the composition of onion species. The determinations have been made both directly on the ethanol extract of onion and on the neutral, basic, and acid amino acid fractions. The methods used for the separation will be described in a more detailed paper elsewhere.

As control compounds, partly preparations isolated in this laboratory from onion bulb, chive and garlic, partly synthesized in this laboratory (racemic mixtures) and partly Beckman type 1 calibration mixture were used. As examples of our results obtained with some onion varieties Table 1 and Fig. 1 are added to this preliminary report.

Both qualitative and quantitative differences occur in the onion varieties studied in regard to amino acids and peptides. At this stage it cannot yet be said to what extent the differences are due to the variety and to what extent due to the growth circumstances, for example differences in the sulfur content of the soil.

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Acid-Catalyzed Rearrangement of 3-Phenyl-2-bromothiophene

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It has been shown that different isomer distributions are obtained on bromination of 3-phenylthiophene (I) [1] with various brominating agents. While bromination with *N*-bromosuccinimide (NBS) in carbon tetrachloride led to the expected 2-bromo-3-phenylthiophene (II), bromination with bromine in refluxing acetic acid yielded 5-bromo-3-phenylthiophene (III) and II in a 2:1 ratio. Further experiments have shown that bromination of I with NBS in acetic acid also yields a mixture of II and III and that I with bromine in CCl_4 yields almost exclusively II. It is thus obvious that the explanation given in Ref. 1 must be incorrect.

A more detailed study of the bromination of I with bromine in acetic acid indicated that II was first formed, but then rearrangement to a mixture of I, II, III, and 2,5-dibromo-3-phenylthiophene (IV) occurred (*cf.* Table 1). Approximately the same mixture was obtained when pure II was refluxed with HBr in acetic acid for 4 h or when III was treated in the same way for 25 h (*cf.* Table 1). After refluxing IV for 25 h, small amounts of II and III could be detected. It thus appears that the bromination of 3-phenylthiophene is reversible and that the ultimately formed product mixture is thermodynamically controlled.

The behaviour of the phenylbromothiophenes thus appears to be more similar to that of halogenopyrroles than to that of halobenzenes. In the pyrrole series protodehalogenation and other types of dehalogenation have been observed with both iodo- and bromopyrroles,[2-5] which therefore are considered to contain "positive" halogen. There is certainly also a connection between the facile halogen-metal exchange in bromothiophenes [6] and the protodehalogenation of 2-bromo-3-phenylthiophene. Similar results to those described above have also been obtained by Wynberg *et al.*[7]

Experimental. *2-Bromo-3-phenylthiophene* was prepared as described in Ref. 1. Column chromatography on alumina (Fluka 507 c, neutral, activity grade 1) with hexane as eluent yielded the analytically pure compound, b.p. 106°C/0.3 mm Hg, $n_D^{20} = 1.6540$. (Found: C 50.0; H 2.91; S 13.4; Br 33.5. Mol.wt. 239. Calc. for $C_{10}H_7BrS$ (239.1): C 50.23; H 2.95; S 13.41; Br 33.41).

5-Bromo-3-phenylthiophene was prepared as described in Ref. 1. Recrystallization from aqueous ethanol yielded the analytically pure compound, m.p. 79–80°C. (Found: C 50.6; H 2.89; S 13.5; Br 33.2. Mol.wt. 239. Calc. for $C_{10}H_7BrS$ (239.1): C 50.23; H 2.95; S 13.41; Br 33.41).

2,5-Dibromo-3-phenylthiophene. 2.02 g (0.0125 mole) of bromine in 20 ml of acetic acid was added dropwise to 1.00 g (0.00625 mole) of 3-phenylthiophene in 20 ml of acetic acid at reflux temperature. After refluxing for 6 h, the mixture was cooled and poured onto ice which caused the precipitation of a brown oil. The mixture was neutralized with 2.5 N

Table 1. Bromination and rearrangement experiments with 3-phenylthiophene and brominated 3-phenylthiophene.

Compounds refluxed with HBr in CH_3COOH	Time (h)	Composition of products formed (wt %)			
		I	II	III	IV
3-Phenylthiophene (I) + Br_2	4	9.5	12.1	56.9	21.5
2-Bromo-3-phenylthiophene (II)	4	8.5	13.6	54.8	23.1
5-Bromo-3-phenylthiophene (III)[a]	25	12.1	13.1	57.2	17.6
2,5-Dibromo-3-phenylthiophene (IV)	25	—	1.3	6.0	92.7

[a] Containing 3.8 % of I.

sodium hydroxide solution and extracted with ether. The combined ether phases were washed with N hydrochloric acid, sodium bicarbonate solution and water, dried over $MgSO_4$ and the ether removed *in vacuo*, leaving 1.9 g of a brown oil. VPC indicated that this oil contained about 7 % of monobromo compounds. Column chromatography in the same way as above with hexane as eluent yielded at least 1.3 g of analytically pure 2,5-dibromo-3-phenylthiophene, b.p. 110°C/0.3 mm Hg, $n_D^{20} = 1.6754$, NMR (DMSO): $\tau_H = 2.69$ ppm, $\tau_{C_6H_5} \approx 2.55$ ppm. (Found: C 37.8; H 1.89; S 10.05; Br 50.5. Mol.wt. 318. Calc. for $C_{10}H_6Br_2S$ (318.0): C 37.77; H 1.90; S 10.08; Br 50.25).

Rearrangement experiments. 200 mg of the compound (2-bromo-3-phenylthiophene, 5-bromo-3-phenylthiophene, or 2,5-dibromo-3-phenylthiophene) was refluxed with 5 ml of a solution of 6.7 g HBr in 100 ml acetic acid. The reaction mixture was poured into water and the mixture extracted with ether. The ether was evaporated *in vacuo* and the residue analyzed. GLC analyses were carried out on a 2 m × 1/8″ column packed with apiezon L (20 %) on Chromosorb P (60—80 mesh) at a column temperature of 260°C, using a Perkin Elmer F 11 Gas chromatograph. The retention times were for I 3.1 min, for II 5.2 min, for III 7.4 min, and for IV 11.4 min. The different peaks were calibrated with known amounts and the results are collected in Table 1.

Bromination of 3-phenylthiophene with bromine in hydrogen-bromide-acetic acid. 7.78 g (0.0486 mole) of bromine in 40 ml of acetic acid was added drop-wise to 7.78 g (0.0486 mole) of 3-phenylthiophene in 40 ml of a solution of 6.7 g HBr in 100 ml of acetic acid. The mixture was refluxed for 4 h, poured onto ice and after standing over night, the crystalline precipitate (10.15 g) was filtered off. Only a few mg of substance could be isolated from the ether extract of the mother liquor. The result of the GLC analyses is given in Table 1.

Bromination of 3-phenylthiophene in acetic acid with a deficit of bromine. 0.465 g (2.9 mmole) of bromine in 5 ml of acetic acid was added during 2.5 min to 0.930 g (5.8 mmole) of 3-phenylthiophene in 10 ml of acetic acid, The mixture was then refluxed for 2.5 min, poured into water and extracted with ether. Evaporation of the solvents yielded 0.783 g of a product which by GLC analysis was shown to consist of 36.4 % of 3-phenylthiophene, 44.8 % of 2-bromo-3-phenylthiophene, 17.7 % of 5-bromo-3-phenylthiophene and 1.1 % of 2,5-dibromo-3-phenylthiophene.

Molecular weights were determined mass spectroscopically using an LKB 900 mass spectrometer. The elementary analyses were carried out at the Analytical Department of the Chemical Institute. NMR spectra were recorded with a Varian A-60 NMR spectrometer, tetramethyl silane serving as internal standard.

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