Polymers and Copolymers of C_4O_3, the Anhydride of Acetylenedicarboxylic Acid

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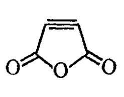
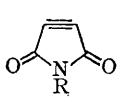
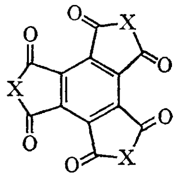
THE diesters of acetylenedicarboxylic acid are well known, but neither the free acid nor the anhydride (I) has been reported. A recent isotopic study[1] has clearly demonstrated that the cyclic heteryne (I), previously postulated as an intermediate in the formation of carbon suboxide by pyrolysis of diacetyltartaric anhydride or diethyl oxaloacetate in the presence of an excess of acetic anhydride does not in fact intervene.



(I)



(II)



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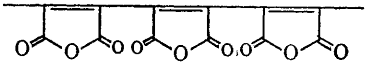

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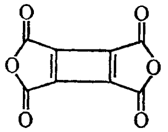
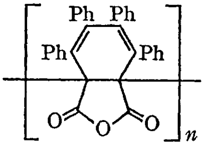
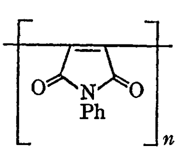


(V)



(VI)



(VII)

However, Draber[2] has furnished evidence for the transient formation of the imides (II; R = H, Me, Ph·CH_2) in the reaction of the corresponding 1,4-dithiintetracarboxydi-imides with pyridine at 120° and their polymerisation to the cyclic trimers (III; X = NR). Attempts by the author to prepare or to demonstrate the intermediate occurrence of the anhydride (I) have invariably led to the formation of a jet black, conjugated polymer $(C_4O_3)_n$ (IV), with no trace of the trimer, mellitic trianhydride (III; X = O), or the unlikely dimer (V).

In the Finkelstein reaction, simple exchange of iodine for chlorine occurs with dichloromaleic anhydride (VIII) to give di-iodomaleic anhydride (IX), m.p. 117·5° (lit.[3] 116°). When (IX) was heated above its melting point, free iodine was liberated and a black polymer $(C_4O_3)_n$ was obtained with a very low iodine content, which is presumably derived from end groups. The polymer showed little structure in the infrared spectrum. When the reaction was conducted in boiling xylene solution, slow evolution of iodine occurred but the black polymer obtained in this case had a carbon content higher than expected, and there was evidence of the participation of the solvent in the reaction. Treatment of (VIII) with metals (Cu or Zn) also led to exclusive polymer formation.

Reaction with thiourea did not prove a suitable method of dehalogenation, owing to the intervention of ring opening.

In aryne chemistry, tetracyclone (X) has been used to intercept the reactive species. Attempts to form the Diels–Alder adduct of (I) by condensing (IX) with (X) at 220° gave a polymeric product which was readily soluble in benzene. By chromatography on alumina a major fraction was separated with composition $(C_{32}H_{20}O_3)_n$, corresponding to (VI). In refluxing bromobenzene, the condensation of monochloromaleic anhydride with (X) is reported to proceed with loss of hydrogen chloride and carbon monoxide to give tetraphenylphthalic anhydride.[4] In this instance, it is likely that hydrogen chloride is eliminated from the adduct first formed.

When *N*-phenyldi-iodomaleimide (XI), m.p. 191° (lit.[5] 171—172°), was heated in a sealed tube at 275° for 24 hr., iodine (quantitative yield) sublimed and settled on the cool wall of the exposed part of tube, leaving a black polymeric residue which analysed correctly for $(C_{10}H_5NO_2)_n$.

Based on infrared-spectral evidence, this is assigned the conjugated polymeric imide structure (VII). On heating in a high vacuum at 250°, no crystalline sublimate was observed, thus ruling out the presence of any trimer (III; X = N·Ph).

Various copolymers of (VIII) with other

monomers, *e.g.*, styrene, have been prepared. Application of the Finkelstein reaction to these copolymers is being investigated. As another approach to copolymer systems incorporating the C_4O_3 moiety, the dehydrohalogenation of the copolymers is also being explored. The synthesis of an alternating copolymer of *p*-phenylene and (I) will be the subject of a forthcoming communication.

No evidence was found for the formation of the C_4O_3 ion or the ions of the dimeric or trimeric species on electron-impact induced fragmentation of (VIII) or (IX) in the mass spectrometer (M.S.9). The significant fragment ions in the mass spectrum of (IX) are those due to $[C_3OI]^+$ (34%), I_2^+ (10%), $[HI]^+$ (5%), and I^+ (13%). The ion $[C_3OI]^+$ is the base peak of the spectrum (M^+ 22%), and infers loss of $CO_2 + I$ from the molecular ion, *m/e* 350. A similar fragmentation pattern was observed with (XI), but (VIII) behaved very differently, exhibiting a series of strong ions (10—20%) as shown in the Table. No Cl_2^+ was observed and only small peaks due to HCl^+ and Cl^+.

TABLE

Ion intensities (% Σ *I*)

Fragment Ions	Parent Compound		
(X = Cl or I)	(VIII)	(IX)	(XI)
M	33·6	21·6	10·7
C_3OX_2	13·7		
C_2X_2	18·7	2·1	<1·0
C_3OX	9·4	34·3	10·4
C_2X	10·2		<1·0
C_2O	2·1		
CX	6·3		
X_2		9·7	1·1
HX		4·8	1·0
X		13·4	0·9
CO_2	1·9	8·9	3·2
CO	0·3	5·1	8·2

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[3] O. Diels and M. Reinbeck, *Ber.*, 1910, **43**, 1274.

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[5] L. Clarke and E. K. Bolton, *J. Amer. Chem. Soc.*, 1914, **36**, 1906.