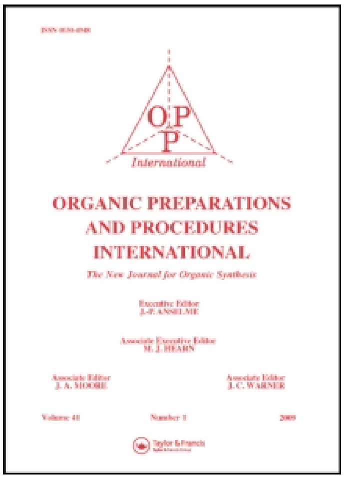


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

THE SYNTHESIS OF 2,3,7,8-TETRAAMINODIBENZOTHIOPHENE-5,5-DIOXIDE

F. E. Arnold[a]
[a] Air Force Materials Laboratory, Wright-Patterson Air Force, Base, Ohio

To cite this Article Arnold, F. E.(1975) 'THE SYNTHESIS OF 2,3,7,8-TETRAAMINODIBENZOTHIOPHENE-5,5-DIOXIDE', Organic Preparations and Procedures International, 7: 3, 123 — 127
To link to this Article: DOI: 10.1080/00304947509355131
URL: http://dx.doi.org/10.1080/00304947509355131

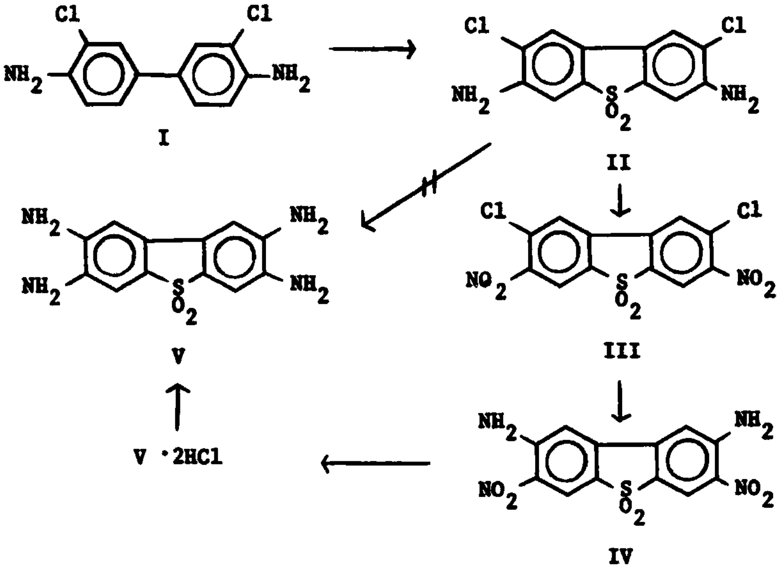
ORGANIC PREPARATIONS AND PROCEDURES INT. 7(3), 123-127 (1975)

THE SYNTHESIS OF
2,3,7,8-TETRAAMINODIBENZOTHIOPHENE-5,5-DIOXIDE

F. E. Arnold

Air Force Materials Laboratory
Wright-Patterson Air Force Base
Ohio 45433

Fused aromatic heterocyclic tetraamines containing two sets of o-amino functions have been prepared with phenazine,[1] dibenzo-p-dioxin,[2] diquinoxalpyrene,[3] dibenzofuran[4] and pyridine[5] ring systems. The latter two heterocyclic tetraamines are of special interest since the hetero atom imparts a variance in amine nucleophilicity, thereby leading to specific geometric isomers in certain polycondensation reactions. This paper describes the four-step synthesis of 2,3,7,8-tetraaminodibenzothiophene-5,5-dioxide V, a new fused heterocyclic tetraamine where two of the four amine groups are different in reactivity from the others.



Sulfonation of 3,3'-dichlorobenzidine (I) with fuming sulfuric acid led to 2,8-dichloro-3,7-diaminodibenzothiophene-5,5-dioxide (II). Attempts to aminate II with ammonia and cuprous chloride at high pressure and temperature to give the tetraamine V directly were unsuccessful. The chloro groups had to be activated for amination by oxidation of the 3,7-amino groups to nitro groups with trifluoroperacetic acid to give 2,8-dichloro-3,7-dinitrodibenzothiophene-5,5-dioxide III. Amination of III proceeded very smoothly at low temperature and without the aid of a catalyst to give 2,8-diamino-3,7-dinitrodibenzothiophene-5,5-dioxide (IV) in excellent yields. The reduction of IV to V was carried out using stannous chloride in concentrated hydrochloric acid. The tetraamine was isolated from the reaction mixture as a dihydrochloride salt which exemplifies the difference of amino reactivity. Although the exact position of salt formation was not determined; one would presume the 3,7-positions to be the site of protonation, from the chemistry of the fused heterocyclic system. The free amine is liberated from its hydrochloride by treatment with ammonium carbonate. The light tan amine could be recrystallized from water and exhibits excellent shelf life when stored in the dark under a nitrogen atmosphere.

EXPERIMENTAL

2,8-dichloro-3,7-diaminodibenzothiophene-5,5-dioxide (II). - To 150 ml of 30% fuming sulfuric acid at 0°, was added 50 g (0.153 mole) of 3,3'-dichlorobenzidine dihydrochloride. The solid was added in small quantities in order to maintain the temperature between 5-15°. After the addition was complete, the mixture was heated to 75° and maintained at that temperature for 15 hours. The solution was then allowed to cool to 30° and poured onto 5 kg of ice to precipitate the compound. The yellow precipitate was collected, washed with water and 8% ammonium carbonate solution, then air dried. The product was recrystallized from m-cresol to give 40 g (83%) of small yellow crystals which did not melt up to 400°. IR (KBr) 3340, 3425 (N-H).

Anal. Calcd. for $C_{12}H_8N_2Cl_2O_2S$: C, 45.72; H, 2.56; N, 8.89

Found: C, 45.69; H, 2.49; N, 8.31

2,8-dichloro-3,7-dinitrodibenzothiophene-5,5-dioxide (III). - To 200 ml of methylene chloride containing 10 ml of 90% hydrogen peroxide was added dropwise 45 ml of trifluoroacetic anhydride. The temperature of the mixture was not allowed to exceed 35° during the addition of the anhydride. To the mixture was then added 10 g (0.0317 moles) of 2,8-dichloro-3,7-diaminodibenzothiophene-5,5-dioxide. The mixture was heated to reflux and maintained at reflux for 10 hours. On cooling to room temperature, a bright yellow material crystallized which was collected, washed with water and air dried. The yellow material was dissolved in tetrahydrofuran and passed through a one foot alumina column using tetrahydrofuran as the elution solvent. The tetrahydrofuran was removed under reduced pressure to give 6.2 g (52%) of bright yellow crystals, mp. 321-322°. IR (KBr) 1449, 1590 (NO_2).

Anal. Calc. for $C_{12}H_4N_2O_6SCl_2$: C, 38.42; H, 1.07; N, 7.07

Found: C, 38.53; H, 1.45; N, 7.38

2,8-diamino-3,7-dinitrodibenzothiophene-5,5-dioxide (IV). - To a pressure bottle was added 40 ml of p-dioxane, 10 ml of concentrated ammonium hydroxide and 5 g (0.0131 mole) of 2,8-dichloro-3,7-dinitrodibenzothiophene-5,5-dioxide. The bottle was sealed and slowly heated to 140°. After 15 hours at 140°, the pressure bottle was allowed to cool to room temperature and the orange solid collected by filtration. The material was washed with water, dried under reduced pressure, and recrystallized

from nitrobenzene to afford 3.8 g (86%) of the product, mp. > 400°.
IR (KBr) 3340, 3440 (N-H).

Anal. Calcd. for $C_{12}H_8N_4O_6S$: C, 42.86; H, 2.39; N, 16.66
Found: C, 42.76; H, 2.39; N, 16.16

2,3,7,8-Tetraaminodibenzothiophene-5,5-dioxide · 2HCl (V). - To a solution containing 33 g (0.148 mole) of stannous chloride dihydrate dissolved in 200 ml of concentrated hydrochloric acid was added 5 g (0.0148 mole) of 2,8-diamino-3,7-dinitrodibenzothiophene-5,5-dioxide at such a rate as to maintain the temperature at 60 to 70°. The mixture was heated for 4 hours between 65 - 70° and then cooled to 0°, thereby precipitating the dihydrochloride as a gray solid. The dihydrochloride was recovered by filtration and dissolved in 300 ml of 50% aqueous methanol. Concentrated hydrochloric acid in the amount of 300 ml was added to the solution. Cooling produced white needles of the dihydrochloride salt which were collected and pressed dry while under a stream of nitrogen. The dihydrochloride salt was washed several times with diethylether and dried under reduced pressure to give 5.7 g (87% yield) of V · 2HCl.

Anal. Calcd. for $C_{12}H_{14}N_4Cl_2SO_2$: C, 41.27; H, 4.04; N, 16.04; Cl, 20.30
Found: C, 41.30; H, 4.35; N, 15.65; Cl, 20.25

2,3,7,8-tetraaminodibenzothiophene-5,5-dioxide (V). - The dihydrochloride salt was suspended in deoxygenated water and ammonium carbonate was added portionwise to free the tetraamine. The free amine was purified by recrystallization from deoxygenated water, mp. > 300°.
IR (KBr) 3335, 3415 (N-H).

Anal. Calcd. for $C_{12}H_{12}N_4SO_2$: C, 52.00; H, 4.65; N, 20.21; S, 11.57
Found: C, 52.12; H, 4.72; N, 19.88; S, 11.62

REFERENCES

1. E. Mietzki and H. Muller, Ber., 22, 440 (1889).
2. J. K. Stille and E. L. Mainen, Macromolecules, 1, 36 (1968).
3. F. E. Arnold, J. Polymer Sci., 8, 2079 (1968).
4. A. J. Sciree, F. E. Arnold and R. L. Van Deusen, J. Polymer Sci., 12, 265 (1974).
5. R. L. Williams and S. A. Cohen, J. Heterocyclic Chem., 8, 841 (1971).
6. A. H. Gerber, J. Polymer Sci., 11, 1703 (1973).

(Received March 10, 1975; in revised form May 23, 1975)