Reaction of Oxime *p*-Toluenesulfonates and Mercaptans

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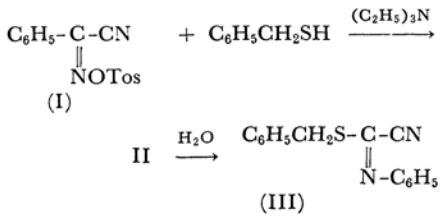
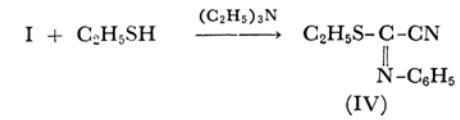
In general, oxime tosylates readily undergo the Beckmann rearrangement,[1] but recently Stevens reported[2] that the tosyl ester of α-oximinobenzyl cyanide (I) appeared to be much more stable than ordinary oxime tosylates; that is, they did not undergo solvolysis in refluxing either in ethanol, or in benzene containing an equivalent of aniline. In our study, I could be recovered unchanged after refluxing in a pyridine or triethylamine solution. The present paper will report a brief study of the nucleophilic attack of the mercapto anion on the carbon atom of the C=N function of this stable oxime tosylate and will compare it with ordinary oxime tosylate.

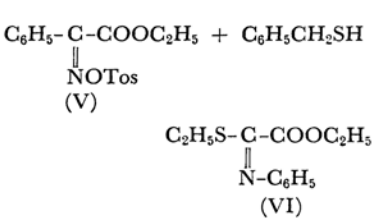
When I was treated with benzyl mercaptan in benzene, no reaction had occured, but in benzene containing an equivalent triethylamine, it was converted with a violent reaction into complex (II), which was very hygroscopic and which decomposed with water to α-benzylmercapto-α-phenyliminoacetonitrile (III) and triethylammonium *p*-toluenesulfonate, which was then saponified with aqueous sodium hydroxide to give triethylamin and sodium *p*-toluenesulfonate.



Also, when I was treated with ethyl mercaptan in benzene containing an equivalent triethylamine, α-ethylmercapto-α-phenyl-iminoacetonitrile (IV) was formed.

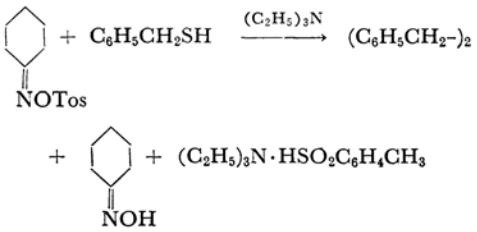


Similarly, when the tosyl ester of ethyl α-phenyl-α-oximino-acetate (V), which was also a stable oxime tosylate like I, was treated with benzyl mercaptan, ethyl α-benzylmercapto-α-phenyl-iminoacetate (VI) was formed.



These reactions seemed to succeed through a nucleophilic attack of the mercapto anion activated by triethylamine on the carbon atom[3] of the C=N function, and through the following rearrangement.

On the contrary, when cyclohexanone oxime *p*-toluenesulfonate (VII) was treated with benzylmercaptan under conditions similar to those described above, dibenzyl disulfide, cyclohexanone oxime, and triethylammonium *p*-toluenesulfinate were formed.



The mechanism of this reaction is not clear.

Experimental

The tosyl ester of α-oximino-benzyl cyanide (I) was prepared according to Stevens' method.[2] Mp 134—135°C.

Tosyl Ester of Ethyl α-Phenyl-α-oximinoacetate (V). To 150 m*l* of an ethanol solution of sodium ethoxide prepared from 11.5 g (1/2 mol) of sodium, 82 g (1/2 mol) of ethyl phenylacetate and 50.2 g (1/2 mol) of *n*-butyl nitrite were added under cooling. After the addition had been completed, the solution was heated at 30°C for one hour. To this solution 100 m*l* of ether were added, and the sodium salt of ethyl α-phenyl-α-oximinoacetate was removed by filtration (73.5 g, 68%). This was suspended in 300 m*l* of benzene, and then 40 g (0.34 mol) of *p*-toluenesulfonyl chloride diluted with 100 m*l* of benzene were added. The mixture was refluxed for one hour. After cooling, the mixture was washed with water, the water layer was extracted with 100 m*l* of ethyl acetate, and the combined organic layer was concentrated to leave 80 g of a residue. The recrystallization of this residue from

1) L. G. Donaruma and W. Z. Heldt, "Organic Reactions," **11**, 1 (1960).
2) T. E. Stevens, *J. Org. Chem.*, **28**, 2436 (1963).
3) F. B. Zienty, B. D. Vineyard and A. A. Schleppnik, *J. Org. Chem.*, **27**, 3140 (1962).

ethanol gave colorless needles of V. Yield, 36.2 g, mp 95—96°C.

Found: C, 58.73; H, 4.89; N, 3.80%. Calcd for $C_{17}H_{17}O_5NS$: C, 58.79; H, 4.93; N, 4.03%.

Tosyl Ester of Cyclohexanone Oxime (VII).[4] A solution of 19.0 (0.1 mol) of *p*-toluenesulfonyl chloride in benzene was stirred, drop by drop, into one of 11.3 g (0.1 mol) of cyclohexanone oxime in 50.5 g (0.5 mol) of triethylamine in an ice bath. The mixture was kept at 0°C for 3 hr and then used in the following experiment without further purification because this substance deflagrated vigorously upon warming to room temperature.

Reaction of the Tosyl Ester of α-Phenyl-α-oximinoacetonitrile (I) with Benzyl Mercaptan. To a solution of 30.0 g (0.1 mol) of I in 50 m*l* of dry benzene containing 10.1 g (0.1 mol) of triethylamine, 12.4 g (0.1 mol) of benzyl mercaptan were added, drop by drop, under cooling. After the addition had been completed, the mixture was refluxed for 10 min and then cooled. The evaporation of the solvent left a very hygroscopic complex (II). The addition of water to this complex formed a water-insoluble material (III), which was filtered and recrystallized from ethanol to give slightly yellowish, silky crystals. Yield, 24.5 g (97%), mp 87—88°C. IR bands (KBr) 2200 cm^{-1} (C≡N), NMR spectrum of III in deuterated chloroform (tetramethylsilane was used as the internal reference): δ 4.43 (2H, singlet) and δ 7.32 (5H, singlet) for $-S-C\underline{H}_2-C_6\underline{H}_5$, and δ 7.1—7.9 (5H, broad) for $=N-C_6\underline{H}_5$.

Found: C, 71.62; H, 4.98; N, 11.35%. Calcd for $C_{15}H_{12}SN_2$: C, 71.41; H, 4.80; N, 11.11%.

Reaction of the Tosyl Ester of α-Phenyl-α-oximinoacetonitrile (I) and Ethyl Mercaptan. The method was the same as that described above. IV was extracted with ether and distilled under reduced pressure. Yield, 89%, bp 87°C/0.007 mmHg. IR bands (liquid film) 2200 cm^{-1} (C≡N). NMR spectrum of IV in deuterated chloroform (tetramethylsilane was used as the internal reference): δ 1.45 (3H, triplet) for $-CH_2-C\underline{H}_3$, δ 3.22 (2H, quartet) for $-C\underline{H}_2-CH_3$, and δ 7.2—7.9 (5H, broad) for $=N-C_6\underline{H}_5$.

Found: C, 63.35; H, 5.19; N, 14.64%. Calcd for $C_{10}H_{10}N_2S$: C, 63.15; H, 5.30; N, 14.73%.

Reaction of the Tosyl Ester of α-Phenyl-α-oximinoacetate (V) and Benzyl Mercaptan. The method was the same as that described above. VI was recrystallized from ethanol to give colorless needles. Yield, 78%, mp 67—68°C. IR bands (KBr) 2200 cm^{-1} (C≡N) and 1710 cm^{-1} (C=O). NMR spectrum of VI in deuterated chloroform (tetramethylsilane was used as the internal reference): δ 1.32 (3H, triplet) for $-C\underline{H}_3$, δ 4.34 (2H, quartet) for $-CH_2-CH_3$, δ 4.35 (2H, singlet) for $-C\underline{H}_2-C_6H_5$, δ 7.32 (5H, singlet) for $-CH_2-C_6\underline{H}_5$ and δ 7.2—7.7 (5H, broad) for $=N-C_6\underline{H}_5$.

Found: C, 68.40; H, 5.79; N, 4.45%. Calcd for $C_{17}H_{17}O_2NS$: C, 68.21; H, 5.73; N, 4.68%.

Reaction of the Tosyl Ester of Cyclohexanone Oxime (VII) and Benzyl Mercaptan. The method was the same as that described above. The separation of dibenzyl disulfide and cyclohexanone oxime was made by the extraction of the oxime with cold ethanol. Yield, dibenzyl disulfide: 85%, mp 71°C, recovered cyclohexanone oxime: 95%, mp 89°C.

4) P. A. S. Smith, *J. Am. Chem. Soc.*, **70**, 323 (1948).