Tetrahedron Letters No. 46, pp 4493 - 4494.

0040-4039/79/1108-4493$02.00/0

NONCLASSICAL THIENO[3,4-c][1,2,5] THIADIAZOLE

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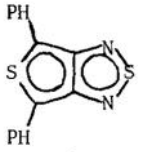
Abstract: Thieno[3,4-c][1,2,5] thiadiazole was generated by the dehydration of the corresponding sulfoxide 8 and characterized by the isolation of its dimer and adducts.

Nonclassical, 10 π-electron thieno[3,4-c]-thiophenes have been studied by several workers.[1-8] Cava and coworkers[2,3] reported the synthesis of 1,3,4,6-tetraphenylthieno[3,4-c]-thiophene, the first stable example of this series. The synthesis or generation of some other nonclassical condensed thiophenes such as thieno [3,4-c] pyrroles, -furan or pyrazole have also been reported.[8,9] Carmack and coworkers[10,11] have synthesized [1,2,5] thiadiazolo[3,4-c][1,2,5] thiadiazole (1a) and the corresponding [1,2,5] selenadiazolo [3,4-c][1,2,5] thiadiazole (1b).

1a: X = S
1b: X = Se

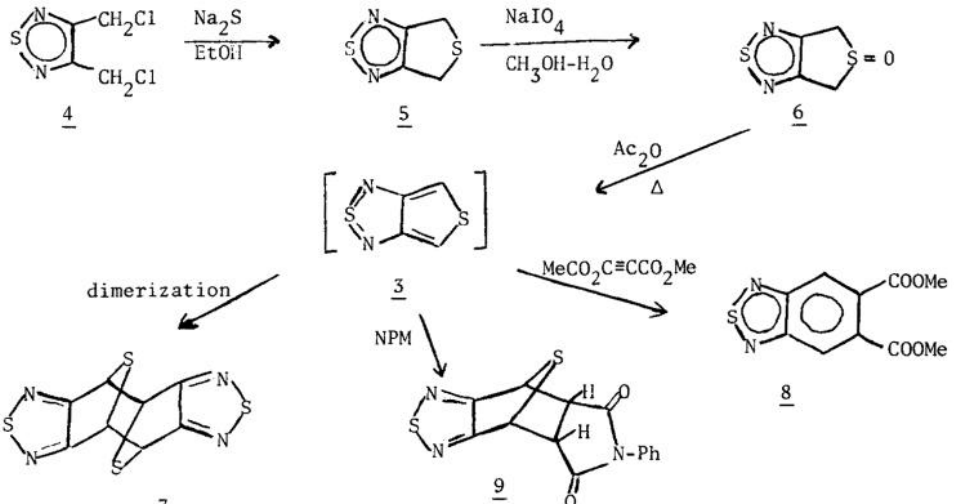


2

3

Schlessinger and Bower[12] reported the synthesis of 2,5-diphenylthieno[3,4-c][1,2,5] thiadiazole (2). In this regard we wish to report the generation of the parent compound, thieno[3,4-c]-[1,2,5] thiadiazole (3) as shown in scheme 1.

SCHEME 1



An ethanolic solution of 3,4-bis(chloromethyl)-1,2,5-thiadiazole[13,14] (49.0 mmol) was slowly added (6 hrs) to a slurry of sodium sulfide nonahydrate (85.0 mmol) in ethanol and allowed to stir at room temperature (20 hrs). Removal of the solvent and recrystallization (methanol) gave 4,6-dihydrothieno [3,4-c][1,2,5]thiadiazole (5) as white crystals [49%, mp 81-83^{o}; m/e 144 (M^+); uv (CH_3OH) 258 (log ε 4.05) and 318 nm (2.26); nmr ($CDCl_3$)δ 4.03 (s)]. A solution of sulfide 5 in methanol was treated with an aqueous solution of sodium periodate and stirred at room temperature for 18 hrs. Concentration of the mixture, extraction with chloroform and recrystallization (methanol) of the product gave white crystals of 4,6-dihydrothieno [3,4-c][1,2,5] thiadiazole-5-oxide [6, 75%, mp 137-139^{o}; m/e 160 (M^+), 112 (M- S=0); ir (KBr) 1020 cm^{-1} (S=0); uv (CH_3OH) 264 (log ε 3.89) and 320 nm (2.37 shoulder)]. The nmr spectrum of 6 showed an AB quartet with absorptions at δ 3.93 (d, 16 CPS, 2H) and δ 4.46 (d, 16 CPS, 2H). Dehydration of sulfoxide 6 in refluxing acetic anhydride (N_2) produced 3 as a fluorescent compound (not stable enough to be isolated) which gradually converted to its dimer [7, mp 278-280^{o} (dec.); m/e 284 (M^+) and 142 (M-142)]. When compound 6 was heated (100^{o}) in acetic anhydride (N_2) in the presence of dimethyl acetylenedicarboxylate, it gave dimethyl 2,1,3-benzothiadiazole-5,6-dicarboxylate (8) as a white solid [70%, mp 110-112^{o}; m/e 252 (M^+), 221 ($M-OCH_3$); ir (KBr) 1750 cm^{-1} (C=0); uv (CH_3OH) 238 (log ε 4.39) and 311 nm (4.04); nmr ($CDCl_3$) δ 4.0 (s, 6H) and 8.4 (s, 2H)]. Dehydration of 6 in acetic anhydride (100^{o}, N_2) in the presence of N-phenylmaleimide gave a crude product which upon elution chromatography on alumina (benzene-hexane) yielded adduct 9 as a white crystalline material [46%, mp 198-200^{o}; m/e 315 (M^+), 173, 142; ir (KBr) 1715 cm^{-1} (C=0); uv (CH_3OH) 298 nm (log ε 3.94); nmr ($CDCl_3$) δ 3.63 (s,2H), 5.12 (s,2H) and 7.25-7.53 (m,5H)]. Based on the nmr position (5.12 δ) of the protons α to the carbonyl groups, compound 9 is shown to be an endo adduct.[3,4]. As is shown, thienothiadiazole 3 is formed as an unstable fluorescent compound. Isolation of dimer 7 and adducts 8 and 9 clearly indicate the generation of this nonclassical aromatic heterocycle in the dehydration of sulfoxide 6.[15]

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15. Elemental analyses on compounds 7. 8. 10 and 11 were in agreement with the structures.

Acknowledgements. We wish to thank the Iranian Ministry of Science and Higher Education and Shiraz University for the support of this project.

(Received in UK 10 September 1979)