

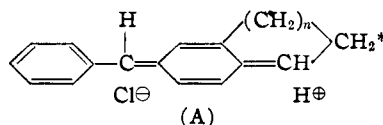
of the transition state by hyperconjugation (*i.e.*, no-bond resonance) has been most invoked to explain<sup>1</sup> this observation.

We have now measured solvolysis rates for compounds I, II and III at 0 and 25° in acetone-water (4:1) with the following results:

Compound	$(k \times 10^4 \text{ sec.}^{-1})$	
	0°	25°
I	214	3996
II	147	2717
III	103	2066

I ( $n = 1$ ); II ( $n = 2$ ); III ( $n = 3$ )

By analogy with the corresponding cyclic amines<sup>2</sup> and cyclic ketones<sup>3</sup> containing five-, six- and seven-membered rings, and in agreement with molecular models, the carbon atom marked C\* lies at increasing distances from the plane of the benzenoid ring as one passes through the series I, II and III. Consequently, the energy required to form a quinoidal type transition state (represented by "A") must increase regularly in the order I < II < III.



In order to explain adequately these rate differences, it has become necessary to assume steric inhibition of hyperconjugation. We believe this to be the first experimental evidence in support of the concept.

Analytically pure samples of I, II and III, employed in this study, were prepared from highly purified crystalline alcohols using newly devised synthetic routes and special techniques which will be described in detail at a later date. It is now clear that the incorrect rate constants reported earlier<sup>4</sup> for compounds I and II resulted from erroneous analytical data.

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(1) E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 949 (1940).

(2) W. G. Brown and S. Fried, *THIS JOURNAL*, **65**, 1841 (1943).

(3) R. G. Kadesch, *ibid.*, **66**, 1207 (1944).

(4) R. T. Arnold, K. Murai and R. M. Dodson, *ibid.*, **72**, 4193 (1950).

(5) Du Pont Postdoctorate Fellow, 1949-1950.

### THE STRUCTURE OF ZrMo<sub>2</sub><sup>1</sup>

Sir:

The existence of an intermediate phase in the zirconium-molybdenum system having the composition ZrMo<sub>3</sub> and the Al<sub>5</sub> (beta-wolfram) structure has been reported.<sup>2</sup> We have prepared the alloys of compositions ZrMo<sub>2</sub> and ZrMo<sub>3</sub> by arc melting (using a technique which has been described elsewhere<sup>2,3</sup>) followed by heating for four hours at 1370° in an atmosphere of high-purity helium.

(1) This work was done under contract number DA-04-495-ORD-18 with the Army Ordnance Department, Washington, D. C.

(2) H. J. Wallbaum, *Naturwiss.*, **30**, 149 (1942).

(3) C. H. Schramm, P. Gordon and A. R. Kaufmann, *Trans. AIME*, **188**, 195 (1950).

Powder patterns were then taken, using radiation from a copper target filtered through nickel foil, and a camera of 22.92 cm. diameter. Inspection of the two patterns showed at once that they were identical except for a few weak lines, and that the common lines could readily be indexed on the basis of a face-centered cubic lattice with a parameter of 7.58 Å. Relative intensities were computed on the assumption that this face-centered cubic phase is ZrMo<sub>2</sub> with the Cl<sub>5</sub> (MgCu<sub>2</sub>) structure, taking into account the Lorentz, polarization, multiplicity, and structure factors. The calculated relative intensities were found to be in very good agreement with those estimated visually from the powder patterns.

We accordingly propose that the intermediate phase in the zirconium-molybdenum system has the ideal stoichiometric composition ZrMo<sub>2</sub> and the Cl<sub>5</sub> crystal structure, and that there is no ZrMo<sub>3</sub> phase. ZrMo<sub>2</sub> thus has the same structure as that previously reported for ZrW<sub>2</sub>.<sup>3,4</sup>

(4) A. Claassen and W. G. Burgers, *Z. Kryst.*, (A) **86**, 100 (1933).

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### THE SYNTHESIS OF METHYL GROUPS FROM SERINE AND ITS BEARING ON THE METABOLISM OF ONE-CARBON FRAGMENTS<sup>1</sup>

Sir:

Further investigations on the conversion of the β-carbon of serine to the methyl groups of choline<sup>2</sup> and thymine<sup>3</sup> have shown that both β-hydrogen atoms accompany the carbon in this process. Following the administration of 2,3-deuterio-3-C<sup>14</sup>, N<sup>15</sup>-L-serine<sup>4</sup> to rats the choline from the internal organs was degraded and the C<sup>14</sup> activity and D concentration<sup>5</sup> of the methyl groups determined. The data (Table I) show that the C<sup>14</sup> and D of the

TABLE I

THE UTILIZATION OF THE β-CARBON AND β-HYDROGEN ATOMS OF L-SERINE FOR THE SYNTHESIS OF METHYL GROUPS

Expt.	Serine administered		Choline methyl groups		Dilution	
	β-C <sup>14</sup> , c.p.m. <sup>a</sup> × 10 <sup>-3</sup>	β-Deuterium, D per β-carbon <sup>b</sup>	C <sup>14</sup> , c.p.m. <sup>a</sup>	D, atoms per methyl group	C <sup>14</sup>	D
1 <sup>c</sup>	3.13	0.725	2970	0.0061 <sup>d</sup>	106	119
2 <sup>e</sup>	0.626	.575	461	.0041 <sup>f</sup>	136	140

<sup>a</sup> Counts per minute per dish of carbon at infinite thickness and under standard conditions. <sup>b</sup> Atom per cent. excess D in serine × 10<sup>-2</sup> × 7/2. See footnote 8. <sup>c</sup> Fed 0.47 mM. per 100 g. of body weight per day for 2 days. <sup>d</sup> Calculated from D concentration in betaine derived from choline (unpublished method). <sup>e</sup> Fed 0.53 mM. per 100 g. body weight per day for 2 days. <sup>f</sup> Atom per cent. excess D in [(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>H<sub>2</sub>PtCl<sub>6</sub> × 10<sup>-2</sup> × 10/3 (V. du Vigneaud, *et al.*, *J. Biol. Chem.*, **140**, 625 (1941)).

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(2) A. Weissbach, D. Elwyn and D. B. Sprinson, *THIS JOURNAL*, **72** 3316 (1950).

(3) D. Elwyn and D. B. Sprinson, *ibid.*, **72**, 3317 (1950).

(4) D. Elwyn and D. B. Sprinson, *J. Biol. Chem.*, **184**, 465 (1950).

(5) J. Graf and D. Rittenberg, *in press*.