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New Sulfur Containing Polymers

5. Monomer Syntheses

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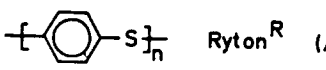
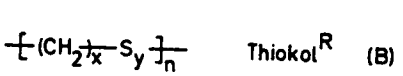
SUMMARY

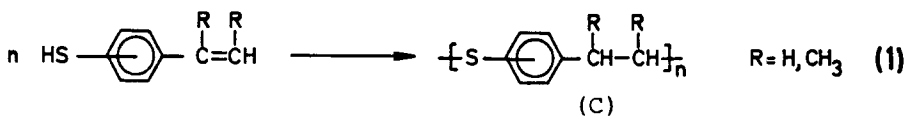
Different pathways for the syntheses of Monomers, containing both an olefinic and a thiol group in the same molecule are described in detail.

GENERAL

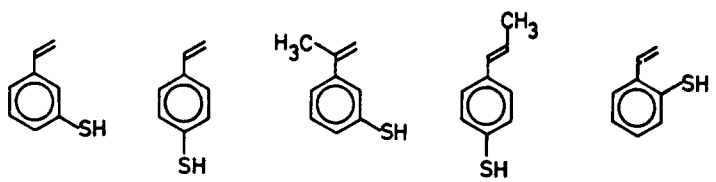
Commercial interest in sulfur containing polymers of the general structures A and B suggested that the syntheses of mixed aliphatic-aromatic polysulfides C would perhaps yield materials with interesting properties







A possible synthesis of polymers having structure C would involve the polymerization of compounds containing both a thiol and a vinyl group such as 1 - 5.



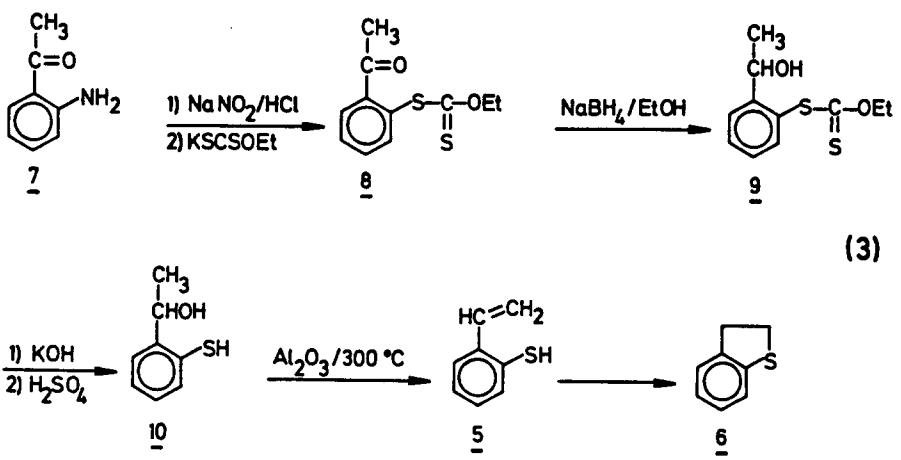
1 2 3 4 5

We recently demonstrated that 1 - 4 react by intermolecular anti-Markovnikov addition of the thiol group to the C=C leading to polymers (NUYKEN et al. 1980, NUYKEN et al. 1981). In contrary, for 5 an intramolecular cyclization is favored and yields 6. In this case no polymer was formed and thus this reaction provides an alternative route for the preparation of 2,3-dihydro-benzo- b -thiophene (KLOOSTERZIEL et al. 1973;

ARESTA et al. 1973; v. BRAUN 1925; KARAULOVA et al. 1967; KHUSHVAKHTOVA et al. 1972)

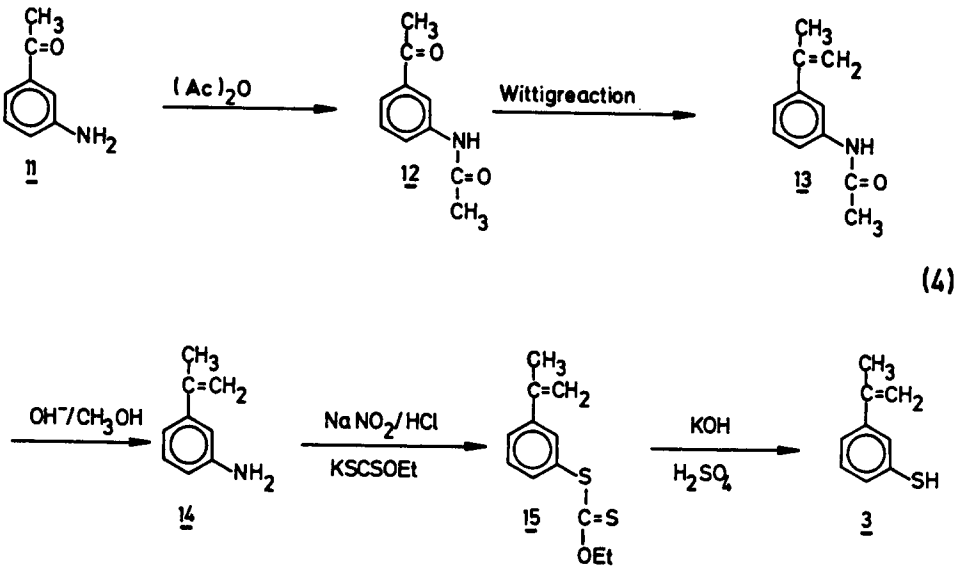
(2)

Although there are several methods available for the introduction of a vinyl or a thiol group into an aromatic ring, there are few syntheses available for compounds containing both a thiol and a C=C bond (v. BRAUN at al. 1926; v. BRAUN et al. 1934) As far as we know, none has been described where both groups are bonded directly to a single aromatic system. Compounds 1-5 were synthesized according to the reaction scheme given in Eq. 3 or that in Eq. 4 depending on their structure and the availability of the starting materials.



(3)

Amine 7 was converted into xanthate 8 followed by reducting the carbonyl group to the corresponding alcohol 9. Hydrolysis of the xanthate group to yield the free thiol 10, followed by generating the C=C bond by dehydration of the alkyl chain over a heated Al_2O_3 catalyst gave 5 (Eq.3). The alternative method (Eq. 4) involved initial protection of the amino group followed by conversion of amide 12 to 13 by a Wittig reaction. Hydrolysis of the amide then yielded the free amine 14 which was finally converted into a thiol 3 via the corresponding xanthate.



EXPERIMENTAL SECTION

^{1}H NMR and ^{13}C NMR Spectra were recorded on a Varian FT80A spectrometer (TMS). IR Spectra were run using a Beckman 4240. MS Spectra were obtained on a Varian MAT CH 5.

Reaction scheme (3)

2-(1-Hydroxyethyl(benzenethiol (10) A solution of 14 g (0.2 mole) of $NaNO_2$ dissolved in 30 ml of distilled water was added dropwise to a solution of 27 g (0.2 mole) of 1-(2-aminophenyl) ethan-1-one (7) in 45 ml of conc. HCl and 50 g of ice. Throughout the addition the temperature was kept below 5°. The resulting, cool, diazonium salt solution was then slowly added (over 2 hrs) to a solution of 40 g of potassium-O-ethyldithiocarbonate dissolved in 55 ml distilled water kept at 45°. After a further 30 min of stirring at room temperature, the red, oily xanthate (8) was extracted with ether. The ethereal solution was dried over $MgSO_4$ and the solvent was then removed by distillation. The residual, crude xanthate was dissolved in 40 ml of ethanol and then a solution of 7.4 g of $NaBH_4$ in 250 ml of ethanol was slowly added to this mixture under nitrogen at about 20°. To the resulting mixture 25 g of KOH dissolved in 150 ml of water was added dropwise. The solution was then heated and kept at reflux for ca. 8 hrs. After removal of four fifth of the ethanol, the solution was acidified (pH 5) by careful addition of 3 M H_2SO_4 (ice cooled). The solution was then extracted with ether and the ethereal extract was dried over $MgSO_4$. Removal of the ether and distilling of the residue in vacuo gave 9.1 g (30%) of an orange oil, bp. 82°/0.3 torr.

Anal. Calcd. for $C_8H_{10}OS$: C, 62.30, H, 6.54, S, 20.79
Found: C, 62.39, H, 6.62, S. 20.65
^1H NMR (d_6-acetone): δ : 1.40 (d, CH_3), 4.20 (broad, SH, OH), 5.10 (q, CH) 7.30 (m, C_6H_4),
IR($CHCl_3$): 3560, 3420, 2950, 2560 cm^{-1}

4-(1-Hydroxyethyl)benzenethiol (10a) was synthesized using the same procedure as described for 10, Yield: 40 % of 1-(aminophenyl) ethan-1-one, bp. 88°/0.2 torr.

Anal. Calcd. for $C_8H_{10}OS$: C, 62.30, H, 6,54, S, 20.79
Found: C, 62.45, H, 6.50, S, 20.71
^1H NMR ($CDCl_3$): δ : 1.35 (d, CH_3), 3.50 (s, SH), 3.75 (s, OH), 4.65 (q, CH), 7.20 (s, C_6H_4).
IR($CHCl_3$): 3590, 3420, 3060, 2960, 2580 cm^{-1}.

4-(1-Hydroxypropyl)benzenethiol (10b) was also synthesized usind the procedure as described for 10. Yield: 33 % of 1-(4-aminophenyl)propan-1-one, bp. 108°/0.5 torr.

Anal. Calcd. for $C_9H_{12}OS$: C, 64.24, H, 7.19, S, 19.06
Found: C, 64.15, H, 7.16, S, 19.15
^1H NMR ($CDCl_3$): δ : 0.8 (t, CH_3), 1.58 (m, CH_2), 3.90 (s, SH), 4.45 (m, CH), 7.13 (s, C_6H_4),
IR($CHCl_3$). 3590, 3420, 2920, 2580 cm^{-1}

3-(1-Hydroxyethyl)benzenethiol (10c) was synthesized using the technique described for 10 but the reduction of 1-(3-aminophenyl)ethan-1-one was carried out before converting the amino group to SH. Yield: 60% of 1-(3-aminophenyl)ethan-1-one, bp. 76°/0.05 torr.

Anal. Calcd. for $C_8H_{10}OS$: C, 62.30, H, 6.54, S, 20.79
Found: C, 62.25, H, 6.53, S, 20.83
^1H NMR ($CDCl_3$): δ : 1.40 (d, CH_3), 1.95 (s, OH), 3.75 (s, SH) 4.80 (q,CH), 7.20 (d, C_6H_4),
IR($CHCl_3$): 3660, 3600, 3100, 2950, 2400 cm^{-1}

2-Vinylbenzenethiol (5) 15.4 g (0.1 mole) of 10 were distilled in vacuo. The vapor from 10 was passed through a 30 cm long tube (30 mm Ø) containing an Al_2O_3 catalyst (Aktive Tonerde SL 11-4, Guilini, Ludwigshafen/West Germany, particle size: 1-2 mm) and heated to 300° with the aid of a heating ribbon before being condensed and collected in a cooled flask (T=-30°). This reaction and also the preparation of 1-4 must be carried out in complete darkness (sodium lamp can be used) to avoid cyclozation (5 ⟶ 6) or polymerization (1-4 ⟶ polymer). Yield: 8 g, 60 % of 10, bp. 32°/0.4 torr.

Anal. Calcd. for C_8H_8S: C, 70.53, H, 5.92, S, 23.54
Found: C, 70.69, H. 5.79, S, 23.61
^1H NMR ($CDCl_3$): δ : 3.25 (s, SH), 5.22 (d, CH_2), 5.54 (d, CH_2) 6.98 (m, CH and C_6H_4)

4-(1-Propenyl)benzenethiol (4) was synthesized using the same procedure as described for 5. Yield: 45% of 10a, bp. 50°/0.4 torr.

Anal. Calcd. for $C_9H_{10}S$: C, 71.95, H, 6.71, S, 21.34
Found: C, 71.91, H, 6.68, S, 21.51
^1H NMR ($CDCl_3$): δ : 1.82 (d, CH_3), 3.35 (s, SH), 6.24 (m, CH=), 7.15 (m, C_6H_4)

4-Vinylbenzenethiol (2) was synthesized using the same method as described for 5. Yield: 60 % of 10 b, bp. 40°/0.4 torr.
Anal. Calcd. for C_8H_8S: C, 70.53, H, 5.92, S, 23.54
Found: C, 70. 61, H, 5.92, S, 23.41
^{1}H NMR ($CDCl_3$): δ : 3.45 (s, SH), 5.20 (d, CH_2), 5.67 (d, CH_2), 6.65 (dd, CH), 7.20 (m, C_6H_4).

3-Vinylbenzenethiol (1) was also synthesized using the procedure described for 5. Yield: 60 % of 10c, bp. 46°/0.45 torr.
Anal.Calcd. for C_8H_8S: C, 70.53, H. 5.92, S, 23.54
Found: C, 70.60, H, 5.93, S, 23.58
^{1}H NMR ($CDCl_3$): δ : 3.40 (s, SH), 5.25 (d, CH_2), 5.70 (d, CH_2) 6.65 (dd, CH), 7.25 (m, C_6H_4).

2,3-Dihydrobenzo- b -thiophene (6) 5 was almost quantitatively converted into 6 in the presence of daylight. This reaction also takes place in the dark. Although the ligth induced reaction is complete in a few minutes, the dark reaction at 50° is complete only after 4 hrs. This reaction can be followed easily by ^{1}H NMR spectroscopy observing the disappearance of SH and $=CH_2$ and appearance of CH_2CH_2S units. Thus it is clear that the synthesis as described for 5 but in the presence of light becomes a preparative route for 6. Yield: ca. 100 % of 5, bp. 35°/0.6 torr.
Anal. Calcd. for C_8H_8S: C, 7Q53, H, 5.92, S, 23.54
Found: C, 70.55, H, 5.78, S, 23.59
^{1}H NMR ($CDCl_3$): δ : 3.14 (m, CH_2CH_2), 7.07 (m, C_6H_4)
^{13}C NMR ($CDCl_3$): δ : 33.18 (SCH_2), 36.16 ($ArCH_2$), 122-154 (C_6H_4)
MS (70 eV), m/e: 137 (9%), 136 (75%), 135 (100 %), 134 (43 %), 91 (69 %), 67 (34%), 65 (29 %), 63 (47%), 51 (44%)

Reaction scheme (4)

N-(3-acetylphenyl)-acetamide (12) 165 g (1.62 mole) of acetic anhydride was added to a solution of 150 g (1.11 mole) 11, dissolved in 1000 ml acetone at room temperature. The mixture was then refluxed for a further hour. After hot filtration and evaporation of about half of the solvent the product started to precipitate. The crystals were separated by filtration and washed with water and dried. Yield: 160 g (90 %), mp. 129° (dil.ethanol).
^{1}H NMR (d_6-acetone): δ : 2.06 (s, CH_3), 2.51 (s, CH_3), 7.71 (m, C_6H_4), 9.31 (s, NH)

N- 3-(1-methylethenyl)phenyl -acetamide (13) 198 g (0.55 mole) of methyltriphenylphosphonium bromide and 0.54 g ($1.5 \cdot 10^{-3}$ mole) of dibenzo- 18 -crown-6-ether were suspended in 750 ml of 1,2-dimethoxyethane. Then 62.6 g (0.55 mole) of potassium-t- butoxide were added in small portions. The yellow color indicated the reaction had started. The temperature was kept at ca. 20°. Then 97 g (o.55 mole) of 12 were added avoiding a temperature increase. The mixture was kept at room temperature for further two hrs. The 1,2-dimethoxyethane and the t-butanol formed during the reaction were then distilled. The mixture was extracted with ether. The ether phase was dried and the product (13) was isolated by removal of the ether. The product was used for the next step without further purification.
1-Amino-3-(1-methylethenyl)benzene (14) the whole amount of

the crude 13 was added to a solution of 76 g (1.35 mole) of KOH in 50 ml of water and 250 ml of methanol and the mixture refluxed for 12 hrs. This solution was then extracted with ether. The ether solution was dried over $MgSO_4$ and, after removal of ether the product was isolated by fractional distillation. Yield: 28 g (38 % of 12), bp. 74°/0.2 torr

Anal. Calcd. for $C_9H_{11}N$: C, 81.11, H, 8.32, N, 10.56
Found: C, 81.50, H, 8.25, N, 10.61

^{1}H NMR (d_6-acetone): δ : 2.06 (s, CH_3), 4.36 (s, NH_2), 5.03 (s, CH_2), 5.32 (s, CH_2), 6.81 (m, C_6H_4)

IR($CHCl_3$): 3450, 3370, 3100, 1610, 895 cm^{-1}.

3-(1-methylethenyl)benzenethiol (3) The conversion of the amino group in 14 to a xanthate 15 was carried out as already described (7 → 8). The crude xanthate was then dissolved in a mixture of 110 ml of ethanol and 110 ml of 1,2-dimethoxyethane. Then 36 g of KOH were added in small portions. After a further 8 hrs refluxing the main part of the solvent was distilled and 100 ml of water were added. By careful addition of 3 M H_2SO_4 the solution was acidified (pH 5), then extracted with ether. The ethereal solution was dried over $MgSO_4$ and the ether removed by distillation. The product was purified by fractional distillation. Yield: 6.3 g (22 % of 14), bp. 49°/0.3 torr.

Anal. Calcd. for $C_9H_{10}S$: C, 71.95, H, 6,71, S, 21.34
Found: C, 71.89, H, 6.81, S, 21.45

^{1}H NMR ($CDCl_3$): δ : 2.08 (s, CH_3), 3.40 (s, SH), 5.06 (s, CH_2), 5.32 (s, CH_2), 7.15 (m, C_6H_4).

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