Sodium salt of 2-thiophenecarbaldehyde tosylhydrazone (1a) was allowed to react with an equimolar amount of acrylonitrile at 120 C for 30 min in anhydrous diglyme. Separation and purification of the reaction mixture with thin-layer chromatography on silica gel afforded an oil of a 1:1 mixture of cis- (2a) and trans-cyclopropane (3a) derivatives and crystals of a pyrazoline derivatives (4a) in 65.0 and 9.2% yields, respectively. On the other hand, in the same type of reaction, but using ten-molar equivalents of acrylonitrile, no 2a, 3a, or 4a were detected but crystals of a N-substituted pyrazoline derivative (5a) were obtained in 45.4% yield. An analogous result was obtained with 3-thiophenecarbaldehyde tosylhydrazone (1b) as shown in the Table.[5]

The structures of the products were deduced on the basis of their spectral, especially NMR, spectral properties and confirmed by comparisons of these spectral properties with those of the analogous compounds.[4,6,7]

				
1a : 2-thienyl		2a , 3a	4a	5a
Yield	1:1*	65.0%**	9.2%	0%
	1:10*	0%**	0%	45.4%
1b : 3-thienyl		2b , 3b	4b	5b
Yield	1:1*	67.4%**	19.7%	0%
	1:10*	0%**	0%	50.8%

* Molar ratio of 1:acrylonitrile. ** Yield of a mixture of 2 and 3.



The reaction is considered to proceed as follows.[8] The pyrolysis of the sodium salt (1) affords the diazo compound (6) leaving sodium p-toluenesulfinate. In the presence of an excess amount of acrylonitrile, 6 reacts with acrylonitrile to give 8 via 1,3-dipolar addition through the ionic intermediate (7). Hydrogen migration in 8 gives the pyrazoline derivative (4), which reacts with acrylonitrile to give the N-substituted pyrazoline derivative (5). If there is no such an excess amount of acrylonitrile, 6 decomposes to give the carbene (9). The 1,2-addition of 9 to acrylonitrile forms the cyclopropane derivatives (2,3).[9]
In the reactions of 1 with stilbene, dimethyl fumarate, dimethyl maleate, and styrene derivatives no pyrazoline derivatives corresponding to 4 or 5 have been detected at all but only the cyclopropane derivatives corresponding to 2 or 3 were afforded.[4] This difference is considered to be attributable to the high reactivity of acrylonitrile to diazo compounds.

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1) W. Kirms, "Carbene Chemistry", Academic Press (1964); J. Hine, "Divalent Carbon", Ronald Press (1964)

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3) K. Saito and H. Ishihara, Heterocycles, 24, 1291 (1986) and 26, 1891 (1987).

4) G. Maas and C. Hummel, Chem. Ber., 113, 3679 (1980), K. Saito, H. Ishihara, T. Murase, Y. Horie, and E. Maekawa, Bull. Chem. Soc. Jpn., 60, 4317 (1987).

5) The physical properties of the products are as follows.

2a or 3a: HRMS: 149.0279. Calcd. for C_8H_7NS: 149.0299. Mass m/z (rel intensity): 149 (M^+, 100), 121 (40). IR (oil): 2240 cm^{-1}. UV (EtOH): 238 nm (log , 3.78). NMR ($CDCl_3$) ppm: 1.38 (m, 1H), 1.53 (m, 2H), 2.72 (m, 1H), 6.84 (m, 1H), 6.91 (m, 1H), 7.12 (m, 1H).

3a or 2a: HRMS: 149.0311. Calcd. for C_8H_7NS: 149.0299. Mass m/z (rel intensity): 149 (M^+, 100), 121 (48). IR (oil): 2240 cm^{-1}. UV (EtOH): 238 nm (log , 3.78). NMR ($CDCl_3$) ppm: 1.42 (m, 2H), 1.70 (m, 1H), 2.52 (m, 1H), 6.93 (m, 2H), 7.18 (m, 1H).

4a: mp 53-54 C. HRMS: 177.0322. Calcd. for $C_8H_7N_3S$: 177.0335. Mass m/z (rel intensity): 177 (M^+, 100), 143 (35), 121 (15). IR (KBr): 2230 cm^{-1}. UV (EtOH): 285 nm (log , 3.99). NMR ($CDCl_3$) ppm: 2.99 (q, 1H, J=18 and 10 Hz), 3.34 (q, 1H, J=18 and 12 Hz), 5.31 (q, 1H, J=12 and 10 Hz), 6.60 (s, 1H), 7.02 (m, 2H), 7.31 (m, 1H).

5a: mp 90-91 C. HRMS: 230.0620. Calcd. for $C_{11}H_{10}N_4S$: 230.0626. Mass m/z (rel intensity): 230 (M^+, 85), 189 (100), 163 (26). IR (KBr): 2260, 2220 cm^{-1}. UV (EtOH): 291 nm (log , 3.99). NMR ($CDCl_3$) ppm: 2.71 (t, 2H, J=7 Hz), 3.03 (q, 1H, J=18 and 12 Hz), 3.36 (m, 3H), 5.00 (q, 1H, J=12 and 11 Hz), 7.02 (m, 1H), 7.24 (m, 1H), 7.37 (m, 1H).

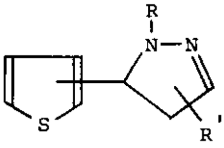
Mixture of 2b and 3b: HRMS: 149.0312. Calcd. for C_8H_7NS: 149.0299. Mass m/z (rel untensity): 149 (M^+, 100), 121 (45). IR (oil): 2240 cm^{-1}. UV (EtOH): 238 nm (log , 3.72). NMR ($CDCl_3$) ppm: 1.2-1.8 (m, 3H), 2.3-2.8 (m, 1H), 6.7-7.4 (m, 3H).

4b: HRMS: 177.0348. Calcd. for $C_8H_7N_3S$: 177.0335. Mass m/z (rel intensity): 177 (M^+, 1), 148 (100), 122 (46). IR (oil): 2230 cm^{-1}. UV (EtOH): 282 nm (log , 3.85). NMR ($CDCl_3$) ppm: 2.90 (q, 1H, J=18 and 10 Hz), 3.31 (q, 1H, J=18 and 12 Hz), 5.16 (q, 1H, J=18 and 10), 6.63 (s, 1H), 7.04 (m, 1H), 7.32 (m, 2H).

5b: mp 108-109 C. HRMS: 230.0625. Calcd. for $C_{11}H_{10}N_4S$: 230.0626. Mass m/z (rel intensity): 230 (M^+, 74), 189 (100), 163 (21). IR (KBr): 2250, 2230 cm^{-1}. UV (EtOH): 291 nm (log , 4.05). NMR ($CDCl_3$) ppm: 2.65 (m, 2H), 2.97 (q, 1H, J=18 and 13 Hz), 3.30 (m, 3H), 4.87 (q, 1H, J=13 and 11 Hz), 7.16 (m, 1H), 7.42 (m, 2H).

6) N. S. Bacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "NMR Spectra Catalog", The National Press (1985); C. J. Powchert and J. R. Campbell, "The Aldrich Library of NMR Spectra", Aldrich Chemical Company Inc. (1974); A. R. Katritzky, "Handbook of Heterocyclic Chemistry", Pergamon Press (1985).

7) The absorption maxima in the UV spectra of 4 and 5 (ca. 290 nm), which appear at longer wave length than those of 2 and 3 (238 nm) or thiophene (231 nm), show that 4 and 5 have double bonds conjugated with thiophene moiety. This fact indicates that 4 and 5 are pyrazoline derivatives bearing the thienyl group at the 3-position but not at the 5-position such as 10.



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8) K. Bowden and M. J. Price, J. Chem. Soc., B, 1970, 1466; E. K. Launio and T. G. Frey, J. Org. Chem., 36, 345 (1971); K. Saito, Bull. Chem. Soc. Jpn., 60, 2105 (1987).

9) The referee suggested a possibility of that the adduct 8 can be the common reaction intermediate for the formation of both 5 and the cyclopropanes 2, 3, and suggested to examine the reaction by changing the reactant concentration. The reaction of 1b with ten molar equivalents of acrylonitrile was carried out in five times diluted concentration comparing to that of the table. 5b was afforded in 38.0% yield but no cyclopropanes 2,3 were detected. This fact is considered to show that 2 and 3 were afforded via the carbene 9, but not via 8. The authors thank to the referee for this suggestion.

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