in 15 ml of acetic acid and 75 ml of water was stirred for 90 min at 0–5°, followed by 90 min at ambient temperatures. Undissolved zinc was removed and the solution was added slowly with stirring to a solution of *p*-bromobenzaldehyde (567 mg, 1.1 moles) in absolute alcohol (18 ml). White crystals separated immediately. The mixture after its being heated briefly at 60°, was stirred at ambient temperatures for 15 min and cooled in ice. White crystals of compound **4b** (filtrate A, 750 mg, 89%, mp 211° from 95% alcohol) which separated were washed with water. This material was identical (mixture melting point and infrared spectrum) with a sample obtained from the methylation reactions previously described.[2]

Anal. Calcd for $C_9H_9BrN_6$: C, 38.43; H, 3.20. Found: C, 38.15; H, 3.04.

The filtrate (A) was extracted with ether (four 100-ml portions). Evaporation of the ethereal solution under a current of warm air yielded a solid mingled with a brownish gum. This residue was stirred in ether (30 ml) and the ethereal solution, after its being filtered to remove some intractable material, yielded a white solid (210 mg, 87–95°) on evaporation of the ether. Recrystallization of this solid from benzene (5 ml) gave white crystals (140 mg) of 2-methyl-5-aminotetrazole (mixture melting point and infrared spectrum) of mp 102°. Addition of pentane (40–60°) to the benzene filtrate yielded a second crop (44 mg, mp 94–98°) of this material (188 mg, 63%). The yields are based on 100% yields of both degradation products.

When 1.5 g (2.5 moles) of *p*-bromobenzaldehyde was used in the above experiment, the ethereal extract on evaporation deposited white flakes (60 mg, mp 163–167°) mingled with a yellow oil. The oil was removed in cold ether (15 ml). Some of the white solid which dissolved was recovered by fractional evaporation of the ether. This material, compound **5b** (mp 166–167° from 95% alcohol), was also prepared as follows.

A solution of 2-methyl-5-aminotetrazole (105 mg) and *p*-bromobenzaldehyde (196 mg) in 95% alcohol (20 ml) was boiled for 10 min and allowed to stand at ambient temperatures for 36 hr with periodic stirring. On cooling the solution in ice white crystals (50 mg, mp 166–167°) of compound **5b** separated.

Anal. Calcd for $C_9H_8BrN_5$: C, 40.60; H, 3.01; Br, 30.07; N, 26.32. Found: C, 40.61; H, 3.40; Br, 30.10; N, 26.90.

Addition of water to the alcoholic filtrate resulted in the precipitation of a further crop (95 mg, mp 165–167°) of this material along with some unreacted aldehyde which was removed by stirring the precipitate in cold ether (10 ml). Yield of compound **5b** was 145 mg (50%).

Arylidene-2-methyl-2H-tetrazol-5-ylhydrazones (4).—Amyl nitrite (2.6 ml) was added to a solution of 2-methyl-5-aminotetrazole (1 g) in 20 ml of acetic acid and 10 ml of water at 0°, and the resulting mixture was stirred for 1 hr at 0–5°. Water (80 ml) was then added to the solution followed by zinc dust (2.65 g) and the mixture was stirred for 1 hr further at 0–5° and for 3 hr at ambient temperatures. Residual zinc was removed and the solution was added to benzaldehyde (1 ml) in 95% alcohol (20 ml), stirred for 45 min at ambient temperatures, and cooled in ice. The glistening, white crystals of compound **4a** (840 mg, 81%) were washed with water and had mp 136–137° (from aqueous alcohol).

Anal. Calcd for $C_9H_{10}N_6$: C, 53.46; H, 4.95; N, 41.58. Found: C, 53.72; H, 5.15; N, 41.84.

By a similar procedure using the appropriate aldehydes, compounds **4b** and **4c** (mp 164–166° from 95% alcohol. *Anal.* Calcd for $C_{10}H_{12}N_6$: C, 55.65; H, 5.35. Found: C, 55.74; H, 5.29) were obtained in 72.5 and 99% yields, respectively.

Efforts to prepare these hydrazones by the established procedure[6] of diazotization of the amine followed by reduction were unsuccessful. The attempted reduction of an acidic solution of the amine (1) and sodium nitrite with stannous chloride resulted in the evolution of a gas from the reaction mixture and the only materials encountered on work-up were decomposition gums.

Registry No.—2, 7593-32-0; **6c**, 4314-09-4; **7b**, 7593-34-2; **7c**, 7593-35-3; **4a**, 7593-36-4; **4b**, 7593-37-5; **4c**, 7593-38-6; **8b**, 7593-39-7; **8c**, 7593-40-0; 2-methyl-5-aminotetrazole, 6154-04-7; **5b**, 7593-42-2.

Acknowledgment.—We are deeply indebted to Dr. J. Feeney and Miss A. Heinrich, Varian Associates, Walton-on-Thames, for assistance with measuring and interpreting the nmr data.

The Use of 2,5-Dichlorothiophene in the Synthesis of 3,4-Disubstituted Thiophenes

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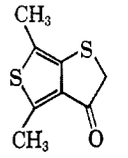
The facile electrophilic substitution of the 2 and 5 positions of the thiophene ring has rendered the direct synthesis of 3-substituted and 3,4-disubstituted thiophene derivatives somewhat difficult. The ready availability of 3-thenyl bromide[2] and 3-bromothiophene[3] has somewhat reduced this difficulty. However, ring closure from a 3-substituted thiophene with both the 2 and 4 positions unsubstituted, results in exclusive substitution in the 2 position.[4] Only when the 2 position is blocked may ring closure take place at the 4 position.[5]

The use of 2,5-dichlorothiophene to introduce useful substituents into the 3 position of the thiophene ring has been reported by several workers.[6] By virtue of the facile removal of the 2,5-chlorine atoms from certain substituted 2,5-dichlorothiophenes, the method becomes useful for the synthesis of 3,4-disubstituted thiophenes. In the present work, 2,5-dichlorothiophene is utilized as starting material in the synthesis of a number of cyclopenta[*c*]thiophene derivatives.

The literature records a small number of thiophenes possessing a five-membered ring fused across the 3,4 positions of the thiophene ring. The compounds I[5b] and II to V[7] have been reported. As far as we have been able to ascertain, neither the parent compound, cyclopenta[*c*]thiophene, nor any of its derivatives have been reported in the literature.



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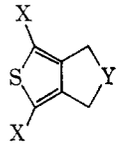

II, X = CO_2CH_3; Y = S
III, X = CO_2CH_3; Y = SO_2
IV, X = CO_2H; Y = S
V, X = H; Y = S

Treatment of 2,5-dichloro-3-thenyl chloride (VI) according to the method of Lawesson and Busch[8] afforded the malonic ester (VII) in 60% yield. Saponi-

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(2) E. Campaigne and B. F. Tullar, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 921.

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(6) (a) J. A. Blanchette and E. V. Brown, *J. Am. Chem. Soc.*, **73**, 2779 (1951); (b) S. Gronowitz, *Arkiv Kemi*, **8**, 441 (1955); (c) E. Profft and G. Solf, *J. Prakt. Chem.*, **24**, 38 (1964).

(7) H. Wynberg and D. J. Zwanenburg, *J. Org. Chem.*, **29**, 1919 (1964).

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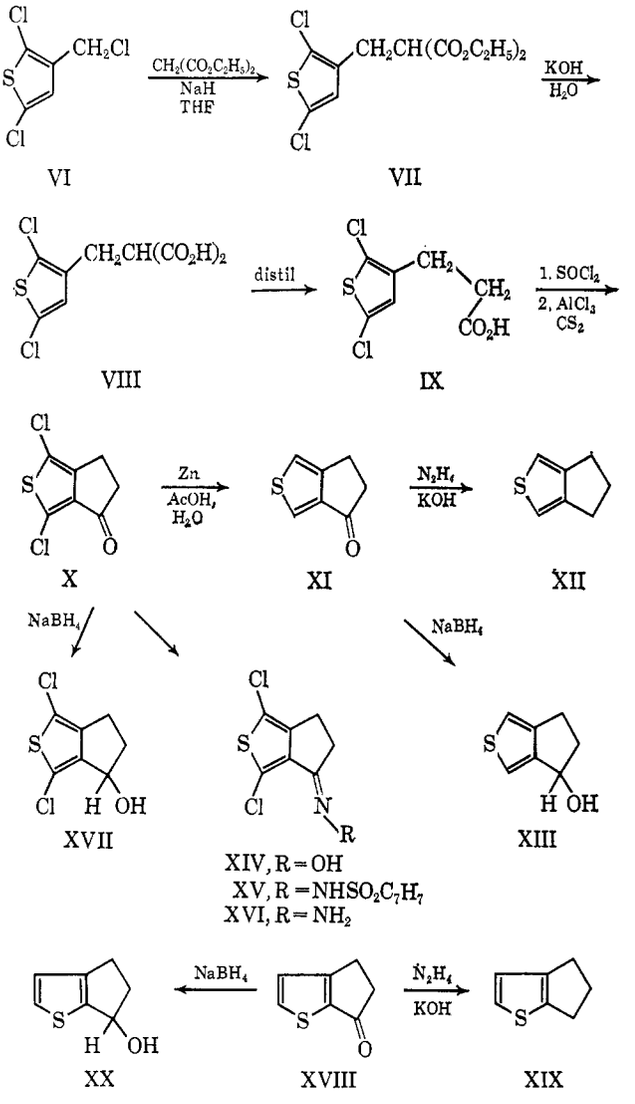
fication afforded an isolable malonic acid (VIII) which was decarboxylated by distillation under reduced pressure. The resulting propionic acid (IX) was converted to the acid chloride and cyclized with aluminum chloride to the dichloro ketone (X) in 81% yield. Attempted removal of the halogen atoms using sodium amalgam in aqueous methanol afforded no useful product. Treatment of X with zinc dust in aqueous acetic acid afforded a 67% yield of halogen-free ketone (XI). Wolff–Kishner reduction of this ketone led to the parent hydrocarbon cyclopenta[*c*]thiophene (XII) as a clear colorless liquid in 76% yield. Reduction of XI with sodium borohydride afforded the corresponding alcohol (XIII).

The analogous cyclopenta[*b*]thiophene (XIX) was prepared in 50% yield from ketone XVIII[4c] by Wolff–Kishner reduction. The ketone was prepared by two different methods; firstly by treatment of β-(3-thienyl)-propionyl chloride[9] with stannic chloride and secondly by treatment of β-(3-thienyl)propionic acid[9] with anhydrous hydrogen fluoride. Reduction of XVIII with sodium borohydride afforded the corresponding alcohol (XX) (see Scheme I).

SCHEME I



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Experimental Section[10]

Diethyl 2,5-Dichloro-3-thenylmalonate (VII).—2,5-Dichlorothiophene (Columbia Organic Chemical Co.) was distilled before use (bp 160°). Chloromethylation of 2,5-dichlorothiophene according to the method of Gronowitz[6b] afforded 2,5-dichloro-3-thenyl chloride (VI), bp 73–74° (1 mm) in 59% yield [lit.[6b] bp 107–110° (14 mm)].

To a flask fitted with stirrer and condenser and containing 30 g of 50% sodium hydride dispersion in mineral oil suspended in 200 ml of dry tetrahydrofuran was added a solution of 102.5 g (0.64 mole) of diethyl malonate in 100 ml of tetrahydrofuran. To the stirred mixture was added dropwise a solution of 125 g (0.61 mole) of VI in 625 ml of tetrahydrofuran solution. The mixture was stirred at room temperature for 12 hr. The mixture was then heated and about two thirds of the tetrahydrofuran was removed by distillation. Ice and water were added to the cooled mixture along with solid sodium chloride. The whole was thoroughly extracted with ether. The ether extracts were dried ($MgSO_4$) and distilled. A foreurn of 20 g of diethyl malonate, bp 65° (0.01 mm), was followed by 121.3 g (60%) of VII, bp 138–140° (0.05 mm). The infrared specturm showed absorption at 1730 cm^{-1} (C=O of ester, neat); the nmr spectrum showed absorptions at τ 3.33 (1 H singlet, aromatic), 5.81 (4 H quartet, CH_2 of ethyl, J = 7 cps), 6.40 (1 H triplet, CH, J = 8 cps), 6.91 (2 H doublet, CH_2, J = 8 cps), and 8.79 (6 H triplet, CH_3, J = 7 cps). Repeated distillation of a small portion of VII, bp 138–140° (0.07 mm), failed to provide an analytical sample; so the corresponding barbiturate was prepared as follows. To a solution of sodium ethoxide prepared from 1.0 g of 50% sodium hydride dispersion in mineral oil and 30 ml of absolute ethanol was added a mixture of urea (1.3 g 0.023 mole) and diethyl 2,5-dichloro-3-thenylmalonate (6.98 g 0.02 mole). After refluxing for 6 hr the mixture was cooled and added to 50 ml of water. Extraction with ether left an aqueous layer which upon acidification with hydrochloric acid gave a white precipitate (4.2 g), mp 209–211°. Recrystallization from water gave analytically pure barbiturate, 3.8 g (65%), mp 212–213°.

Anal. Calcd for $C_9H_6Cl_2N_2O_3S$: C, 36.88; H, 2.06; N, 9.56. Found: C, 37.03; H, 2.21; N, 9.76.

2,5-Dichloro-3-thenylmalonic Acid (VIII).—A mixture of VII (50 g, 0.15 mole) and potassium hydroxide (50 g) in 200 ml of water was heated under reflux for 4 hr. At the end of this period the mixture was cooled and extracted with ether. The aqueous portion was poured into a mixture of ice and hydrochloric acid. A yellow oil separated which was taken up in ether, washed with water, and dried over $MgSO_4$, and the solvent was removed. The oily residue crystallized upon removal of the solvent. Recrystallization from hexane gave 38.6 g (95%) of the malonic acid (VIII), mp 134–138°. An analytical sample prepared by crystallization from hexane had mp 138–139°.

Anal. Calcd for $C_8H_6Cl_2O_4S$: C, 35.71; H, 2.25; Cl, 26.35; S, 11.90. Found: C, 35.79; H, 2.21; Cl, 26.59; S, 12.05.

β-(2,5-Dichlorothienyl)propionic Acid (IX).—Malonic ester VII (100 g, 0.32 mole) was saponified as described above and unpurified malonic acid VIII was distilled under reduced pressure. Evolution of carbon dioxide gas occurred and a clear, yellow distillate was collected over the range 150–160° (1 mm), approximately 70 g (97%). The oily distillate solidified upon cooling and was crystallized from hexane to give 64 g (89%) of product, mp 65–67°. The infrared spectrum (KBr) showed a characteristic acid hydroxyl absorption at 3000 and carbonyl absorption at 1700 cm^{-1}; the nmr spectrum ($CDCl_3$) showed a singlet at τ −1.22 (1 H, acid), a singlet at 3.33 (1 H, aromatic), and a complex multiplet 6.95–7.57 (4 H, CH_2).

Anal. Calcd for $C_7H_6Cl_2O_2S$: C, 37.35; H, 2.69; Cl, 31.51; S, 14.25. Found: C, 37.51; H, 2.58; Cl, 31.79; S, 14.45.

4-Oxo-1,3-dichlorocyclopenta[*c*]thiophene (X).—A mixture of 20 g (0.89 mole) of IX and 30 g of thionyl chloride in ether (35 ml) containing 3 drops of pyridine was heated under reflux for 3 hr. Removal of the solvent followed by distillation afforded the acid chloride as a pale yellow oil, bp 102–103° (0.2 mm), 19.3 g (88%). Treatment of a small portion of the acid chloride with

(10) All temperature readings are uncorrected. Microanalysis were performed by Galbraith Laboratories, Knoxville, Tenn. Nmr spectra were recorded on a Varian HA-60 using tetramethylsilane as an internal standard and solvents as specified. The ultraviolet spectra were determined in 95% ethanol on a Perkin-Elmer Model 350 spectrometer. The infrared spectra were recorded on a Perkin-Elmer Infracord Model 137 spectrophotometer.

concentrated aqueous ammonia afforded the corresponding amide, mp 101–102° after sublimation.

Anal. Calcd for $C_7H_7Cl_2NOS$: C, 37.51; H, 3.15; N, 6.25. Found: C, 37.28; H, 3.13; N, 6.16.

To a stirred mixture of $AlCl_3$ (20 g, 0.15 mole) and carbon disulfide (300 ml), cooled in an ice bath, was added dropwise over a 0.5-hr period a solution of the acid chloride (31 g, 0.12 mole) in carbon disulfide (120 ml). The mixture was heated under reflux with stirring overnight. The cooled mixture was poured onto ice and concentrated hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with sodium bicarbonate solution and water and dried over $MgSO_4$. Removal of the solvent left a golden yellow residue which was distilled to give a total of 25.8 g of a pale yellow oil, bp 105–110° (0.5 mm). The distillate solidified upon cooling and was recrystallized from hexane to give 20.1 g (81%) of white crystals, mp 64–66°. An analytical sample prepared by recrystallization from hexane melted at 65–66°. The infrared spectrum (KBr) showed carbonyl absorption at 1700 cm^{-1}; $\lambda_{max}^{95\%\ EtOH}$ 219 mμ (ε 11,980), 256 (sh, 8240), 263 (10,150), 304 (3450); the nmr spectrum ($CDCl_3$) showed τ 7.00–7.33 (complex multiplet, aliphatic ring hydrogens).

Anal. Calcd for $C_7H_4Cl_2OS$: C, 40.60; H, 1.95; Cl, 34.24; S, 15.50. Found: C, 40.80; H, 2.10; Cl, 34.40; S, 15.61.

The following derivatives of ketone X were prepared. Oxime XIV was obtained as white needles (ethanol), mp 228° dec. *Anal.* Calcd for $C_7H_5Cl_2NOS$: C, 37.85; H, 2.27; N, 6.37. Found: C, 37.82; H, 2.47; N, 6.50. Tosylhydrozone XV was obtained as white, fluffy needles (ethanol), mp 229–231° dec. *Anal.* Calcd for $C_{14}H_{12}Cl_2N_2O_2S_2$: C, 44.80; H, 3.22; N, 7.47. Found: C, 44.65; H, 3.20; N, 7.21. Hydrazone XVI had mp 124–125°, pale yellow needles. *Anal.* Calcd for $C_7H_6Cl_2N_2S$: C, 38.02; H, 2.74; N, 12.67; S, 14.17. Found: C, 38.20; H, 2.84; N, 12.59; S, 14.48.

4-Oxocyclopenta[*c*]thiophene (XI).—A mixture of dichloroketone X, (5.0 g, 0.24 mole), zinc (20 mesh granules, 20 g), acetic acid (50 ml), and water (50 ml) was heated under reflux for 22 hr. The mixture was poured onto ice and thoroughly extracted with ether. Careful washing of the ether extracts with sodium carbonate solution gave an acid-free solution which was dried ($MgSO_4$). Removal of the ether left 3.4 g of crude ketone which was recrystallized from hexane (Norit) to give 2.2 g (67%) of white needles mp, 80–81°. An analytical sample prepared by sublimation had mp 81–82°. The infrared spectrum showed ketone carbonyl absorption at 1670 cm^{-1} (fluorolube); $\lambda_{max}^{95\%\ EtOH}$ 259 mμ (ε 12,790); the nmr spectrum ($CDCl_3$) showed absorptions at τ 2.36 and 3.00 (1 H doublets, aromatic hydrogens, J = 2.5 cps), and at 7.00 (4 H singlet, aliphatic ring hydrogens).

Anal. Calcd for C_7H_6OS: C, 60.83; H, 4.38; S, 23.21. Found: C, 60.95; H, 4.50; S, 23.40.

Cyclopenta[*c*]thiophene (XII).—In a 25-ml flask with an attached distillation head and condenser was placed a mixture of the ketone XI (1.0 g, 0.0072 mole), diethylene glycol (10 ml), 95% hydrazine (1.5 ml), and potassium hydroxide (1 g). The mixture was heated slowly in an oil bath to 200° while the distillate was collected. The distillate contained water-soluble and water-insoluble material. The reaction mixture was cooled to 100° and water (5 ml) was added. The mixture was then heated again and any distillate was collected. This procedure was repeated once more. The combined distillates were extracted with ether and the ether was dried (Na_2SO_4). Removal of the ether left a pale yellow liquid which was distilled to give a colorless distillate: bp 81–82° (20 mm), 0.68 g (78%), $n^{20}D$ 1.5657. This compound would solidify to a white solid on cooling to −30° but liquified on standing at room temperature. The infrared strongest absorption occurred at 770 cm^{-1} (neat); $\lambda_{max}^{95\%\ EtOH}$ 244 mμ (ε 7370); the nmr spectrum (CCl_4) showed absorptions at τ 3.35 (1 H singlet, aromatic) and 7.17–7.84 (3 H complex multiplet, aliphatic ring hydrogens).

Anal. Calcd for C_7H_8S: C, 67.69; H, 6.49; S, 25.82. Found: C, 67.71; H, 6.69; S, 25.63.

4-Hydroxycyclopenta[*c*]thiophene (XIII).—To a solution of ketone XI (280 mg, 0.002 mole) in 10 ml of methanol was added sodium borohydride (200 mg) in one portion. An immediate effervescence was accompanied by a slight rise in temperature. After 1 hr the mixture was poured into saturated sodium chloride solution and extracted with ether. Removal of the ether left an oil, (290 mg) which solidified on standing in a deep freeze. Recrystallization from hexane gave 210 mg (74%), mp 66–67°, of white solid. An analytical sample (hexane) melted at 67–68°. The nmr spectrum ($CDCl_3$) showed absorptions at τ 3.03 (1 H doublet) and 3.30 (1 H multiplet, aromatic hydrogens), at 5.05 (1 H broad doublet, alcohol proton), and at 7.10–8.12 (5 H complex multiplet, aliphatic ring protons).

Anal. Calcd for C_7H_8OS: C, 59.96; H, 5.74; S, 22.87. Found: C, 60.12; H, 5.75; S, 23.01.

4-Hydroxy-1,3-dichlorocyclopenta[*c*]thiophene (XVII).—A mixture of the dichloro ketone (X, 2.0 g, 0.0096 mole) and sodium borohydride (0.3 g) in 20 ml of methanol was allowed to stand at room temperature for 3 hr. The mixture was worked up as above. Removal of the ether left a crude, yellow oil (*ca.* 2 g) which crystallized upon standing in a refrigerator. Recrystallization from hexane gave 1.62 g (81%) of white needles, mp 59–60°. An analytical sample had mp 59–60°. The nmr spectrum ($CDCl_3$) showed absorptions at τ 4.95 (1 H broad triplet, hydroxyl proton) and at 6.95–8.00 (5 H complex multiplet, aliphatic ring protons).

Anal. Calcd for $C_7H_6Cl_2OS$: C, 40.21; H, 2.89; S, 15.34. Found: C, 40.26; H, 2.87; S, 15.57.

6-Oxocyclopenta[*b*]thiophene (XVIII). Method A.—A solution of β-(3-thienyl)propionyl chloride (9.0 g, 0.05 mole) in 10 ml of dry carbon disulfide was added dropwise under nitrogen with stirring to an ice-cold mixture of 18.6 g (0.07 mole) of anhydrous stannic chloride in 50 ml of dry carbon disulfide. After completing the addition (10 min), the dark red contents were stirred at 0° for 0.5 hr and then refluxed for 45 min. The contents were poured onto ice and stirred. The organic layer was separated and the aqueous layer was saturated with sodium chloride and extracted thoroughly with ether. The combined ether layers were washed with dilute sodium bicarbonate solution and water. The organic solution was dried ($MgSO_4$) and distilled giving 2.5 g (28%) of white solid, bp 97–99° (0.9 mm), mp 90–92° [lit.[4c] 90–91°]. Sublimation at 60° (0.3 mm) gave white needles, mp 92–93°.

Method B.—The ring closure was carried out on 5.0 g (0.032 mole) of β-(3-thienyl)propionic acid using a threefold excess of anhydrous hydrogen fluoride which had been freshly condensed in a polyethylene container according to the method of Sam,[4c] yielding 2.65 g (60%), mp 92–93° (hexane). The infrared spectrum (KBr) showed carbonyl absorption at 1700 cm^{-1} (C=O); the ultraviolet spectrum showed λ_{max} at 261 mμ (ε 15,100); the nmr spectrum ($CDCl_3$) showed doublets at τ 2.16 and 2.99 (1 H doublets, aromatic J = 5 cps) and a singlet at 7.03 (4 H, CH_2).

Anal. Calcd for C_7H_6OS: C, 60.83; H, 4.38; S, 23.21. Found: C, 60.64; H, 4.25; S, 22.95.

The 2,4-dinitrophenylhydrazone derivative, mp 255.0–255.5°, was obtained as red prisms from ethyl acetate.

Anal. Calcd for $C_{13}H_{10}N_4O_4S$: C, 49.05; H, 3.17; N, 17.61. Found: C, 49.26; H, 3.12; N, 17.37.

Cyclopenta[*b*]thiophene (XIX).—A mixture of 2.7 g (0.02 mole) of 6-oxocyclopenta[*b*]thiophene (XVIII, 3.3 g (0.06 mole) of potassium hydroxide, 2 ml of 95% hydrazine, and 20 ml of diethylene glycol was placed in a 100-ml flask fitted with a distilling head and condenser. The mixture was heated slowly to 200° while the distillate was collected. The flask was cooled, 50 ml of water was added, the contents were distilled, and the distillate was collected. This procedure was repeated once more. The distillate was extracted with ether and the ether solution was dried ($MgSO_4$). Removal of the ether gave a yellow liquid which was distilled at 71–72° (15 mm) giving 1.25 g (50%) of clear, colorless product, mp −17° approximately. An analytical sample distilled at 79–80° (22 mm), $n^{25}D$ 1.5522. The infrared spectrum showed the absence of carbonyl absorption; the ultraviolet spectrum showed λ_{max} 226 mμ (ε 4580) and 241 mμ sh (ε 4000); the nmr spectrum (CCl_4) showed doublets at τ 2.94 and 3.29 (1 H doublets, aromatic, J = 5 cps) and a complex multiplets at 7.00–7.75 (6 H, CH_2).

Anal. Calcd for C_7H_8S: C, 67.69; H, 6.49; S, 25.82. Found: C, 67.73; H, 6.62; S, 25.60.

6-Hydroxycyclopenta[*b*]thiophene (XX).—Compound XVIII (2.0 g, 0.0145 mole) was dissolved in 10 ml of 95% ethanol. Sodium borohydride (1 g) was added in small portions to the stirred solution. A white solid precipitated and the stirring was continued for 12 hr. The mixture was poured into 50 ml of ether and shaken vigorously with 50 ml of water. The ether layer was separated and dried ($MgSO_4$) and the ether was removed leaving an oil which distilled at 92–102° (3 mm). Crystallization of the oil from hexane gave 1.3 g (64%) of white solid, mp 44–46°. Sub-

limation gave an analytical sample, mp 49–50.5°. The infrared spectrum (neat) showed absorption at 3300 cm^{-1} (OH); the nmr spectrum ($CDCl_3$) showed doublets at τ 2.70 and 3.21 (1 H doublets, J = 5 cps, aromatic), a broad absorption at 4.70–4.93 (1 H, OH), and a complex multiplet at 6.80–8.00 (5 H, aliphatic ring hydrogens).

Anal. Calcd for C_7H_8OS: C, 59.97; H, 5.75; S, 22.87. Found: C, 60.00, 59.97; H, 5.83, 5.85; S, 22.67, 22.53.

Registry No.—2,5-Dichlorothiophene, 3172-52-9; VII, 7687-77-6; VIII, 7695-30-9; IX, 7687-78-7; X, 7687-79-8; XI, 7687-82-3; XII, 7690-98-4; XIII, 7687-83-4; XIV, 7687-80-1; XV, 7690-97-3; XVI, 7687-81-2; XVII, 7687-84-5; XVIII, 5650-52-2; XVIII 2,4-dinitrophenylhydrazone, 7687-86-7; XIX, 5650-50-0; XX, 7687-88-9; acid chloride of IX, 7687-74-3; corresponding amide of IX, 7690-96-2.

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A Facile Cyclization of 4-(2-Chloroethyl)-3-methyl-2-pyrazolin-5-one to a Spirocyclopropane Derivative

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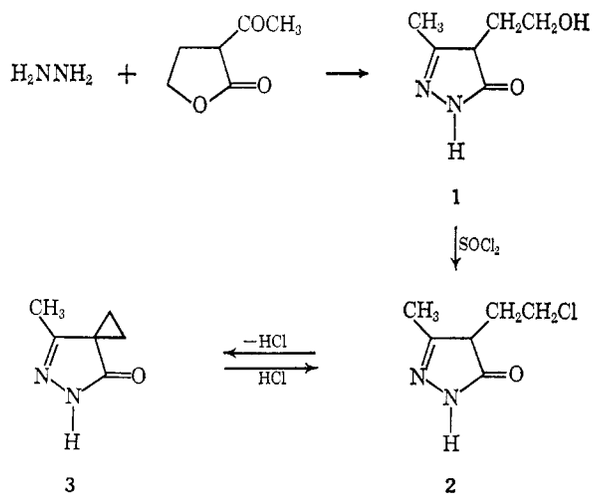
During the preparation of pyrazolin-5-one derivatives over the last few years it was noticed that one of the derivatives, 4-(2-chloroethyl)-3-methyl-2-pyrazolin-5-one (**2**), underwent a facile cyclization to 4-methyl-7-oxo-5,6-diazaspiro[2.4]hept-4-ene (**3**). A recent publication reporting similar findings[1] prompted us to report our results. The reaction path followed by us is outlined in Scheme I.

SCHEME I



Compound **2** was reported by Wamhoff and Korte[1] as an intermediate, but was not isolated. We have isolated **2** and its hydrochloride salt. Compound **3** was originally reported by von Rothenburg[2] who synthesized it from 1-acetyl-1-carbethoxycyclopropane and hydrazine. Von Rothenburg reported his melting point for **3** as 197°. The melting point as found by Wamhoff and Korte[1] and by us was 148–150°. We have attempted to repeat von Rothenburg's synthesis and were unable to isolate any pure material. The physical and chemical constants found by Korte and us are in agreement and indicate that the spiro structure assigned to **3** is the correct one.

The nmr spectrum of **3** using tetramethylsilane as an internal standard in $CDCl_3$ shows peaks at 9.75 (amide H) and 1.86 (CH_3), and a multiplet between 1.85 and 1.5 ppm (cyclopropyl) having an A_2B_2 spin-coupling pattern. These assignments were in agreement with those of Wamhoff and Korte.[1] The 0.2- to 0.3-ppm shift to higher field of the methyl protons can be explained by the shielding effects of the cyclopropyl ring which is fixed in a plane at right angle to the plane of the pyrazolinone ring. The spectrum was also run in pyridine in an attempt to separate methyl and methylene peaks; the resonances were shifted upfield, but the pattern remained unchanged.

The synthesis of **3** by Wamhoff and Korte[1] was carried out by treatment of **1** with either sulfuric acid or thionyl chloride followed by basification and extraction. We have instead, isolated **2** and its hydrochloride salt by reaction of **1** with thionyl chloride. Compound **2** was stable in refluxing water, alcohol, and pyridine. In water, the pH of a suspension of **2** dropped from 6 to about 3.2. Apparently an equilibrium was set up in water: $2 \rightleftarrows 3 + HCl$. The liberation of HCl prevents further conversion to **3** since **2** can be recovered almost quantatively from refluxed aqueous suspensions. When **2** was suspended in water, addition of aqueous sodium hydroxide brought the pH up momentarily after which it dropped again. After 1 equiv had been added, all of **2** was converted to **3** and the pH remained stable at 5.9. During the addition, the pH was never allowed to go higher than 6.0. In one attempt to convert **2** (HCl salt) to its base, 2 equiv of sodium hydroxide solution was added in error. In the time it took to bring the pH back to 7, all the material had cyclized. Compound **3** could be reconverted to **2** by heating in concentrated hydrochloric acid. Wamhoff and Korte[1] claim that the formation of **3** from **1** on treatment with concentrated sulfuric acid proceeds by dehydration. We have tried heating at 190° and also treatment with dicyclohexylcarbodiimide in an attempt to convert **1** to **3**. In both cases starting material was recovered. Bachman and Heisey[3] also attempted dehydration of **1** by treatment with potassium hydroxide and with disodium hydrogen phosphate in an attempt to make vinyl compounds, but were unable to isolate any identifiable material. We believe, therefore, that the reaction of **1** with sulfuric acid produces a 4-(2-hydrogensulfato)ethyl compound which on treatment with base undergoes γ elimination of sulfuric acid to give **3**.

(1) H. Wamhoff and F. Korte, *Chem. Ber.*, **99**, 2962 (1966).

(2) R. von Rothenburg, *J. Pract. Chem.*, [2] **51**, 60 (1895).

(3) G. B. Bachman and L. V. Heisey, *J. Am. Chem. Soc.*, **71**, 1985 (1949).