

alkylmercury compounds by mercuric bromide (reaction 2), and the exchange of alkyl groups in dialkylmercury compounds in the presence of alkylmercuric salts.<sup>10</sup>

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CHEMICAL EVIDENCE FOR AT LEAST TWO  
DIFFERENT PRECURSORS TO CYCLOHEXENE  
FORMED BY ELECTRON IRRADIATION OF  
CYCLOHEXANE

Sir:

By observation of the cyclohexene yield,  $G(\text{C}_6\text{H}_{10})$ , obtained by electron irradiation of cyclohexane containing a number of solutes, we have shown that there are at least two different modes for the formation of cyclohexene. Table I contains the experimental results.

TABLE I  
 $G(\text{C}_6\text{H}_{10})$  IN THE PRESENCE OF SOLUTES<sup>a</sup>

Solute	Concn., $M$	Dose $\times 10^{-20}$ ev./ml.	$G(\text{C}_6\text{H}_{10})$
None	..	3.55	2.3
Iodine	0.02	3.55	1.1
	.05	3.55	0.9
Benzyl chloride	.05 <sup>b</sup>	5.54	1.3
	.11 <sup>b</sup>	5.68	0.9
	.20	5.73	.8
	.55	5.73	.8
	3.48	5.97	.3
Toluene	0.097	4.84	1.8

<sup>a</sup> Irradiations were carried out on deoxygenated samples unless noted. <sup>b</sup> Irradiated both in the presence and absence of air, with the same results within experimental error.

The high-energy source used in this work was a 2-Mev. G. E. Resonant Transformer delivering 1 ma. beam current. Irradiations were performed in a multiple-cell sample holder previously described.<sup>1</sup> Dosimetry was accomplished by means of a flow calorimeter developed in this Laboratory. Cyclohexene was analyzed by means of quantitative gas-liquid chromatography. A 20-ft. column of 15% tricresyl phosphate on 30-60 mesh acid-washed Chromosorb, operated at 65°, separated cyclohexene from all other products.

It is postulated that cyclohexene is produced by processes other than thermalized radical reactions. Cyclohexyl radicals do not disproportionate efficiently to form cyclohexene.<sup>2,3</sup> We have found that for pure cyclohexane  $G(\text{C}_6\text{H}_{10}) = 2.3 \pm 0.2$  (Table I), in agreement with Dewhurst's value.<sup>4</sup> When the irradiation is carried out on samples containing 0.02  $M$  iodine in cyclohexane the  $G$ -yield drops to 1.1. As suggested by the work of Burton, *et al.*,<sup>5</sup> this result clearly shows that iodine

(0.02  $M$ ) does not completely prevent the formation of cyclohexene. Benzyl chloride (0.1  $M$ ) has an effect similar to that of iodine, reducing  $G(\text{C}_6\text{H}_{10})$  to about 1.0. When the benzyl chloride concentration is varied from 0.05  $M$  to 3.48  $M$  (25% benzyl chloride by volume),  $G(\text{C}_6\text{H}_{10})$  is decreased from 1.3 to 0.3. The reduction in cyclohexene is not linear with solute concentration. It drops rapidly with the initial addition of 0.05  $M$  benzyl chloride, and then decreases slowly as the concentration is raised to 3.48  $M$ . The fast initial drop of cyclohexene yield followed by the slow reduction on further addition of solute indicates that at least two different processes lead to cyclohexene. Addition of solutes quenches the formation of cyclohexene from one of these intermediates.

There is a gradation of effectiveness of different solutes with regard to ability to inhibit cyclohexene formation. The data in Table I demonstrate that at the same concentration iodine is more efficient than benzyl chloride which in turn is more effective than toluene.

At present, speculation as to the nature of these species is of little value and will be deferred until more of the variables have been studied (*e.g.*, effect of temperature, phase, viscosity, etc.).<sup>6</sup>

(6) Results similar to these have been published recently, see H. A. Dewhurst, *J. Phys. Chem.*, **63**, 813 (1959).

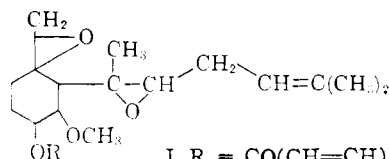
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THE STRUCTURE OF FUMAGILLIN<sup>1</sup>

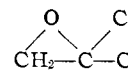
Sir:

Consideration of previous information<sup>2-10</sup> and of results now presented shows that fumagillin and its neutral saponification product "alcohol-I" possess structures I and II.



I, R =  $\text{CO}(\text{CH}=\text{CH})_4\text{COOH}$   
II, R = H

The presence in II of the epoxide group<sup>5,6,10</sup>



(1) Supported in part by Grant E-1138 of the U. S. Public Health Service.

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(3) C. G. Swain, L. J. Schaad and A. J. Kresge, *THIS JOURNAL*, **80**, 5313 (1958).

(4) H. A. Dewhurst, *J. Chem. Phys.*, **24**, 1254 (1956).

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