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1,3-Dithian-2-one Tosylhydrazone. Synthesis and Carbenoid Decomposition

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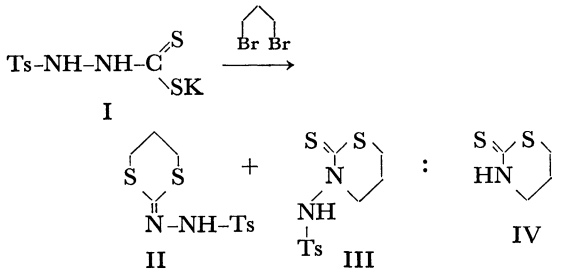
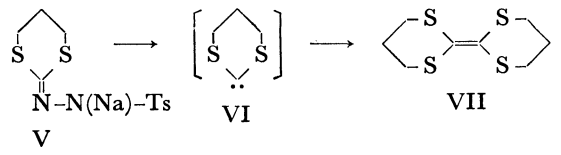
Synopsis. 1,3-Dithian-2-one tosylhydrazone was prepared by the reaction of potassium 3-tosyldithiocarbazate and 1,3-dibromopropane. Carbenoid reactions of the tosylhydrazone were investigated.

Much attention has been paid on the synthesis of 1,3-dithiane derivatives and their application in organic synthesis as a nucleophile of acyl anion equivalent.[1] In the carbene analog, however, only a few acyclic dithiocarbenes[2-4] and ethylenedithiocarbene[2] to give fragmentation products have been reported. As compared with these carbenes, trimethylenedithiocarbene is of great interest both in its reactivity and as synthetic tool. In this paper I present a convenient synthesis of 1,3-dithian-2-one tosylhydrazone (II) and its carbenoid decomposition under several conditions.

Potassium 3-tosyldithiocarbazate (I) prepared[3] from tosylhydrazine and carbon disulfide in the presence of KOH in methanol was alkylated with 1,3-dibromopropane. After chromatography on silica gel were obtained tosylhydrazone (II) and 3-(tosylamino)tetrahydro-1,3-thiazine-2-thione (III) in 36 and 28% yields, respectively, along with 11% recovery of tosylhydrazine. The structures of II and III were established by the elemental analysis and spectroscopic data. The structure of III was confirmed by reduction with zinc in acetic acid to give tetrahydro-1,3-thiazine-2-thione (IV) in 74% yield, the structure of which was determined by direct comparison with a sample prepared by the authentic route.[5]



Sodium salt (V) was prepared from II and NaH in hexane and was subjected to carbenoid decomposition, the Bamford-Stevens reaction.[6] Thermal decomposition of V in pyridine and in DMF at 90—95 °C for 2 h gave 2,2'-bi(1,3-dithianylidene) (VII) in 36 and 29% yields, respectively. Similarly, irradiation of V in DMF with 500 W high-pressure mercury lamp yielded VII in 23% yield along with unknown products. The structure of VII was established by elemental analysis and mass and NMR spectra.



The formation of the dimer VII seems to be a good indication that trimethylenedithiocarbene (VI) is a real intermediate[7] in both thermal and photochemical reactions of V. This carbene is in marked contrast to ethylenedithiocarbene[2] in reactivity, which gave no dimerization product but only fragmentation products, ethylene and carbon disulfide.

Experimental

Reaction of Potassium 3-Tosyldithiocarbazate (I) with 1,3-Dibromopropane. A solution of KOH (1.74 g, 0.031 mol) in methanol (10 ml) was added to I (9.32 g, 0.031 mol) prepared by the method of Schöllkopf and Wiscott[3] and the mixture was stirred at 50 °C for 10 mim. To this solution was added dropwise 1,3-dibromopropane (8.08 g, 0.04 mol) in methanol (10 ml) during a period of 1 h under stirring and the mixture was stirred for 2 h at room temperature. Removal of the solvent and addition of benzene caused precipitation. After filtration, the filtrate was concentrated and the residue was chromatographed on silica gel. Elution with benzene gave 1,3-dithian-2-one tosylhydrazone (II) (3.28 g, 36%), mp 172—173 °C from hexane–CH_2Cl_2.

Found: C, 43.72; H, 4.64; N, 9.48%; mol wt: 302 (mass). Calcd for $C_{11}H_{14}O_2N_2S_3$: C, 43.71; H, 4.67; N, 9.72%, mol wt: 302.4. IR(KBr): 3160 (νN–H) and 1520 cm^{-1} (νC=N). NMR($CDCl_3$): δ 2.16 (m, 2H), 2.42 (s, 3H), 3.04 (m, 4H), 7.50 (s, 1H), and 7.80 (d, 2H). Elution with benzene–CH_2Cl_2 (2: 1) gave 3-(tosylamino)tetrahydro-1,3-thiazine-2-thione (III) (2.65 g, 28%), mp 100—101 °C from hexane–CH_2Cl_2.

Found: C, 43.79; H, 4.72; N, 9.78%; mol wt: 302 (mass). Calcd for $C_{11}H_{14}O_2N_2S_3$: C, 43.71; H, 4.67; N, 9.27%; mol wt: 302.4. IR(KBr): 3140 (νN–H) and 1540 cm^{-1} (νC=S). NMR($CDCl_3$): δ 2.42 (s+t, 5H), 3.00 (t, 2H), 4.10 (t, 2H), 7.28 (d, 2H), 7.70 (d, 2H), and 9.46 (d, 2H). Further elution with CH_2Cl_2 gave tosylhydrazine (0.66 g, 11%).

Redution of III with Zinc in Acetic Acid. 1.0 g Zn was added to a solution of III (0.40 g, 1.3 mmol) in AcOH (15 ml) and the resulting mixture was refluxed for 3 h. After filtration, the filtrate was concentrated and dried under reduced pressure. The residue was chromatographed on silica gel. Elution with CH_2Cl_2 gave tetrahydro-1,3-thiazine-2-thione (IV) (0.13 g, 74%), mp 132—133 °C from hexane–CH_2Cl_2 (lit,[5] mp 132 °C).

Thermal Decomposition of Sodium Salt of Tosylhydrazone (V) in Pyridine. A solution of V (1.0 g, 3.3 mmol) in pyridine (20 ml) was heated at 90—95 °C for 2 h with stirring under argon. After evaporation of the solvent under reduced pressure, CH_2Cl_2 solution of the residue was washed with water and dried with $MgSO_4$. After eveporation of CH_2Cl_2, the residue was chromatographed on silica gel. Elution with benzene gave 2,2'-bi(1,3-dithianylidene) (VII) (0.28 g, 36%), mp 140—141 °C from CH_2Cl_2-hexane (lit,[8] mp 140.8—141.6 °C).

Found: C, 40.43; H, 5.12%; mol wt: 236 (mass). Calcd for $C_8H_{12}S_4$: C, 40.68; H, 5.12%; mol wt: 236.4. NMR-($CDCl_3$): δ 2.16 (m, 4H) and 2.94 (t, 8H).

Photochemical Decomposition of V in DMF. A solution of

V (1.0 g, 3.3 mmol) in DMF (20 ml) was irradiated with 500 W highpressure mercury lamp for 5 h at room temperature under argon. After a similar work-up to that mentioned above, chromatographing on silica gel of the mixture gave VII (0.18 g, 23%).

References

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