Thiophene Chemistry

XIV.* Thiomaleic Anhydride

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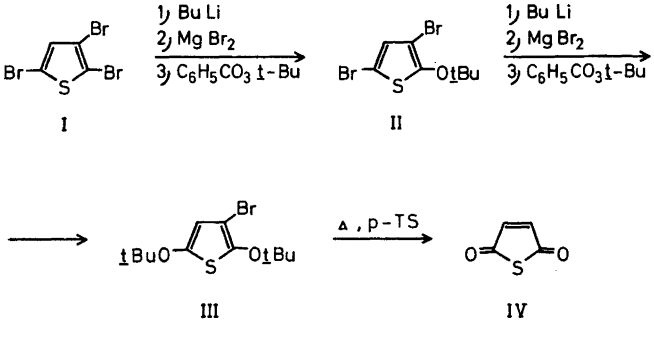
In recent years there has been great interest in the preparation of thiomaleic anhydride: Mayer *et al.*[1] failed to prepare it, but according to a recent patent [2] it was prepared in low yields by catalytic oxidation of thiophene. Quite recently [3] it was also obtained, although in low overall yields, in a 2-step synthesis, starting from 4,5,8,9-tetrahydrophthalic anhydride. In connection with our general studies of potential mono-,[4] di-,[5] and tri[6]-hydroxythiophenes we have found another method for the preparation of thiomaleic anhydride, which is described below. In forth-coming publications the scope of this reaction and the synthetic and spectroscopic investigations of the title compound will be published.

2,3,5-Tribromothiophene, I, is reacted with butyllithium at −40°C to give 3,5-dibromothienyllithium,[7] which is treated with anhydrous magnesium bromide, followed by *t*-butyl perbenzoate [4] to give 2-*t*-butoxy-3,5-dibromothiophene, II. In the same way 2,5-di-*t*-butoxy-3-bromothiophene, III, is prepared from II. By heating III in the presence of catalytic amounts of *p*-toluenesulphonic acid, thiomaleic anhydride is isolated in 91 % yields after isobutylene and HBr-elimination. Physical constants of IV and also UV, IR, and NMR data were identical with earlier published ones.[3]

Experimental. 2-t-Butoxy-3,5-dibromothiophene, II. 3,5-Dibromothienyllithium was prepared from 130 g (0.41 mole) of 2,3,5-tribromothiophene in 300 ml of ether and 168 ml (0.42 mole) of butyllithium.[7] Then 0.5 mole of anhydrous $MgBr_2$ (prepared from 16.4 g of magnesium and 80 g of bromine in 200 ml of ether) was added rapidly with stirring. After 75 min, when the temperature had raised to zero, 65 g (0.33 mole, 60 ml) of *t*-butyl perbenzoate in 100 ml of ether was added, during 30 min, to the solution, kept at 0°C. After stirring for another 4 h the mixture was worked up in the usual way.[4] B.p. 90−91°C/0.3 mm Hg; $n_D^{20} = 1.5620$; yield: 98 g (95 %). (Found: C 30.67; H 3.35; Br 50.94; S 10.34. Calc. for $C_8H_{10}OSBr_2$: C 30.57; H 3.18; Br 50.96; S 10.19).

2,5-Di-t-butoxy-3-bromothiophene, III. The title compound was prepared as above from 72 g (0.25 mole) of II and worked up as usual. B.p. 62−64°C/0.1 mm Hg; $n_D^{20} = 1.5165$; yield: 59 g (90 %). (Found: C 47.35; H 5.88; Br 25.78. Calc. for $C_{12}H_{19}O_2SBr$: C 46.97; H 5.22; Br 26.38).

Thiomaleic anhydride, IV. III (crude product from above) was placed in a Vigreux distillation set, heated with 5 mg of *p*-toluenesulphonic acid at 110−120°C under vacuum. After isobutylene and HBr-elimination has ceased, the product was distilled immediately. B.p. 68−70°C/10 mm Hg; m.p. ≈ 26°C (lit.[3]: b.p. 72−74°C/10 mm Hg; m.p. 28°C); $n_D^{30} = 1.5606$. (Found: C 41.82; H 1.83. Calc. for $C_4H_2O_2S$: C 42.12; H 1.77). UV: (hexane) λ_{max} 230, 318 (ε 9220, 620). IR: (CCl_4) 1690 (s), 1730(v). NMR: ($CDCl_3$) a single peak at 433 cps.



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Received March 28, 1968.

An Electron Diffraction Study of Tetracyanoethylene

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The crystal structure of monoclinic tetracyanoethylene (TCNE) was first reported by Bekoe and Trueblood.[1] They observed a rather short central C=C distance of 1.317 Å (e.s.d. 0.009 Å). Penfold and Lipscomb determined the structure of diaminomaleonitrile,[2] and found the C=C distance in that compound to be 1.363 Å (e.s.d. 0.004 Å). According to the discussion by these authors there seems to be no obvious reason for the C=C bonds to be so different in the two compounds. It was therefore felt to be of interest to study the structure of the TCNE molecule by the gas phase electron diffraction method.

Electron diffraction diagrams were recorded photographically with the sector method at nozzle to plate distances of about 12, 19, and 48 cm, using an electron wavelength of about 0.065 Å. The intensity data were treated in the usual manner,[3] giving a useful observed molecular intensity function for the range $s = 1.25$ Å^{-1} to $s = 55$ Å^{-1} from which a radial distribution curve was computed.

A planar, symmetric molecular model with C−C≡N linear was fitted to the radial distribution curve by adjusting structural parameters to give the closest possible correspondence between experimental and theoretical radial distribution curves.

Table 1. Tetracyanoethylene. Interatomic distances and root-mean-square amplitudes of vibration.

Atoms	Distance	R.m.s. amplitude
C(1)−C(2)	1.357 Å	0.046 Å
C(1)−C(3)	2.430	0.060
C(1)−N(4)	3.495	0.120
C(1)−C(9)	1.435	0.047
C(1)−N(10)	2.597	0.060
C(3)−N(4)	1.162	0.035
C(3)−C(5)	2.460	0.090
C(3)−N(6)	3.515	0.120
C(3)−C(7)	3.754	0.074
C(3)−N(8)	4.871	0.089
C(3)−C(9)	2.835	0.097
C(3)−N(10)	3.575	0.120
N(4)−N(6)	4.452	0.144
N(4)−N(8)	5.980	0.096
N(4)−N(10)	4.030	0.192
∠C(1)−C(2)−C(3)	121.1°	

The molecular dimensions and corresponding root-mean-square amplitudes of vibrations are listed in Table 1, with the numbering system indicated in Fig. 1.

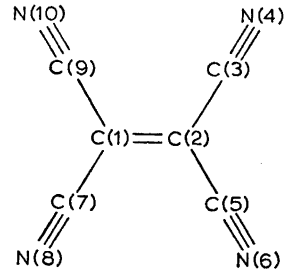

Fig. 1. Molecular model for tetracyanoethylene with indication of numbering system used.

The parameters in Table 1 were used in the calculation of the theoretical intensity curve shown in Fig. 2(*b*), and in the theoretical radial distribution curve in Fig. 3(*b*) (a damping function $\exp(-0.0009s^2)$ was used for the curves in Fig. 3).