Pentacarbanilino-D-glucose Diethyl Mercaptal

To a solution of 3.0 g. (10.5 millimoles) of D-glucose diethyl mercaptal (m.p. 125°) in 75 ml. of dry pyridine, maintained at 100°, was added all at once 11.4 ml. (105 millimoles) of phenyl isocyanate. The mixture was stirred at 100° for 6.5 hours, cooled, and added to 300 ml. of absolute ethanol. This clear solution on dilution with an equal volume of water gave 9.1 g. (98.5% of the theoretical amount) of crude pentacarbanilino-D-glucose diethyl mercaptal. Two recrystallizations from hot *n*-butanol in the proportion of 50 ml. of solvent per gram of crude compound gave an analytically pure material melting at 207–210°, $[\alpha]^{26}D$ +41.8° (*c* 0.9, pyridine). Recovery of purified material was approximately 83% at each recrystallization step.

Anal. Calcd. for $C_{45}H_{47}N_5O_{10}S_2$: C, 61.3; H, 5.3; N, 7.9; S, 7.3. Found: C, 61.3; H, 5.5; N, 7.7; S, 7.3.

J. E. Hodge prepared the D-glucose diethyl mercaptal and C. H. Van Etten performed the microanalyses.

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U. S. DEPARTMENT OF AGRICULTURE I. A. WOLFF
PEORIA, ILLINOIS P. R. WATSON

RECEIVED JULY 30, 1951

COMMUNICATIONS TO THE EDITOR

RETENTION OF Br^{80} IN COMPLEX BROMIDES, FOLLOWING ISOMERIC TRANSITION[1]

Sir:

The 18 minute bromine nascent from the isomeric transition decay of Br^{*80} is known to possess a high chemical reactivity. Disruption of the parent molecule appears always to occur, in the case of aqueous bromate ion and of various organic bromides, although in pure condensed systems some recombination of the primary fragments has been postulated. This reactivity is due to the high positive charge on the bromine which results from the Auger ionization that follows internal conversion.[2] It seemed possible that a bromine-containing Werner complex might more easily tolerate such a positive increment in charge, especially if the complex ion were negative in sign to begin with. Results are here reported for $Co(NH_3)_5Br^{+2}$ and $PtBr_6^{-2}$.

The general procedure was to prepare a solution of the complex, labelled with 4.4 hour Br^{80} (in equilibrium with the 18 minute daughter), and then to precipitate the complex as bromopentamminecobaltate(III) nitrate or as ammonium bromoplatinate(IV). Sodium bromide, if not already present, was added before the separation. The degree of retention of the 18 minute isomer was determined from the growth curve of the precipitated complex. Retention in the solid state was determined by dissolving the solid complex, adding sodium bromide, and immediately reprecipitating the complex. Ordinary exchange of bromide ion with either complex was negligible in the *ca.* two hours time involved (in the dark).

TABLE I

Complex	Concn. of complex, *M*	% retention	
$Co(NH_3)_5Br^{+2}$	0.01	0	
$[Co(NH_3)_5Br](NO_3)_2$	(solid)	14	
$PtBr_6^{-2}$	0.00166	52	52
	0.0005	70[a]	53
	0.0005 with 0.003 *M* NaBr	54	
$(NH_4)_2PtBr_6$	(solid)	100	

[a] Possibly some photocatalyzed exchange.

Evidently, disruption of the bromopentamminecobaltate(III) ion occurred upon every isomeric transition, and without recombination of fragments or any re-entry of bromine into another molecule of complex. Recombination of primary fragments to give the original complex might be expected to be improbable since the complex ion is unstable in solution and aquates slowly; the process might be responsible for the small retention in the solid. Re-entry of the "hot" 18 minute bromine into a different molecule of complex would be unlikely in solution because of the low concentration of the complex.

The high retention by aqueous bromoplatinate(IV) ion cannot be due to re-entry, by the same argument as above, and also in view of the lack of dependence of the effect upon concentration and upon added free bromide ion. Furthermore, it seems unlikely that the retention was due to a recombination of primary fragments, again because the complex ion is unstable toward aquation. Interestingly, the same high retention was observed when free bromide ion was initially present, indicating that isomeric transition did not so activate the complex as to permit exchange.

These results suggest that the degree of reactivity induced by isomeric transition is strongly dependent upon the charge of the parent molecule, but the two complex ions studied are too dissimilar for this conclusion to be more than tentative. Further work on this and related systems is in progress.

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RECEIVED AUGUST 28, 1951

STERIC INHIBITION OF HYPERCONJUGATION

Sir:

For *p*-alkylbenzhydryl chlorides, the first order rates of solvolysis decrease in the order $CH_3 > CH_3CH_2 > (CH_3)_2CH > (CH_3)_3C$. Stabilization

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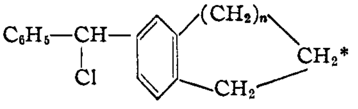
[1] This work was carried out under contract N6onr23809 between the University of Southern California and the Office of Naval Research.

[2] For a recent bibliography see S. Goldhaber, R. S. H. Chiang and J. E. Willard, THIS JOURNAL, **73**, 2271 (1951).

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

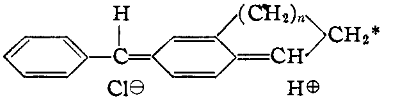
We have now measured solvolysis rates for compounds I, II and III at 0 and 25° in acetone–water (4:1) with the following results:



Compound	($k \times 10^6$ 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[2] and cyclic ketones[3] 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.



(A)

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[4] for compounds I and II resulted from erroneous analytical data.

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RICHARD T. ARNOLD
WILLIAM L. TRUETT[5]

RECEIVED OCTOBER 9, 1951

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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 $ZrMo_2$[1]

Sir:

The existence of an intermediate phase in the zirconium–molybdenum system having the composition $ZrMo_3$ and the A15 (beta-wolfram) structure has been reported.[2] We have prepared the alloys of compositions $ZrMo_2$ and $ZrMo_3$ by arc melting (using a technique which has been described elsewhere[2,3]) followed by heating for four hours at 1370° in an atmosphere of high-purity helium. 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 $ZrMo_2$ with the C15 ($MgCu_2$) 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 $ZrMo_2$ and the C15 crystal structure, and that there is no $ZrMo_3$ phase. $ZrMo_2$ thus has the same structure as that previously reported for ZrW_2.[3,4]

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

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POL DUWEZ
CHARLES B. JORDAN

RECEIVED SEPTEMBER 28, 1951

THE SYNTHESIS OF METHYL GROUPS FROM SERINE AND ITS BEARING ON THE METABOLISM OF ONE-CARBON FRAGMENTS[1]

Sir:

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

	Serine administered		Choline methyl groups			
Expt.	β-C^{14}, c.p.m.[a] $\times 10^{-5}$	β-Deuterium, atoms D per β-carbon[b]	C^{14}, c.p.m.[a]	D, atoms per methyl group	Dilution C^{14}	D
1[c]	3.13	0.725	2970	0.0061[d]	106	119
2[e]	0.626	.575	461	.0041[f]	136	140

[a] Counts per minute per dish of carbon at infinite thickness and under standard conditions. [b] Atom per cent. excess D in serine $\times 10^{-2} \times 7/2$. See footnote 8. [c] Fed 0.47 mM. per 100 g. of body weight per day for 2 days. [d] Calculated from D concentration in betaine derived from choline (unpublished method). [e] Fed 0.53 mM. per 100 g. body weight per day for 2 days. [f] Atom per cent. excess D in $[(CH_3)_3N]_2 \cdot H_2PtCl_6 \times 10^{-2} \times 10/3$ (V. du Vigneaud, *et al.*, *J. Biol. Chem.*, **140**, 625 (1941)).

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(1) This work was supported by a grant from the American Cancer Society, recommended by the Committee on Growth of the National Research Council, and in part, by a grant from the Lederle Laboratories Division of the American Cyanamid Company.

(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. Graff and D. Rittenberg, in press.