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5*H*,7*H*-Bisindeno[2,3-*b*:3',2'-*d*]thiophene

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It has been reported (1) that the reaction between sulfur and indene gives as one of several products a compound thought to be I, melting at 290-292°, which was very insoluble in organic solvents and showed fluorescence in benzene solution. The structure was proposed as I mainly on the basis of elemental analysis. The properties which we have found for I, prepared by an unambiguous method, suggest that the early literature reports are incorrect in proposing that the product from the reaction of sulfur and indene is I. Attempts to repeat the reaction between sulfur and indene by us gave only asphalt-like unworkable material.

In connection with a study of the synthesis of thiophene compounds related to fluorene, we have prepared 5*H*,7*H*-bisindeno[2,3-*b*:3',2'-*d*]thiophene (I). Reduction of 5*H*,7*H*-bisindeno[2,3-*b*:3',2'-*d*]thiophene-5,7-dione (IV) with lithium aluminum hydride and aluminum chloride (2) gave a 22 percent yield of I as a yellow solid melting at 215-216°. Compound I was non-fluorescent and soluble in many organic solvents. The methylene peak occurred at τ 6.21 in the nmr spectrum of I. The methylene peak of fluorene also occurred at τ 6.21. Ketone IV, m.p. 334.5-335°, was formed in 27 percent yield as a bright orange solid from the ring closure of 3,4-diphenyl-2,5-thiophenedicarboxylic acid chloride (III). Treatment of 3,4-diphenyl-2,5-thiophenedicarboxylic acid (II) (3) with excess thionyl chloride gave III as a yellow solid in 90 percent yield.

EXPERIMENTAL

Melting points are uncorrected. The ultraviolet spectra were determined in 95% ethanol on a Perkin-Elmer Model 350 spectrophotometer. The infrared spectra were determined on a Perkin-Elmer Infracord. The nmr spectrum was determined on a Varian HA-60 spectrometer. Elemental analysis were performed by Galbraith Laboratories Inc., Knoxville, Tennessee.

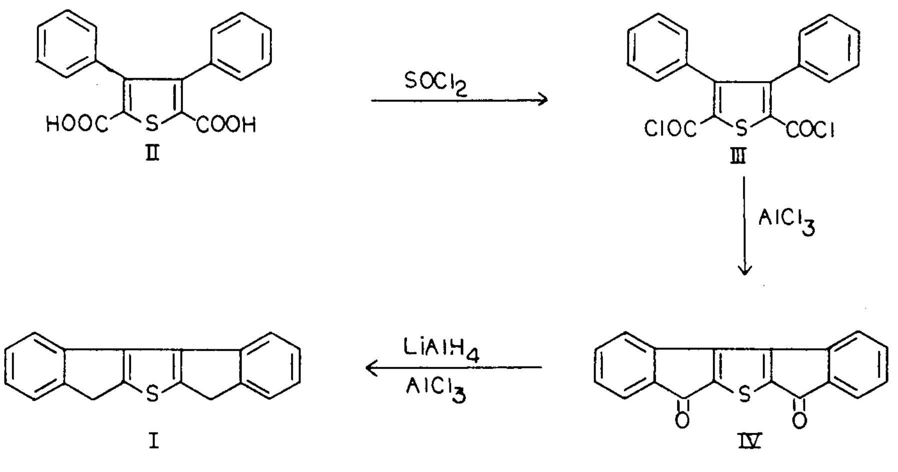
3,4-Diphenyl-2,5-thiophenedicarboxylic Acid Chloride (III).

A suspension of II (3) (20 g., 0.061 mole) in 40 ml. of thionyl chloride was stirred under gentle reflux for 12 hours. Excess thionyl chloride was removed from the resulting dark solution under reduced pressure leaving a dark, viscous oil which was dissolved in hexane, treated with norit, and filtered. Upon cooling, a yellow solid crystallized and weighed 20 g. (90%), m.p. 115-118°. Recrystallization from carbon tetrachloride-hexane gave long, yellow needles, (18.9 g., 85%) m.p. 121-122°. The infrared spectrum (chloroform) showed absorption at 1760 cm^{-1} (C=O).

Anal. Calcd. for $C_{18}H_{10}Cl_2O_2S$: C, 59.84; H, 2.79; S, 8.88; Cl, 19.63. Found: C, 59.74; H, 2.75; S, 9.00; Cl, 19.64.

5*H*,7*H*-Bisindeno[2,3-*b*:3',2'-*d*]thiophene-5,7-dione (IV).

To a stirred mixture of aluminum chloride (10 g., 0.075 mole) and dry carbon disulfide (100 ml.) was added a solution of III (12 g., 0.033 mole) in 100 ml. of dry carbon disulfide. The reaction mixture was cooled to 0° in an ice bath during the addition. After the addition was completed, the contents were stirred for an additional 4 hours at 0°. The stirring was discontinued and the reaction mixture was allowed to warm to room temperature and remain for 12 hours. The mixture consisted of a black solid and a carbon disulfide suspension. The suspension was poured onto ice causing an orange solid to form which was collected by filtration after the carbon disulfide had been evaporated. Treatment of the black solid with cold water caused an orange solid to form which was collected and combined with the solid obtained from the carbon disulfide suspension. This was washed with dilute sodium carbonate solution until no coloration occurred in the filtrate. The remaining yellow solid was very insoluble in most organic solvents. Several recrystallizations from chloroform (500 ml. of solvent per gram of IV) gave long orange needles, 2.6 g. (27%), m.p. 334.5-335°.



Anal. Calcd. for $C_{18}H_8O_2S$: C, 75.00; H, 2.79; S, 11.29. Found: C, 74.95; H, 2.81; S, 11.29.

The ultraviolet spectrum exhibited λ max 230 mμ (ε, 58,100), 264 (52,900), 310 (22,600) and 331 (17,600). The infrared spectrum (potassium bromide) contained absorptions at 1735 and 1705 cm^{-1} (C=O).

5*H*,7*H*-Bisindeno[2,3-*b*:3′,2′-*d*]thiophene (I).

To a mixture of lithium aluminum hydride (0.2 g., 6 mmoles) and dry ether (20 ml.) a solution of aluminum chloride (1.6 g., 12 mmoles) in 25 ml. of ether was added dropwise with stirring. Ketone IV (0.5 g., 1.8 mmoles) was added directly in the flask in small portions causing a slight effervescence to occur with each addition. The contents were heated to reflux and stirred for 2 hours. The resulting gray-orange mixture was cooled to 0° and decomposed by the careful addition of cold water. Acidification with cold dilute sulfuric acid followed by thorough extraction with ether gave an orange ethereal solution which was dried (sodium sulfate) and evaporated to give a red solid. Sublimation at 180-190° gave 0.1 g. (22%) of a yellow powder, m.p. 195-199°. Two recrystallizations from benzene-hexane gave yellow needles, m.p. 215-216°.

Anal. Calcd. for $C_{18}H_{12}S$: C, 83.03; H, 4.65; S, 12.32. Found: C, 82.85; H, 4.71; S, 12.17.

The ultraviolet spectrum showed λ max 221.5 mμ (ε, 23,100), 249 (21,300), 259.5 (29,900), 276 (20,000) and 283 (18,200). The infrared spectrum (potassium bromide) did not contain carbonyl absorption and showed strongest absorption at 750 cm^{-1}. The nmr spectrum (deuteriochloroform) exhibited peaks at 2.00-3.00 (8H multiplet, aromatic), and 6.21 (4H singlet, CH_2).

REFERENCES

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Received March 6, 1967 Morgantown, West Virginia 26506