

CYCLIC ETHERS FROM THE SELF-CONDENSATION OF

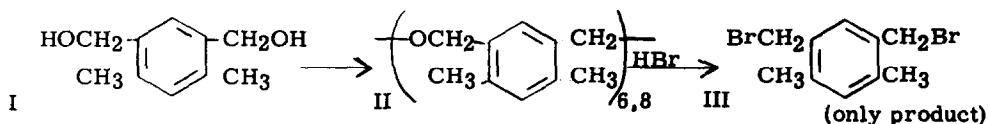
4, 6-DIMETHYLOL-m-XYLENE

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(Received 2 October 1959)

ACID-CATALYZED condensations of dimethylolbenzenes generally lead to the expected hydroxy-ended linear polyethers. While such reactions for para-dimethylolbenzenes are detailed by Rhoad and Flory¹, they noted briefly that some meta-analogs also condense in this way. During the course of similar study, but with 4, 6-dimethylol-m-xylene (I) and greater catalyst concentration, we detected no linear polyether of this type in the final product, but, instead, observed the quantitative formation of compounds whose characteristics are best represented by the cyclic poly (xylylene ether) (II). Molecular weight determinations indicated that, in separate experiments, the product isolated consisted of 6 and 8 monomeric units, respectively. Similar cyclic structures have not been previously reported.



4, 6-Dimethylol-m-xylene, I, ($C_{10}H_{14}O_2$, m.p. 150-151°) was prepared by the method of v. Braun and Nelles². It was heated, under N_2 , with 1% by

¹ M. J. Rhoad and P. J. Flory, J. Amer. Chem. Soc. 72, 2216 (1950).

² J. v. Braun and J. Nelles, Ber. 67, 1094 (1934).

weight of sulfamic acid at 200° for 0.5 hour. In each of the three successive experiments, the weight loss exactly equaled that had one mole of water been lost per mole of I. In each case the white product failed to exhibit hydroxyl function, in microchemical³ and I. R. analyses. The products were purified through separation from xylene solution by the addition of methanol.

Exp't. No.	Determinations on the Purified Products			Analysis, % ^e		
	M. P. ^a	M. W. ^e	C	H	O ^b	
1	135.7-136.6°	890 ^c , 885 ^d , av. 888	81.04 81.16	8.04 8.19	10.92 10.65	
2	135.3-136.4°	882 ^c , 903 ^d , av. 893	81.24 81.20	8.21 8.26	10.55 10.55	
3	136-137°	1204 ^c , 1092 ^c , av. 1148	81.14 81.22	8.20 8.03	10.66 10.75	

^a All melting points corrected; ^b % O, by difference; ^c Signer-Barger method; ^d Rast method; ^e Schwarzkopf Microanalytical Lab., Woodside 77, New York, M. W. accuracy within 5-10%.

Calculated from the analytical data, the empirical formula in each instance is C₁₀H₁₂O, exactly one H₂O less than the original diol (I) (C₁₀H₁₄O₂); This confirms the experimentally-observed weight loss. Structure II has the identical empirical formula, C₁₀H₁₂O: its 6-membered cycle has a calculated m.w. (888) comparing well with the determined values of products from experiments 1 and 2. The 8-membered cycle has a m.w. (1184) differing by only 3% from the average m.w. determined on the product from experiment 3.

The possibility of methylene-bridged functions, observed in small amounts in the self-condensation of p-xylylene glycol¹, was precluded in our case by the isolation of a single product, 4,6-bis-(bromomethyl)-m-xylylene (III), m.p. 110-111° (lit. val.², 111°), by treatment of these isolated products with 48% HBr. Structure II would behave exactly this way.

³ F. Feigl, Spot Tests in Organic Analysis, Elsevier, N.Y., 5th Ed. (1956).

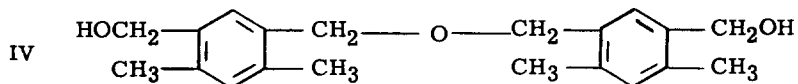
It is interesting to note that we did isolate a product containing, apparently, some methylene-bridged cross-links, by the self-condensation of dimethylol-mesitylene with 1% sulfamic acid. The product, m.p.265-270°, was so appraised by its insolubility in aromatic solvents. Rhoad & Flory, employing .1% sulfamic acid in an otherwise identical reaction, obtained a composition, m.p.245-250°, that was soluble in phenylcyclohexane, and which was considered solely a linear polyether. The ten-fold difference in catalyst concentration could account for this variance.

Further evidence for the cyclic nature of these condensation products is to be found in comparative melting points. It is seen that the melting points are quite sharp and are considerably lower than that of the starting diol (I). The sharpness is indicative of the relative purity and single nature of the product, while the lower melting point is significant of the absence of hydroxy function. On the other hand, the linear polyethers reported by Rhoad & Flory increased in melting point with increasing degree of polymerization, the melting points in all cases being higher than that of starting diol. This is quite consistent with their assignment of hydroxyl end-groups to these polymers.

It may be noted, finally, that, owing to the limited solubility of the linear polyethers, their molecular weights could not be determined by conventional means¹. As reported, their degrees of polymerization were estimated from their carbon analyses, the starting monomer having the minimum % C, and the latter increasing with degree of polymerization to the maximum at infinite chain length. The only other condition of maximum % C is that justified by a cyclic polyether. Since our products were sufficiently soluble, conventionally determined m.w.'s (by Signer-Barger & Rast methods) were obtained and from them the degrees of polymerization, 6 and 8, as discussed, were calculated. The % C determined in each case was the maximum possible (equal to that calculated for infinite linear- or cyclic-structure). This, together with m.w., lack of hydroxyl

function, low m.p. and high solubility, affords considerable validity to the cyclic structure (II) that we have assigned to these products.

In another experiment employing I with .1% sulfamic acid, as the only variation, the observed weight loss was equivalent to the loss of one-half mole of water per mole of I. Here hydroxyl groups were positively identified. While the product was not further characterized, structure IV seems to correlate most aptly with these observations.



On the assumption that this dimer (IV) is the correct structure resulting from the use of .1% catalyst, it might be proposed that m-diols, such as I, react in pairs and, under the influence of more vigorous catalysis (1% sulfamic acid), these pairs then react to form the proposed cyclic systems. By the use of Stuart and Briegleb molecular models, we have found that the 6-unit cyclic structure is the smallest of this homologous series in which complete freedom of rotation is possible for each substituent group. The 8-unit structure is likewise stable. Since rings larger than these should have at least as much steric freedom, it does not seem probable that larger rings first formed and disproportionated into the 6- and 8-unit structures; if such disproportionations were to occur, the 6- and 8-unit cyclic ethers would also be subject to such, forming larger rings - which were not observed. This absence might also preclude a random, heterogeneous condensation. The possibility of sequential linear build-up, *i. e.*, polymer reacting only with monomer, might also be ruled out since the sterically-stable 7-unit cycle should also be formed; it has not been found. (The 5-10% accuracy of the m. w. determinations, however, limits the validity of its absence.)