65–87°. After two recrystallizations from ethanol, 5.4 g. (83%) of colorless leaflets, m.p. 94.5–96°, was obtained. Admixture of product from procedure (B) did not depress the m.p.

(B).—Under anhydrous conditions a mixture of 13.6 g. of pentaerythritol, 85.5 g. of chloroacetic anhydride and 0.5 g. of fused zinc chloride was boiled at 20 mm. pressure under reflux until the initial vigorous reaction had subsided, and then heated below the boiling point on a steam-bath for three hours. The (hot) mixture was poured into 200 ml. of water and allowed to stand overnight. The product separated as an oil. Addition to the mixture of 100 ml. of ethanol failed to cause crystallization. The aqueous ethanolic phase was separated and discarded. On addition of 50 ml. more ethanol to the non-aqueous phase, crystallization occurred. By filtration and washing with ethanol, 14.5 g. of colorless crystals, m.p. 55–56°, was obtained.

Recrystallization of 11.6 g. from 200 ml. of absolute ethanol gave 7.0 g. (16%) of colorless leaflets, m.p. 100.5–101°.

Anal. Calcd. for $C_{13}H_{16}Cl_4O_8$: C, 35.32; H, 3.65. Found: C, 35.42; H, 3.47.

By procedure (A) one obtains the product in much higher yield, and its purity is satisfactory for most purposes.

The compound gave a positive Beilstein halogen test, but reacted with alcoholic silver nitrate only after many minutes of boiling.

Reaction of α-*p*-Nitrophenylbutyryl Chloride with Pentaerythritol.—Finely divided, dry portions of *d,l*-α-*p*-nitrophenylbutyric acid (m.p. 118–120°)[4,5] (5.0 g.) and of phosphorus pentachloride (5.1 g.) were mixed. The mixture soon liquefied, with evolution of hydrogen chloride. The mixture was gently boiled for ten minutes, then phosphorus oxychloride was removed by vacuum distillation. The residue upon vacuum distillation gave 4.67 g. (86%) of *d,l*-α-*p*-nitrophenylbutyryl chloride as a bright yellow liquid of b.p. 172–174° (10 mm.), $n^{26}D$ 1.5505, which could not be induced to crystallize. To characterize the product, it was treated with ethanol and sodium hydroxide under Schotten–Baumann conditions, giving *d,l*-ethyl α-*p*-nitrophenylbutyrate, b.p. 145–150° (2–3 mm.), $n^{24}D$ 1.5202, d^{28} 1.133. The constants are in good agreement with those for the ester prepared[5] directly from the acid.

When the acid chloride (5.7 g.) was heated with 0.55 g. of pentaerythritol at 150° for 20 minutes, the product was obtained as a yellow oil, which solidified on prolonged shaking with ethanol to give 3.3 g. of material, m.p. 90–122°. After seven recrystallizations from ethanol the colorless product (0.66 g., 30%) still melted over a wide range (130–153°). The molecular weight (Rast method) was found to be 810 (theor. for $C_{45}H_{48}N_4O_{16}$, 901). It is presumably a mixture of the three theoretically possible racemic forms, and has not been further characterized.

***d,l*-Pentaerythritol Tetra-[2-(carbo-2-methylbutoxy)-6-nitrobenzoate].**—Under anhydrous conditions, 5.0 g. of *dextro*-2-methylbutyl 2-carboxy-6-nitrobenzoate[6] (m.p. 160–161°, $[\alpha]^{25}D$ +2.56° (acetone, *c*, 32)) was refluxed with 10 ml. of thionyl chloride for one hour. After removal of thionyl chloride by vacuum distillation, the residue was recrystallized from dry petroleum ether, giving colorless leaflets of m.p. 60–62°. After two more recrystallizations, 4.5 g. (84%) of *dextro*-2-methylbutyl 2-chloroformyl-6-nitrobenzoate, m.p. 61–62°, $[\alpha]^{25}D$ +0.69° (ethyl acetate, *c*, 17.3), was obtained.

To one gram of the acid chloride in 2 ml. of dry pyridine was added 0.10 g. of pentaerythritol. The warm mixture was cooled, and after 17 hours at 25° was added at 0° to 10 ml. of 10% sulfuric acid. The aqueous phase was decanted and the semi-solid organic residue recrystallized twice from ethanol, giving 0.75 g. (86%) of fine colorless needles, m.p. 111–114°. A sample was recrystallized again for analysis, and dried at 80° (10 mm.); m.p. 113–115°.

Anal. Calcd. for $C_{57}H_{64}N_4O_{24}$: C, 57.57; H, 5.43; N, 4.71. Found: C, 57.18; H, 5.17; N, 5.12.

Recrystallization from benzene–ligroin changed the m.p. to 85–95°, but when this low-melting form was recrystallized from ethanol the m.p. was restored to 113–115°.

The product gave no optical rotation and was apparently racemic.[7] An identical product was obtained when the same reactions were carried out with the 3-nitrophthalate of *d,l*-2-methylbutanol. A mixed m.p. on the two final products showed no depression.

Three racemic forms are theoretically possible for the pentaerythritol ester but thus far only the product above has been isolated.

(4) C. S. Marvel and T. Chu, THIS JOURNAL, **55**, 2841 (1933).
(5) A. L. Wilds and W. R. Biggerstaff, *ibid.*, **67**, 789 (1945).
(6) A. McKenzie, *J. Chem. Soc.*, **79**, 1135 (1901).
(7) Since the observed rotation of the acid chloride from the *dextro*-3-nitrophthalate was only + 0.12°, the racemization may have occurred during chlorination.

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Chloromycetin.[1] Related Compounds. The β-*p*-Nitrophenylserines

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Chloromycetin has been shown to be D_G-(−)-*threo*-2-dichloroacetamido-1-*p*-nitrophenyl-1,3-propanediol.[2] In exploring related substances, several authors[3,4,5] have reported on β-*p*-nitrophenylserine and its N-dichloroacetyl derivative which differs from Chloromycetin in having a carboxyl in place of the primary carbinol group. β-*p*-Nitrophenylserine has been prepared by (1) nitration of the N-acetate of Erlenmeyer's β-phenylserine,[3] by (2) direct nitration of Erlenmeyer's β-phenylserine,[4] by (3) the condensation of *p*-nitrobenzaldehyde with ethyl glycinate over sodium,[6] and recently by (4) the condensation of *p*-nitrobenzaldehyde with ethyl glycinate in alcohol solution without a catalyst.[7]

On the basis of microbiological testing, Billet[8] has claimed from unpublished work, a difference suggesting that the β-*p*-nitrophenylserine obtained by Method 3 was not the same as that from Method 2. Since the Erlenmeyer β-phenylserine has been shown to be of the *threo* configuration, Method 3 was considered to give the *erythro* form. However, the attempt to show non-identity of the two acids and to correlate their configurations with the chloramphenicols by microbiological activities was later reported to be unsatisfactory since the activity difference was too small. The N-dichloroacetyl derivatives were then prepared, but the melting points were the same and no mixed melt was reported.[9] The N-dichloroacetyl-β-*p*-nitrophenylserine prepared in the manner of Method 1 has since been found to have no microbiological activity *vs. S. sonnei*. Since this substance can be shown to be the *threo* modification, it follows that Billet's hope of assigning configuration on the basis of anticipated differing microbiological activities and on the assumption that these must parallel the chloramphenicol activities, must fail.

We have investigated each method of preparation and have been able to demonstrate by chemical methods that the products of Methods 3 and

(1) Parke, Davis & Co. registered trademark for chloramphenicol.
(2) M. C. Rebstock, *et al.*, THIS JOURNAL, **71**, 2460 (1950).
(3) D. W. Woolley, *J. Biol. Chem.*, **185**, 293 (1950).
(4) D. Billet, *Compt. rend.*, **230**, 1358 (1950).
(5) C. F. Huebner and C. R. Scholz, THIS JOURNAL, **73**, 2089 (1951).
(6) C. E. Dalgliesh, *J. Chem. Soc.*, 90 (1949).
(7) E. D. Bergmann, *et al.*, *Compt. rend.*, **231**, 361 (1950).
(8) D. Billet, *ibid.*, **230**, 1074 (1950).
(9) D. Billet, *ibid.*, **231**, 293 (1950).

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 Billet[4] (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-*p*-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 $C_{15}H_{16}N_2O_7Cl_2$: 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 Scholz[5] 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-*p*-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 $C_{13}H_{12}N_2O_5Cl_2$: 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 Structure[1]

BY ALAN W. SEARCY, ROBERT J. PEAVLER AND H. J. YEARIAN

In a brief note Wallbaum[2] 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).