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Meta and Para Rings[1]

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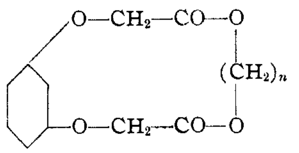
The closure of rings through the *m*- and *p*-positions of the benzene nucleus is one of the conventional problems of organic chemistry that long resisted solution. As soon as a rational theory of ring closure had been developed,[2] it became apparent that success might easily be achieved by the use of either the dilution or the interchange principle. Meanwhile, Ruzicka, Buijs and Stoll[3] applied their thorium salt method to the acids p-$C_6H_4[(CH_2)_6COOH]_2$ and m-$C_6H_4[(CH_2)_6COOH]_2$ and from the latter obtained a small amount of the 16-membered cyclic ketone, while Ziegler and Luttringhaus[4] have applied the dilution method to the nitriles m- and p-C_6H_4-$[O(CH_2)_6CN]_2$. The cyclic iminonitriles of 18 and 19 atoms were obtained in good yields.

In the experiments presently reported, the acids m- and p-$C_6H_4(OCH_2COOH)_2$ were esterified with glycols of the series $HO(CH_2)_nOH$ and the resulting polyesters depolymerized. In this manner, we have obtained *m*-rings (I) of 13, 14, 15, 17, 20 and 21 atoms, in yields ranging from 16 to 35%. In the *p*-series (II) none of the 14- or 15-membered ring was obtained, but those of 16, 18 and 22 atoms were isolated in yields of 12 to 18%.



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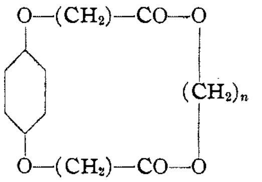

II

Data concerning yields and properties are shown in Table I.

These results demonstrate clearly the formation and stable existence of a 13-membered *m*-ring, and they suggest that in the *p*-series a ring of 16 atoms is the smallest possible, but caution must be used in extending or generalizing these conclusions. On the one hand, it has already been shown[5] that the replacement of —CH$_2$— by —O— in a chain considerably increases the ease of ring formation; thus, in the carbocyclic series the limits may lie at values different from those obtained for rings containing two ester groups and two ether oxygens. On the other hand, the failure to obtain a ring by no means demonstrates that its formation is impossible or that it would be very unstable if formed. Nevertheless, in view of the observed facts and the implications of space models, it seems that *m*-rings much smaller than 13 atoms and *p*-rings much smaller than 16 atoms are not likely to be obtained.

Experimental

Preparation and Properties of Polymers.—Polymeric resorcinol diacetates were prepared by heating equivalent amounts of the acid and glycol at 190–200° for about three hours and finally heating the residue to 210° in vacuum for one or two hours. The polymers were light brown viscous resins. Nonamethylene resorcinol diacetate, however, crystallized on long standing; the melting point of the crude polymer was 35–40°.

Owing to the high melting point of the acid, polymeric hydroquinone diacetates were prepared by heating equivalent amounts of the glycol and the ester (ethyl hydroquinone diacetate) with a small crystal of stannous chloride to 190° for about three hours. Final traces of alcohol were removed by heating the mixture in a vacuum to 210°. Ethylene and trimethylene hydroquinone diacetates are low-melting brown glassy resins. The remaining polymers were solids which had the following melting points:

Tetramethylene hydroquinone diacetate	45–50°
Hexamethylene hydroquinone diacetate	50–55°
Decamethylene hydroquinone diacetate	60–65°

Depolymerization.—The polyesters were depolymerized at 270° (1 mm.) in an 800-cc. vapor-heated still or depolymerizer of the type described in the preceding paper,[6] using 1 to 2% of $SnCl_2 \cdot 2H_2O$ as catalyst. Rates, yields and melting points are given in Table I. The monomers, purified by crystallization from alcohol, are all pure white sharply macrocrystalline solids. They

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(1) Paper XXVI on Polymerization and Ring Formation; Paper XXV, THIS JOURNAL, **57**, 929 (1935).

(2) *Ibid.*, **51**, 2548 (1929); **54**, 1569 (1932); **55**, 5043 (1933).

(3) Ruzicka, Buijs and Stoll, *Helv. Chim. Acta*, **15**, 1220 (1932).

(4) Ziegler and Luttringhaus, *Ann.*, **511**, 1 (1934).

(5) THIS JOURNAL, **55**, 5050 (1933).

(6) *Ibid.*, **57**, 929 (1935).

TABLE I

PROPERTIES AND SUMMARY OF PREPARATION OF META AND PARA RINGS

Polyester diacetate	Polyester, g.	Heating, hrs.	Crude yield, %	Pure yield, %	M. p. of monomer, °C.	Ring size of monomer
Ethylene resorcinol	23	2.5	30	21	100	13
Trimethylene resorcinol	29	3.5	41	24	134	14
Tetramethylene resorcinol	22	5	23	16	112	15
Hexamethylene resorcinol	22	3	45	35	115	17
Nonamethylene resorcinol	20	5	45	35	86	20
Decamethylene resorcinol	20	5	55	35	86	21
Ethylene hydroquinone	48	14	9	0	..	..
Trimethylene hydroquinone	35	6.5	10	0	..	..
Tetramethylene hydroquinone	28	4	42	12	140	16
Hexamethylene hydroquinone	50	7	30	12	124	18
Decamethylene hydroquinone	50	7	38	18	58	22

TABLE II

ANALYTICAL DATA FOR META AND PARA RINGS

	C	H	Mol. wt.[a]
Ethylene resorcinol diacetate			
Calcd. for $C_{12}H_{12}O_6$	57.14	4.76	252
Found	57.37	4.76	252
Trimethylene resorcinol diacetate			
Calcd. for $C_{13}H_{14}O_6$	58.64	5.96	266
Found	58.69	5.38	260
Tetramethylene resorcinol diacetate			
Calcd. for $C_{14}H_{16}O_6$	60.00	5.71	280
Found	60.04	5.65	290
Hexamethylene resorcinol diacetate			
Calcd. for $C_{16}H_{20}O_6$	62.33	6.49	308
Found	61.96	6.29	302
Nonamethylene resorcinol diacetate			
Calcd. for $C_{19}H_{26}O_6$	65.14	7.43	350
Found	65.02	7.31	360
Decamethylene resorcinol diacetate			
Calcd. for $C_{20}H_{28}O_6$	65.92	7.69	364
Found	66.02	7.75	364
Tetramethylene hydroquinone diacetate			
Calcd. for $C_{14}H_{16}O_6$	60.00	5.71	280
Found	60.33	5.86	268
Hexamethylene hydroquinone diacetate			
Calcd. for $C_{16}H_{20}O_6$	62.33	6.49	308
Found	62.40	6.84	307
Decamethylene hydroquinone diacetate			
Calcd. for $C_{20}H_{28}O_6$	65.92	7.69	364
Found	66.25	7.84	356

[a] Determinations made by freezing point in benzene.

are very soluble in ethyl acetate, benzene, acetone and ether; moderately soluble in petroleum ether and carbon tetrachloride. In the latter solvent, the higher members are more soluble than the lower ones. The compounds are all neutral (*i. e.*, they do not decompose potassium carbonate), and they react only slowly with a carbon tetrachloride solution of bromine. Two of the monomers, hexamethylene hydroquinone diacetate and hexamethylene resorcinol diacetate, were saponified; the corresponding dibasic acids were obtained in good yields and identified by mixed melting points.

Summary

Polyesters prepared from the acids *m*- and *p*-$C_6H_4(OCH_2COOH)_2$ by causing them to react with glycols $HO(CH_2)_nOH$ have been depolymerized. Cyclic monomers were thus obtained in the *m*-series, having rings of 13, 14, 15, 17, 20 and 21 atoms. In the *p*-series none of the 14- or 15-membered rings could be isolated, but those of 16, 18 and 22 atoms were readily formed.

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