# A STUDY OF SOME CONDENSATION PRODUCTS IN THE 2-PHENYLTHIOPHENE SERIES

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A number of previously unreported $\alpha$, $\beta$-unsaturated ketones of the 2-phenylthiophene series has been synthesized by the crotonic condensation of 2-acetyl-5-phenylthiophene with aromatic and heterocyclic aldehydes and of 2-formyl-5-phenylthiophene with aliphatic-aromatic and heterocyclic ketones in an alkaline medium.

There is no information on condensation products in the 2-phenylthiophene series. We have obtained a number of $\alpha$, $\beta$-unsaturated ketones of this series by the crotonic condensation of 2-acetyl-5-phenylthiophene with some aromatic and heterocyclic aldehydes (I–VI, Table 1) and of 2-formyl-5-phenylthiophene with some aliphatic-aromatic and heterocyclic ketones (VII–XIV, Table 2), carrying out the condensation at room temperature in ethanol and using 20% aqueous sodium hydroxide catalyst.

The 2-phenylthiophene was synthesized by Broun and Voronkov's method with a yield of 9.0%, and the 2-acetyl-5-phenylthiophene was obtained by the acetylation of 2-phenylthiophene with acetyl chloride in benzene solution in the presence of tin tetrachloride with a yield of 57.0%; previously, the synthesis of 2-acetyl-5-phenylthiophene had been performed with titanium tetrachloride as catalyst [2]. 2-Formyl-5-thiophene was obtained by the procedure of Lescot et al. [3] by the reaction of 2-phenylthiophene and dimethylformamide in the presence of phosphorus oxychloride in dry xylene with a yield of 38.3%. In order to establish its structure, the aldehyde synthesized was subjected to Kizhner reduction, which gave 2-methyl-5-phenylthiophene [4], permitting the aldehyde to be assigned the structure of 2-formyl-5-phenylthiophene. This was also confirmed by oxidation with 4% aqueous potassium permanganate, which yielded 5-phenyl-2-thiophenecarboxylic acid. The unsaturated ketones obtained formed crystalline substances mainly colored yellow, soluble in benzene, ether, and dioxane, more sparingly soluble in ethanol, and insoluble in water. They possessed halochromic properties and in solution in $H_2SO_4$ their color deepened to blue-violet.

## EXPERIMENTAL

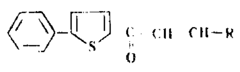
**2-Acetyl-5-phenylthiophene.** A three-necked flask with a reflux condenser, mechanical stirrer, and dropping funnel was filled with 1.1 g (0.0068 mole) of 2-phenylthiophene, 20 ml of anhydrous benzene, and 0.96 g (0.012 mole) of acetyl chloride, after which it was cooled with water, and 2.6 g (0.01 mole) of $SnCl_4$ was added; the mixture was left to stand for 30–40 min and was decomposed with ice-water. The benzene solution was washed with dilute hydrochloric acid, NaOH solution, and water. The aqueous layer was extracted with benzene, the combined benzene extracts were dried with $CaCl_2$. Distillation of the benzene yielded 0.8 g of product, mp 116° C (from gasoline). According to the literature [2], mp 115°–118° C (from gasoline).

**2-Acetyl-5-phenylthiophene.** A three-necked flask with a reflux phosphorus oxychloride was gradually added to a mixture of 2 g (0.0125 mole) of 2-phenylthiophene, 1.25 g (0.0166 mole) of dimethylformamide, and 10 ml of dry toluene, and the mixture was heated in the water bath for 3.5 hr and, after cooling, was extracted with a hot saturated aqueous solution of sodium acetate. The organic layer was extracted repeatedly with ether, washed with dilute aqueous sodium carbonate solution and with water, and dried over $Na_2SO_4$. The solvent was then distilled off and the residue was recrystallized from alcohol. Yield 0.9 g. The aldehyde had mp 76°–80° C. Found, %: S 17.19. Calculated for $C_{11}H_8OS$, %: S 17.03. **Semicarbazone:** Mp 225°–227° C (from ethanol), yellowish needles. Found, %: S 12.99. Calculated for $C_{12}H_{11}N_3OS$, %: S 13.07.

**2-Methyl-5-phenylthiophene.** A mixture of 0.2 g (0.001 mole) of 2-formyl-5-phenylthiophene, 1.03 g (0.02 mole) of 95% hydrazine hydrate, and 3 ml of diethylene glycol was boiled under reflux for 7 hr. After cooling, the reaction mixture was treated with 0.5 g (0.009 mole) of solid KOH and boiled for 2 hr. Then 3.5 ml of 10% hydrochloric acid was added and the mixture was extracted with benzene. The benzene extracts were dried over $CaCl_2$, the solvent was distilled off, and the product was recrystallized from ethanol. Yield 0.08 g, mp 46°–49° C. According to the literature [4], mp 49°–51° C. Found, %: S 18.55. Calculated for $C_{11}H_{10}S$, %: S 18.40.

Table 1

1-(5-Phenyl-2-thienyl)-3-(R)-prop-2-en-1-ones



| Compound | R | Mp*, ° C | Empirical formula | S, % | | Yield, % |
|---|---|---|---|---|---|---|
| | | | | Found | Calculated | |
| I | Phenyl | 155–156 | $C_{19}H_{14}OS$ | 11.13 | 11.04 | 69.7 |
| II | 2-Furyl | 156–158 | $C_{17}H_{12}O_2S$ | 11.47 | 11.44 | 54.0 |
| III | 2-Thienyl | 178–179 | $C_{17}H_{12}OS_2$ | 21.37 | 21.64 | 52.0 |
| IV | 1-Naphthyl | 144–146 | $C_{23}H_{16}OS$ | 9.66 | 9.42 | 74.2 |
| V | 3-Nitrophenyl | 178–180 | $C_{19}H_{13}NO_3S$ | 9.32 | 9.56 | 61.0 |
| VI | 4-Nitrophenyl | 257–258 | $C_{19}H_{13}NO_3S$ | 9.64 | 9.56 | 75.5 |

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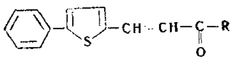
*All the ketones were recrystallized from 95% ethanol.

Table 2

1-(5-Phenyl-2-thienyl)-3-(R)-prop-1-en-3-ones



| Compound | R | Mp, ° C | Empirical formula | S, % | | Yield, % |
|---|---|---|---|---|---|---|
| | | | | Found | Calculated | |
| VII | Phenyl | 110—112* | $C_{19}H_{14}OS$ | 10.93 | 11.04 | 51.0 |
| VIII | 4-Xenyl | 186—188** | $C_{25}H_{18}OS$ | 8.78 | 8.75 | 80.0 |
| IX | 2-Thienyl | 137—141*** | $C_{17}H_{12}OS_2$ | 21.79 | 21.64 | 79.5 |
| X | 5-Phenyl-2-thienyl | 223—225** | $C_{23}H_{16}OS_2$ | 17.30 | 17.21 | 62.5 |
| XI | 2-Naphthyl | 144—146* | $C_{23}H_{16}OS$ | 9.64 | 9.42 | 58.0 |
| XII | 5-(1-Naphthyl)-2-thienyl | 161—163** | $C_{27}H_{18}OS_2$ | 15.25 | 15.17 | 77.0 |
| XIII | 2-Nitrophenyl | 164—166*** | $C_{19}H_{13}NO_3S$ | 9.59 | 9.56 | 47.0 |
| XIV | 5-Nitro-2-thienyl | 223—225*** | $C_{17}H_{11}NO_3S_2$ | 18.49 | 18.78 | 9.2 |

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*The ketones were recrystallized from 95% ethanol. **The ketones were recrystallized from a mixture of benzene and acetone. ***The ketones were recrystallized from acetone.

**5-Phenyl-2-thiophenecarboxylic acid.** With stirring, 3.4 ml of a 4% aqueous solution of $KMnO_4$ was added in small portions to a suspension of 0.22 g (0.0011 mole) of 2-formyl-5-phenylthiophene in 25 ml of 1% aqueous NaOH, the temperature of the reaction mixture being 4°-8° C. A few drops of sodium bisulfite solution was added, the precipitate of $MnO_2$ was filtered off, and the filtrate was acidified with 10% HCl (to Congo Red). The white precipitate that deposited was filtered off, washed with cold water, and dried in the air. Yield 0.07 g, mp 182° C (from ethanol). Found, %: S 15.81. Calculated for $C_{11}H_8O_2S$, %: S 15.69.

**Ketones (I-VI, Table 1; VII-XIV, Table 2).** With stirring, a 20% aqueous solution of caustic soda (0.5-0.8 ml) was added in drops to a solution of equimolar amounts (0.0019 mole) of 2-acetyl-5-phenylthiophene and the appropriate aromatic or heterocyclic aldehyde in a small amount of ethanol (10-40 ml). The reaction mixture was left overnight. The precipitate that deposited was filtered off, washed with aqueous ethanol and water, and recrystallized from ethanol to constant melting point. The unsaturated ketones (VII-XIV) were obtained similarly from equimolar amounts (0.0021 mole) of 2-formyl-5-phenylthiophene and the appropriate aliphatic-aromatic or heterocyclic ketone.

## REFERENCES

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