

4 are identical and diastereoisomeric with the product of Method 1. We have been unable to obtain a satisfactory product from direct nitration of β -phenylserine as reported by Billet⁴ (Method 2).

The amino acids themselves cannot be distinguished satisfactorily by melting point determination. Each isomer has about the same melting point and there is little depression when mixed. Conversion to the ethyl esters gave derivatives with distinctive melting points.

An ethyl β -*p*-nitrophenylserinate (*erythro*), m.p. 115–116°, is obtained in Method 4 by hydrolysis of the Schiff base which is the initial product. The use of equivalent amounts of *p*-nitrobenzaldehyde and ethyl glycinate was found to improve the yield of condensation product to 66%. Further hydrolysis of the ester produces a β -*p*-nitrophenylserine (*erythro*) which can be esterified to the same ester. The β -*p*-nitrophenylserine (*threo*) from Method 1 gave an ethyl ester melting at 132–133°. This higher-melting ester was also obtained from the diastereoisomer of m.p. 115° by thionyl chloride inversion of the N-acetate. Esterification of the β -*p*-nitrophenylserine from Method 3 gave the ester (*erythro*) melting at 115°, identical with that from Method 4.

The ethyl ester (*erythro*) from Method 4 was treated with methyl dichloroacetate and then with acetic anhydride to produce ethyl N-dichloroacetyl-O-acetyl- β -*p*-nitrophenylserinate (*erythro*), m.p. 85–86°. This was compared with the corresponding compound (*threo*), m.p. 126–127°, obtained from Erlenmeyer's *threo*- β -phenylserine by the same reactions followed by nitration. The products were not identical, but on alkaline hydrolysis yielded the same product, m.p. 183–184°, which is believed to be ethyl α -dichloroacetamido- β -nitrocinnamate. Since, in this product, all asymmetry is lost, it could be expected from either diastereoisomer. A second product of the hydrolysis of the 126–127° form was *threo*-N-dichloroacetyl- β -*p*-nitrophenylserine, m.p. 187–189°. Huebner and Scholz have described this method of obtaining N-dichloroacetyl- β -*p*-nitrophenylserine, m.p. 173–175°, and have also obtained and identified the other product of hydrolysis as ethyl α -dichloroacetamido- β -*p*-nitrocinnamate, m.p. 151–155°.

The methods of β -*p*-nitrophenylserine production which involve condensation of *p*-nitrobenzaldehyde with ethyl glycinate thus are shown to yield products of the same diastereoisomeric form which differ from the products of nitration of known *threo*- β -phenylserine derivatives. They are, therefore, assigned the *erythro* configuration.

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ADDED IN PROOF.—Since this note was submitted, the question of the stereochemistry of the β -*p*-nitrophenylserines has been the subject of publications by several groups. The results are not entirely in accord. M. Kopp, *et al.*, *Compt. rend.*, **233**, 527 (1951), have concluded from a chemical investigation that Method 4 leads to the *erythro* form, while E. D. Bergmann, *et al.*, *J. Chem. Soc.*, 2673

(1951), reach the opposite conclusion. D. Molho and L. Molho-Lacroix, *Compt. rend.*, **233**, 1067 (1951), have obtained microbiological evidence of the *erythro* configuration for the product of Method 3 and D. Billet and C. Marnay, *ibid.*, **233**, 961 (1951), support the *erythro* assignment to Method 4 while reporting a modification of the method to yield what is claimed to be the *threo* form. Unfortunately, much of the disagreement is supported by experiment not yet reported in detail or by materials not completely characterized.

Experimental

Ethyl β -*p*-Nitrophenylserinate.—The β -*p*-nitrophenylserines were esterified with absolute ethanol and anhydrous HCl and the liberated amino esters crystallized from aq. ethanol; *threo*, m.p. 132–133°; *erythro*, m.p. 115–116°.

Anal. Calcd. for $C_{11}H_{14}N_2O_5$: C, 51.96; H, 5.55; N, 11.02. Found: *threo*: C, 52.24; H, 5.48; N, 11.00. *erythro*: C, 52.16; H, 5.57; N, 10.95.

Inversion of *erythro*- β -*p*-Nitrophenylserinate.—The *erythro* ester was acetylated with acetic anhydride to the N-acetyl derivative, m.p. 158–159°.

Anal. Calcd. for $C_{13}H_{16}N_2O_6$: C, 52.70; H, 5.44; N, 9.46. Found: C, 52.78; H, 5.50; N, 9.54.

The N-acetate (12 g.) was added during ten minutes to 60 ml. of thionyl chloride. After 40 minutes at room temperature, the mixture was treated cautiously with 120 ml. of water and heated for 1.5 hours on the steam-bath. The chilled solution was neutralized with ammonium hydroxide and the precipitated amino acid separated. The amino acid thus obtained was converted to the ethyl ester, 7.1 g., identical by mixed melting point with the ethyl *threo*- β -*p*-nitrophenylserinate (m.p. 132–133°).

Ethyl N-Dichloroacetyl-O-acetyl- β -*p*-nitrophenylserinate.—The ethyl *erythro*- β -*p*-nitrophenylserinate was treated in methanol solution with methyl dichloroacetate and the product acetylated with acetic anhydride. The acetate melted at 86–87° after crystallization from aq. ethanol.

Anal. Calcd. for $C_{15}H_{18}N_2O_7Cl_2$: C, 44.24; H, 3.96; N, 6.88. Found: C, 44.04; H, 4.06; N, 6.62.

The corresponding *threo* derivative was prepared by the procedure of Huebner and Scholz⁵ and melted at 126–127°.

Anal. Found: C, 44.27; H, 4.06.

Each diastereoisomer on treatment with NaOH in acetone at 0° gave ethyl α -dichloroacetamido- β -nitrocinnamate, m.p. 183–184°; λ_{max} (in H_2O) 310, $E = 16600$; λ_{max} (in OH^-) 362, $E = 14800$. A mixture of the two showed no melting point depression.

Anal. Calcd. for $C_{13}H_{12}N_2O_6Cl_2$: C, 44.97; H, 3.49. Found: C, 45.14, 45.01; H, 3.69, 3.72.

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Preparation of Mo_3Ge and Determination of Its Structure¹

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In a brief note Wallbaum² reported the structures of a number of germanides of transition metals. His note is almost the only report in the literature of this series of compounds. The correspondence in composition and in structure of many of these germanides to silicides of the same elements is of particular interest.

The compounds Mo_3Si ,^{3,4} Cr_3Si ,⁵ V_3Si ,⁶ Cr_3Ge ²

(1) This research was supported by the Office of Naval Research.

(2) H. J. Wallbaum, *Naturwissenschaften*, **32**, 76 (1944).

(3) L. Brewer, A. W. Searcy, D. H. Templeton and C. H. Dauben, *J. Am. Ceram. Soc.*, **33**, 291 (1950).

(4) D. H. Templeton and C. H. Dauben, *Acta Cryst.*, **3**, 261 (1950).

(5) B. Boren, *Arkiv Kemi, Mineral. Geol.*, 11a (no. 10), 1 (1933); *Strukturbericht*, **3**, 628 (1937).

(6) H. J. Wallbaum, *Z. Metallkunde*, **31**, 362 (1939).

and V_3Ge^2 have been prepared and are all isomorphous. It seemed of interest to attempt the preparation of Mo_3Ge .

Samples of molybdenum and germanium powders in atomic ratios of approximately three to one were heated for several hours near 1000° to effect equilibrium. X-Ray diffraction patterns were then obtained with a General Electric powder camera. Filtered copper $K\alpha$ radiation was used ($\alpha_1 = 1.540522 \text{ \AA.}$, $\alpha_2 = 1.544367 \text{ \AA.}$). A sample having the over-all composition $MoGe_{0.33}$ gave a very faint molybdenum pattern and the strong pattern of a cubic phase. A sample of composition $MoGe_{0.37}$ gave a strong pattern of the cubic phase and faint lines of a phase that we have shown to be $MoGe_{0.67 \pm 0.03}$. The composition of the cubic phase, therefore, is $MoGe_{0.35 \pm 0.03}$, or Mo_3Ge , with no observable solid solution range.

Values of the cell constant a obtained from different values of d/n (the distance between crystallographic planes) were plotted against $\cos^2 \theta \cot \theta$, where θ is the angle of reflection of the X-ray beam. The plot was extrapolated to $\theta = 90^\circ$ to obtain the best value of a from each photograph. The diffraction patterns of two different samples containing Mo_3Ge in equilibrium with molybdenum yielded $a = 4.9330 \pm 0.0003 \text{ \AA.}$ and $a = 4.9329 \pm 0.0006 \text{ \AA.}$ A pattern of Mo_3Ge in equilibrium with $MoGe_{0.67}$ yielded $a = 4.9332 \pm 0.0003 \text{ \AA.}$ Variation of the lattice constant with composition is within the uncertainties in the measurements, strengthening the conclusion that Mo_3Ge has no appreciable solid solution range.

The density of a small, porous sample of Mo_3Ge was determined from measurements of its apparent weight in air and in water. This experimental density was $9.7 \pm 0.4 \text{ g. cm.}^{-3}$; the density calculated assuming six molybdenum atoms and two germanium atoms per unit cell of the cubic lattice was $9.97 \pm 0.01 \text{ g. cm.}^{-3}$.

Values for d/n calculated for lines from the diffraction pattern of Mo_3Ge corresponded very closely to those reported by Templeton and Dauben⁴ for Mo_3Si , although six of the weaker lines of the Mo_3Si pattern were missing from the Mo_3Ge pattern. The two phases are obviously isomorphous. Table I lists the hkl assignments, d/n values, and calculated and visual intensities for Mo_3Ge . The calculated intensities were reduced to the same arbitrary scale used by Templeton and Dauben in their determination of the structure of Mo_3Si , and their values for Mo_3Si were included in the table for comparison. The intensities calculated for Mo_3Ge agree satisfactorily with the intensities observed. The six lines observed in the Mo_3Si pattern, but not observed in the Mo_3Ge pattern, all have very low calculated intensities for Mo_3Ge . Thus Mo_3Ge , like Mo_3Si , belongs to space group $O_h^3-Pm\bar{3}n$ and has the β -tungsten⁷ structure. The positions of the atoms are: two Ge in (a) at $0, 0, 0$; $1/2, 1/2, 1/2$; and six Mo in (c) at $1/4, 0, 1/2$; $1/2, 1/4, 0$; $0, 1/2, 1/4$; $3/4, 0, 1/2$; $1/2, 3/4, 0$; $0, 1/2, 3/4$.

Each germanium atom in Mo_3Ge is surrounded

(7) H. Hartmann, F. Ebert and O. Bretschneider, *Z. anorg. Chem.*, **198**, 116 (1931).

TABLE I

DIFFRACTION DATA FOR Mo_3Ge
vs, very strong; s, strong; m, medium; w, weak.

hkl	Mo_3Ge		Mo_3Si	
	d	Visual	Calcd.	$(T + D)^4$ Calcd.
110	3.4724	w ⁻	5	36
200	2.4557	w	45	25
210	2.1993	vs	163	183
211	2.0031	s	96	58
220	Absent	<1	3
310	Absent	1	7
222	1.4215	w	17	25
320	1.3663	w ⁺	34	26
321	1.3167	m	44	26
400	1.2323	w ⁻	21	16
330	Absent	1	4
411				
420	1.1024	w	13	7
421	1.0755	m	34	33
332	1.0506	w ⁻	12	7
422	Absent	<1	2
431	Absent	<1	6
510				
432	0.9158	s	46	43
520				
521	0.9004	m ⁻	23	13
440	0.8720	m ⁺	30	22
433	Absent	<1	5
530				
442	0.8221	w ⁺	20	12
600				
610	0.8110	m	25	27
532	0.8002	s	63	39
611				

by 12 molybdenum atoms at 2.75 \AA. Each molybdenum atom has two molybdenum atoms at 2.46 \AA. , four germanium atoms at 2.75 \AA. and eight molybdenum atoms at 3.02 \AA.

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The Purification and Identification of 1-Methylnaphthalene

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The inefficacies of conventional methods for the liberation of 1-methylnaphthalene from its usual impurity, the 2-methyl isomer, have been pointed out recently by Morrell, Pickering and Smith.² The best method in the literature^{2,3,3b} involves a rather tedious process, *i.e.*, sulfonation, conversion of the sulfonic acids to their *p*-toluidine salts, frac-

(1) Department of Chemistry, Wellesley College, Wellesley, Mass.
(2) S. H. Morrell, G. B. Pickering and J. C. Smith, *J. Inst. Petroleum*, **34**, 677 (1948).

(3) (a) G. T. Morgan and E. A. Coulson, *J. Soc. Chem. Ind.*, **53**, 73 (1934); (b) after this article was submitted it was brought to our attention that a method involving distillation of the hydrocarbon under special conditions in the presence of 5-ethylnonanol as an azeotropic agent was reported by J. Feldman and M. Orchin; Abstracts of Papers, 117th Meeting, American Chemical Society, Chicago, Ill., September 3 to 8, 1950.