J.Sci.I.R.Iran

Vol. 1, No. 5
Autumn, 1990

PHOTOCHEMICAL DECOMPOSITION OF 3-CHLORO-CROTON ALDEHYDE TOSYLHYDRAZONE SODIUM SALT

M. Ghandi* and A. Shahbazi

Department of Chemistry, Faculty of Science, University of Tehran P. O. BOX. 13145-143, Tehran, Islamic Republic of Iran

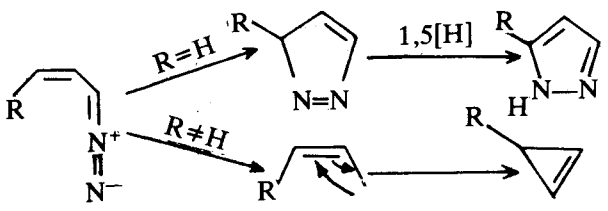
Abstract

The low temperature photochemical decomposition of 3- chloro-croton aldehyde tosylhydrazone sodium salt in tetrahydrofuran results in the formation of 3- chloro- 3- methyl cyclopropene and 5- chloro- 5- methyl- pyrazolenine respectively. In the presence of moisture, the photohydrated compound **3** was obtained as one of the products.

Introduction

The most common reaction of vinylcarbenes and carbenoids is the formation of cyclopropenes, several such reactions have been reported [1]. With some exceptions, most routes to vinylcarbenes are believed to proceed via the initial formation of vinyldiazoalkanes [2]. These compounds are known to arise from the thermal or photochemical decomposition of the tosylhydrazone salts of α, ß- unsaturated carbonyl compounds [3]. Tosylhydrazones are easily prepared in good yield by the reaction of corresponding carbonyl compounds with p-toluenesul - fonhydrazide. Generally, these compounds are highly crystalline, conveniently handled, and very stable at ordinary laboratory temperatures. General interest in the chemistry of tosylhydrazones has arisen as a result of the work of Bamford and Stevens in 1952 [4]. Since then, extensive studies showed that tosylhydrazones are potentially useful intermediates for organic synthesis.

Generally, when the ß-position of tosylhydrazone of α, ß- unsaturated carbonyl compound is not substituted (R=H), pyrazole formation (through cyclization of diazo intermediate) is predominant [5].

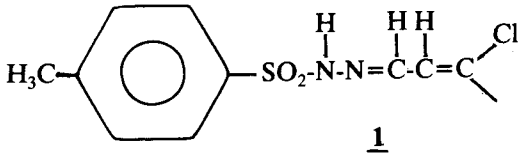


Key words: Tosylhydrazones, Carbenes

As a result of our interest to know the effect of halogen substitution in ß- position on product distribution, we chose the title compound. Certainly, the cyclopropanization of this compound and other derivatives could have led to the formation of 3- chloro- cyclopropenes which must be prepared through classical methods [6].

Results and Discussion

p. Tolutenesulfonylhydrazone **1** was prepared by reaction of ß- chloro- croton aldehyde [7] with p-toluenesulfonhydrazide in ethanol at 50°C (MP 125°C, 52% yield). Identification of **1** was done according to the analysis of spectroscopic properties.



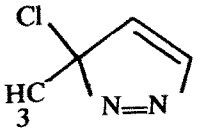
1

The mass spectrum of tosylhydrazone showed the expected molecular ion peak at m/e 272. The H-NMR spectrum (acetone- d6, δ) revealed peaks at 6.8-8.1 (m, 7H, changed to 6H in D_2O), 2.7 (S, 3H), and 2.4 (S, 3H). Anal. calcd. For $C_{11}H_{13}ClN_2O_2S$, C, 48.4%; H, 4.8%; N, 10.3%. Found: C, 49.3%; H, 5.5%; N, 10.5%.

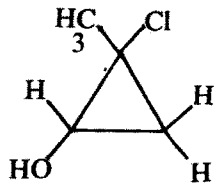
To 0.12M solution of tosylhydrazone **1** in dry THF was added an equivalent mole of sodium methoxide

and the mixture was stirred for 15 minutes. The solution was irradiated at 3660A° in a pyrex vessel under nitrogen atmosphere at-5°C for two hours using two UV lamps. After evaporation of solvent, pyrazoline **2** was obtained as the photoproduct (88% yield). The H-NMR ($CDCl_3$, δ) showed peaks at 6.8-7.2 (dd, AB pattern, J=9 Hz , 2H), and 2.1 (S, 3H).

The experiment was repeated but the wavelength was changed to 2540A°. The product was found to be a mixture of four compounds. Column chromatography separation of mixture on Silica gel using a mixture of 36% chloroform and 70% carbon tetrachloride as elutent gave two products which were identified as pyrazoline **2** and alcohol **3** in 35% and 30% yield respectively.



2



3

4

The structure of alcohol **3** was realized on the basis of its H-NMR ($CDCl_3$, δ) which showed peaks at 2.4 (m, 1H), 1.7 (bs, 1H, disappeared in D_2O), 1.5 (S, 3H) and 0.8 (m, 2H). The alcohol **3** seems likely to have arisen through the photohydration of Cyclopropene **4**. The source of moisture might have been from solvent or nitrogen gas. On the basis of these results, it was concluded that the cyclopropene yield would improve if a high pressure mercury lamp was used and the solvent dried as much as possible in order to avoid further reaction of cyclopropene.

Therefore, the photolysis was repeated with a high pressure mercury lamp for a period of four hours at 20°C through a pyrex filter. Rapid filteration of solution through Silica gel (20g) and evaporation of solvent gave cyclopropene **4** (47% yield). Structure assignment of cyclopropene **4** followed from its H-NMR spectrum which showed peaks at 7.2 (S, 2H), and 2.1 (S, 3H).

It is apparently possible to obtain a significant amount of vinylcarbene from ß- chloro- substituted α,β- unsaturated aldehyde and a simple method to the synthesis of 3- chloro- cyclopropene derivatives.

Acknowledgement

This work was partially supported by the Tehran University Research Council.

References

1- (a)- G. L. Closs, and L. E. Closs, *J. Am. Chem. Soc*, **83**, 1003 (1961).
(b)- G. L. Closs, and L. E. Closs, *ibid*, **83**, 2015 (1961).
(c)- G. L. Closs, and L. E. Closs, *ibid*, **85**, 99 (1963).
(d)- F. Fischer, and D. E. Applequist, *J. Org. Chem.*, **30**, 2089 (1965).
(e)- R. M. Magid, and J. G. Welch, *J. Am. Chem.* Soc., 88, 5681 (1966).
(f)- R. M. Magid, and J. G. Welch, *ibid.*, **89**, 5300 (1967).
(g)- R. M. Magid, and J. G. Welch, *ibid.*, **90**, 5211 (1968).
(h)- R. Köster, S. Arora, and P. Binger, *Angew. Chem.*, **82**, 839 (1970), Angew. Chem. Int. Ed. Engh., 9, 810 (1970).
(i)- R. Köster, S. Arora, and P. Binger, *Justus Liebigs Ann. Chem.*, **1219** (1973).
2- (a)- T. Severin, H. Kramer, and P. Adhikary, *Chem. Ber.*, **104**, 972 (1971).
(b)- J. A. Pincock, R. Morchat, and D. R. Arnold, *J. Am. Chem. Soc.*, **95**, 7536 (1973).
(c)- G. E. Palmer, J. R. Bolton, and D. R. Arnold, *ibid*, **96**, 3708 (1974).
3- (a)- G. Buchi, and J. D. White, *ibid.*, **86**, 2884 (1964).
(b)- H. H. Stechl, Chem. Ber., 97, 2681 (1964).
(c)- H. Dürr, Angew-Chem., 79, 1104 (1967), *Angew: Chem. Int. Ed. Engl.*, **6**, 1084 (1967).
(d)- R. Ya. Levina, L. G. Zaitseva, I. B. Avezoy, and I. C. Bolesov, *Zh. Org. Khim.*, **8**, 1105 (1972).
(e)- M. Jones, Jr, S. D. Reich, and L. T. Scott, *J. Am. Chem. Soc*; **92**, 3118 (1970).
(f)- S. Masamune, R. T. Seidner, H. Zenda, M. Weisel, N. Nakatsuka, and G. Bigam, *ibid*, **90**, 5286 (1968).
(g)- D. G. Farnum, M. Ghandi, S. Raghu, and T. Reitz, *J. Org. Chem.*, **47**, 2598 (1982).
(h)- A. P. Marchand, and R. E. Lehr, Pericyclic Reactions (W. M. Jones and Udo H. Brimker), Ed., Academic Press, New York, 1977, Vol. I, pp 109-198.
4- W. R. Bamford and S. Stevens, *J. Chem. Soc.*, **4735** (1952).
5- (a)- J. L. Brewbaker, and H. Hart, *J. Am. Chem. Soc.*, a, 711 (1969).
(b)- G. L. Closs, E. L. Closs, and W. A. Boll, *ibid*, **85**, 3796 (1963).
6- (a)- R. Breslow, J. T. Groves, and G. Ryna, *ibid*, **89**, 5048 (1967).
(b)- S. W. Tobey and R. West, *ibid.*, **88**, 2478 and 2481 (1966).
(c)- A. Haas, and H. Krachter, *Chem. Ber.*, **121**, 1827 (1988).
(d)- J. Sepiol, and R. L. Soulen, *J. Org. Chem.*, **40**, 3791 (1975).
(e)- K. C. Waterman, D. V. Speer, A. Streitwieser, Jr, C. C. Look, K. O. Nguyen, and J. G. Stack, *J. Org. Chem.*, **53**, 583 (1988).
7- K. Bodenoorf and R. Mayer, *Chem. Ber.*, **98**, 3554 (1965).