SYNTHESIS OF (5-STYRYL-2-THIENYL)-PHENYLACRYLIC ACIDS

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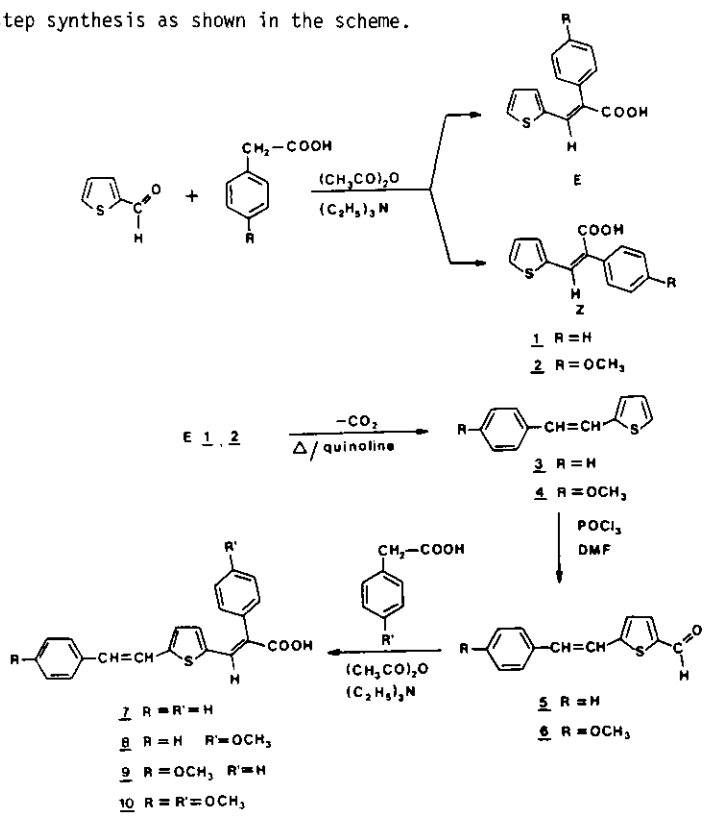
Abstract — We describe the synthesis of E-3-(5-styryl-2-thienyl)-2-phenylacrylic acid 7, E-3-(5-styryl-2-thienyl)-2-(4-methoxyphenyl)acrylic acid 8, E-3-[5-(4-methoxyphenylethenyl)-2-thienyl]-2-phenylacrylic acid 9 and E-3-[5-(4-methoxyphenylethenyl)-2-thienyl]-2-(4-methoxyphenyl)acrylic acid 10 by Oglialoro condesation.

In our earlier work[1,2] we prepared a number of 3-(2-furyl)-2-arylacrylic acids and 3-(5-substituted-2-furyl)-2-arylacrylic acids. Now we report about four new 3-(5-substituted-2-thienyl)-2-arylacrylic acids, substituted in the position 5 of the thiophene nuclei with styryl and substituted styryl groups following the multistep synthesis as shown in the scheme.



First was prepared 3-(2-thienyl)-2-phenyl or substituted phenylacrylic acid by the Oglialoro condensation.[3] The acids so prepared were decarboxylated[4] and the obtained 1-(4-substituted)-2-(2-thienyl)-ethenes were formylated by Vilsmeier formylation.[5] The corresponding 5-styryl-2-formylthiophenes reacted than with phenylacetic acid in the Oglialoro condensation to give the title compounds.

All prepared acids are interesting because of their geometrical structure which were spectroscopically identified. In all cases only the "E" isomers could be isolated. All prepared acids could be interesting as dyes because of their absorption namely fluorescence and also photochemically, as the starting materials for preparing some polycyclic heterocycles with thiophene nuclei.

EXPERIMENTAL

Melting points are uncorrected. Ir spectra were taken on a Perkin-Elmer Model M-257 in KBr discs. The ^1H nmr spectra were recorded on Joel J.M.M.-FX 100 FT spectrometer with tetramethylsilane as the internal reference.

3-(2-Thienyl)-2-phenylacrylic acid 1

3-(2-Thienyl)-2-phenylacrylic acid 1 was prepared by the known method[3] from phenylacetic acid (13.5 g, 0.1 mole) and 2-thiophenealdehyde (14 g, 0.12 mole) in a mixture of triethylamine (20 ml) and acetic acid anhydride (20 ml). The mixture was heated for 3 h at boiling point. After the reaction was over the mixture was cooled, acidified with hydrochloric acid and extracted with ether. The organic layer was washed with water and acid was reextracted by strong shaking in 10% sodium carbonate solution. The alkaline solution of sodium salts was acidified with acetic acid. The precipitated E-isomer was filtered off and recrystallized from methanol giving 13.2 g (97.8%) of white crystals, mp 185-186 °C (Lit.[3], mp 186-188 °C); ir (KBr); 1600 cm^{-1} (C=C), 1670 (C=O); nmr ($CDCl_3$) δ; 6.93-7.24 (m, 8H, thiophenic + aromatic), 8.1 (s, 1H, ethylenic). To the filtrate hydrochloric acid was added and an additional crop consisting of the corresponding Z-isomer was filtered and recrystallized from benzene + petroleum ether. The yield was 1 g (0.8%), mp 135-136 °C; ir (KBr); 1610 cm^{-1} (C=C), 1690 (C=O); nmr ($CDCl_3$) δ 6.86-7.47 (m, 8H, thiophenic + aromatic), 7.47 (s, 1H, ethylenic).

3-(2-Thienyl)-2-(4-methoxyphenyl)acrylic acid 2

Compound 2 was prepared in a manner similar to the preparation of compound 1 from 2-thiophenealdehyde (14 g, 0.12 mole) and p-methoxyphenylacetic acid (16.6 g, 0.1 mole). The yield on the E-isomer was 12.42 g (74.8%), mp 199 °C from methanol (Lit.[3], mp 200-202 °C); ir (KBr); 1600 cm^{-1} (C=C), 1670 cm^{-1} (C=O); nmr ($CDCl_3$) δ 3.86 (s, 3H, OCH_3), 6.98 (2H), 7.19 (2H), $J_{A_2B_2}$ = 9.0 Hz, 6.93-7.17 (m, 3H) 8.1 (s, 1H, ethylenic).

Yield of the Z-isomer was 3.2 g (22%), mp 128-130 °C from methanol; ir (KBr); 1610 cm^{-1} (C=C), 1660 (C=O); ($CDCl_3$) δ 3.82 (s, 3H, OCH_3), 6.91 (2H), 7.42 (2H), $J_{A_2B_2}$ = 8.8 Hz, 7.02-7.3 (m, 3H) 7.48 (s, 1H, ethylenic).

1-Phenyl-2-(2-thienyl)ethene 3

This compound was prepared by decarboxylation of the compound 1. The compound 1 (10 g, 0.043 mole) was heated with 10 g of Cu-powder in 50 ml of quinoline (dried over molecular sieves) during 3 h at the boiling point. The reaction mixture was taken into 50 ml of ether and washed with 70 ml of 10% hydrochloric acid. Ethereal extracts were separated from the water layer, which was extracted twice with ether. All ethereal extracts were collected, washed with water, 10% hydrochloric acid and water and dried over magnesium sulfate. The extract was evaporated and the residue was recrystallized from methanol giving 1.6 g (20%) of white crystals, mp 113-115 °C (Lit.[6] mp 112-115 °C); ir (KBr); 1590 cm^{-1} (C=O), 697 cm^{-1} (cis CH=CH); ($CDCl_3$) δ 6.8-7.5 (m, 10H).

1-(4-Methoxyphenyl)-2-(2-thienyl)ethene 4

This compound was prepared by decarboxylation of the compound 2 (10 g, 0.038 mole) in a manner similar to the preparation of the compound 3. The yield is 2.85 g (34.7%) white crystals, mp 135-137 °C, from methanol; ir (KBr); 1590 cm^{-1}, (C=C), 698 cm^{-1} (cis CH=CH); nmr ($CDCl_3$) δ 3.8 (s, 3H, OCH_3), 6.86 (2H), 7.38 (2H), $J_{A_2B_2}$ = 9.0 Hz, 6.95-7.23 (m, 5H). Anal. Calcd for $C_{13}H_{12}OS$: C, 72.2; H, 5.6. Found: C, 72.6; H, 5.65.

5-Styryl-2-formylthiophene 5

This compound was prepared from 3 by Vilsmeier formylation. A mixture of N,N-dimethylformamide (0.8 ml, 0.01 mole) and $POCl_3$ (0.01 mole), added dropwise and with stirring at 0 °C was stirred for 30 min. To the resulting mixture a solution of 1-phenyl-2-(2-thienyl)ethene 3 (1.6 g, 0.009 mole) in N,N-dimethylformamide (1.6 ml, 0.02 mole) was added dropwise and with stirring at 0-10 °C. The mixture was stirred at room temperature for 1 h and then at 70 °C for 3 h. Ice cold water was added, the mixture was neutralized with sodium carbonate and left overnight. The separated product was filtered off and recrystallized from methanol giving 1.15 g (72%) of white crystals, mp 67-68 °C; ir (KBr): 1645 cm^{-1} ($C\overset{H}{=}O$), 1590 (C=C), 956 (trans CH=CH); nmr ($CDCl_3$) δ 6.8-7.57 (m, 7H), 6.96 (d, 1H, H_3 thiophenic, J=3.8 Hz), 7.65 (d, 1H, H_4 thiophenic, J=3.8 Hz), 9.85 (s, 1H, $C\overset{O}{=}H$). Anal. Calcd for $C_{13}H_{10}OS$: C, 72.9; H, 4.7. Found: C, 72.65, H, 4.82.

5-(4-Methoxyphenylethenyl)-2-formylthiophene 6

This compound was prepared from 4 (2.16 g, 0.01 mole) in a manner similar to the preparation of the

compound 5. The yield was 1.35 g (61.3%) as yellow crystals, mp 85-88 °C from methanol; ir (KBr); 1650 cm^{-1} (C=O), 1595 (C=C), 945 (trans CH=CH); nmr ($CDCl_3$) δ 3.83 (s, 1H, OCH_3), 7.10 (d, 1H, H_3 thiophenic, J=3.8 Hz), 7.64 (d, 1H, H_4 thiophenic, J=3.8 Hz), 6.9 (2H), 7.45 (2H), $J_{A_2B_2}$ = 8.8 Hz, 7.09 (s, 2H), 9.83 (s, 1H, C=O). Anal. Calcd for $C_{14}H_{12}O_2S$: C, 68.8; H, 5.0. Found: C, 67.95; H, 5.3.

E-3-(5-Styryl-2-thienyl)-2-phenylacrylic acid 7

This compound was prepared in a manner similar to the preparation of the compound 1 from 5 (0.5 g, 0.002 mole) and phenylacetic acid (0.3 g, 0.002 mole). The yield was 0.185 g (37%), yellow crystals, mp 196-198 °C from methanol; ir (KBr): 1670 cm^{-1} (C=O), 1590 (C=C), 945 cm^{-1} (trans CH=CH); nmr (DMSO-d_6) δ; 6.68-7.57 (m, 14H), 8.31 (s, 1H, ethylenic). Anal. Calcd for $C_{21}H_{16}O_2S$: C, 75.9; H, 4.9. Found: C, 76.35; H, 4.97.

E-3-(5-Styryl-2-thienyl)-2-(4-methoxyphenyl)acrylic acid 8

This acid was prepared in a manner similar to the preparation of 7 from 5 (0.5 g, 0.002 mole) and 4-methoxyphenylacetic acid (0.4 g, 0.002 mole). The yield was 0.19 g (38%), yellow crystals, mp 202-203 °C from methanol; ir (KBr): 1670 cm^{-1} (C=O), 1600 (C=C), 945 (trans CH=CH), nmr (DMSO-d_6) δ; 3.80 (s, 3H, OCH_3), 6.68-7.56 (m, 13H), 7.98 (s, 1H, ethylenic). Anal. Calcd for $C_{22}H_{18}O_3S$: C, 72.9; H, 5.0. Found: 73.36; H, 5.45.

E-3-[5-(4-Methoxyphenylethenyl)-2-thienyl]-2-phenylacrylic acid 9

This acid was prepared in a manner similar to the preparation of the compound 7 and 8 from 6 (0.4 g, 0.002 mole) and phenylacetic acid (0.24 g, 0.002 mole). The yield was 0.15 g (37.5%), yellow crystals, mp 221-223 °C from methanol; ir (KBr): 1670 cm^{-1} (C=O), 1600 (C=C), 945 (trans CH=CH), nmr (DMSO-d_6) δ; 3.75 (s, 3H, OCH_3), 6.62-7.54 (m, 13H), 8.1 (s, 1H, ethylenic). Anal. Calcd for $C_{22}H_{18}O_3S$: C, 72.9; H, 5.0. Found: C, 73.35; H, 5.4.

E-3-[5-(4-Methoxyphenylethenyl)-2-thienyl]-2-(4-methoxyphenyl)acrylic acid 10

This acid was prepared in a manner similar to the preparation of the compound 7, 8, and 9 from 6 (0.4 g, 0.002 mole) and 4-methoxyphenylacetic acid (0.4 g, 0.002 mole). Yellow crystals were obtained in the yield of 0.16 g (40%), mp 242-245 °C from methanol; ir (KBr) 1670 cm^{-1} (C=O), 1600 (C=C), 950 (trans CH=CH); nmr (DMSO-d_6) δ; 3.75 (s, 1H, OCH_3), 3.81 (s, 1H, OCH_3), 6.68-7.57 (m, 12H), 8.31 (s, 1H, ethylenic). Anal. Calcd for $C_{23}H_{20}O_4S$: C; 70.4; H, 5.1. Found: C, 70.75; H, 5.25.

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