from this equation are shown in column four in Table I.

Temp., °C.	$E°$ (obsd.) (Harned and Ehlers)	$E°$ (obsd.) (int. volts)	$E°$ (calcd.) (int. volts)	$E°$ (calcd.) (abs. volts)	2.30259 RT/F (abs. volts)
0	0.23634	0.23641	0.23639	0.23647	0.054195
5	.23392	.23399	.23398	.23406	.055187
10	.23126	.23133	.23137	.23145	.056179
15	.22847	.22855	.22858	.22865	.057171
18	.....	.....	.22682	.22689	.057766
20	.22551	.22559	.22561	.22568	.058163
25	.22239	.22247	.22247	.22254	.059155
30	.21912	.21920	.21917	.21924	.060147
35	.21563	.21571	.21571	.21578	.061139
37	.....	.....	.21425	.21432	.061536
40	.21200	.21208	.21210	.21216	.062131
45	.20821	.20829	.20834	.20841	.063123
50	.20437	.20446	.20445	.20452	.064115
55	.20035	.20044	.20043	.20050	.065107
60	.19620	.19629	.19628	.19635	.066099

The constants of this equation were multiplied by the factor[2] 1.000330 yielding $E°$ in absolute volts: $E°$ (absolute volts) $= 0.22254 - 6.4471 \times 10^{-4} (t - 25) - 3.277 \times 10^{-6} (t - 25)^2 + 8.99 \times 10^{-9} (t - 25)^3$. Values of $E°$ calculated from this equation are shown in column five in Table I. These results should be used in future calculations of the ionization constants of weak acids and bases.

For convenience, the values of the function 2.30259 RT/F in absolute volts are shown in column six of Table I. These values were calculated using the constants listed by Bearden and Watts,[6] $R = 8.3144$ abs. joules mole⁻¹ deg.⁻¹, $T_0 = 273.16°$K. and $F = 96495.4$ abs. coulombs equiv.⁻¹.

DuMond and Cohen[7] list a slightly different value of the Faraday, 96519.4 abs. coulombs equiv.⁻¹ on the physical scale corresponding to 96493.1 abs. coulombs equiv.⁻¹ on the chemical scale. This value, differing from that of Bearden and Watts by 2 parts in 10⁵, would increase 2.30259 RT/F by one digit in the fifth significant figure but this is within the limits of error of the above calculations.

(6) J. A. Bearden and H. M. Watts, *Phys. Rev.*, **81**, 73 (1951).

(7) J. W. M. DuMond and E. R. Cohen, *ibid.*, **82**, 555 (1951).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF OREGON
EUGENE, OREGON   RECEIVED JULY 18, 1951

A New Synthesis of 4,6-Diamino-2,5-dichloropyrimidine

BY E. C. TAYLOR, JR.,[1] AND P. DRENCHKO

In the course of a program on synthetic pteridines, 4,6-diamino-2-chloropyrimidine was desired as a possible intermediate. Chlorination of 4,6-diamino-2-hydroxypyrimidine with phosphorus oxychloride was unsuccessful; no reaction took place and the starting material was recovered

unchanged. Addition of phosphorus pentachloride to the phosphorus oxychloride reaction mixture resulted in the formation of a clear solution, but the product of the reaction proved to be 4,6-diamino-2,5-dichloropyrimidine and not 4,6-diamino-2-chloropyrimidine as expected. The compound was formed in 64% yield, as contrasted with a 12.2% yield by the only previously reported method involving the treatment of 2,4,5,6-tetrachloropyrimidine with ammonia.[2] Such anomalous introduction of halogen by phosphorus pentachloride has been observed previously in the pyrimidine series. Chlorination of 2-amino-4,6-dihydroxypyrimidine with phosphorus oxychloride and phosphorus pentachloride gives largely 2-amino-4,5,6-trichloropyrimidine and some 2-amino-4,6-dichloropyrimidine, and barbituric acid under the same conditions yields 2,4,5,6-tetrachloropyrimidine.[2] Likewise, 2-hydroxy-4-methylpyrimidine has been reported to yield a compound designated as 2:x:x:x-tetrachloro-4-methylpyrimidine upon treatment with the same reagents.[3] Thus it would appear to be a valid generalization that chlorination in the 5-position of a pyrimidine may readily occur if phosphorus pentachloride is employed.

Experimental

4,6-Diamino-2,5-dichloropyrimidine.—A mixture of 200 ml. of phosphorus oxychloride, 130 g. of phosphorus pentachloride and 20 g. of 4,6-diamino-2-hydroxypyrimidine[4] was heated under reflux for two hours, the excess phosphorus oxychloride removed by distillation under reduced pressure and the sirupy residue poured onto ice. The resulting acid solution was adjusted to pH 8 with sodium bicarbonate and the precipitate which formed was collected by filtration, washed thoroughly with water and dried. The crude product was then placed in a soxhlet cup and continuously extracted with acetone over a period of 20 hours. Removal of the acetone and crystallization of the residue from ether-petroleum ether gave 18.2 g. (64%) of white needles melting at 303–305°. The reported[2] melting point for 4,6-diamino-2,5-dichloropyrimidine is 302–304°.

Anal. Calcd. for $C_4H_4N_4Cl_2$: C, 26.8; H, 2.3; N, 31.3. Found: C, 27.1; H, 2.4; N, 31.1.

(2) S. J. Childress and R. L. McKee, THIS JOURNAL, **72**, 4271 (1950).

(3) J. R. Marshall and J. Walker, *J. Chem. Soc.*, 1004 (1951).

(4) A. Bendich, J. F. Tinker and G. B. Brown, THIS JOURNAL, **70**, 3109 (1948).

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS   RECEIVED OCTOBER 20, 1951

Spallation Products from Cobalt and 240 Mev. Protons

BY GENEVIEVE WAGNER AND EDWIN O. WIIG

The nuclear reactions resulting when thin targets of pure cobalt ($_{27}Co^{59}$) were bombarded with 240 Mev. protons in the 130-inch Rochester cyclotron have been studied. In order to observe the products of the reactions inert carriers were added to a solution of the target and fractions containing the radioisotopes were separated.

The gross decay curve of each chemically separated fraction was resolved to give the half-lives of the individual radioactive species. The specific nuclides shown in Table I were identified on this basis. Further verification was provided by testing for positive and negative β-particles whenever the

activity of the samples was sufficient to permit the use of a simple β-ray spectrometer and by determining the energies of the emitted particles with aluminum or lead absorbers.

The assignment of the activities observed could be made to known nuclides[1] in all cases. The presence of both Co^{58} (β^+, 72-day) and Co^{56} (β^+, 72-day) in the ratio of about 8 to 1 was shown by determining the energies of the emitted positrons. This result was based on a consideration of (1) the contribution of the total counting rate of the two positrons, (2) the counter efficiency for each positron and (3) the probable decay scheme[2] for each isotope.

Mass assignments with respect to the 4-hour activity observed in the scandium fraction could not be made with certainty, since both Sc^{43} and Sc^{44m} emit nearly identical radiations and have similar half-lives (4 hours). Their relative yields are based on the assumption that the two isotopes were formed in equal amounts. Likewise, resolution of the decay curve for the chlorine fraction showed the presence of Cl^{39} (β^+, 1 hour) and one or more shorter lived isotopes. The activity was not sufficient to permit use of other methods of verification. The shorter lived activity was arbitrarily assigned to Cl^{38} in calculating a relative yield. Actually, calculations based on the assumption that only Cl^{38}, only Cl^{34} or equal amounts of each are formed give a yield in each case of the same order of magnitude and agreeing within experimental error.

Because of the time required for chemical separations, activities of half-life less than 20 minutes would normally not have been observed. Careful searches were made for 8.9-minute Fe^{53} (β^+), 21-minute Mn^{52m} (β^+, γ) and 46-minute Mn^{51} (β^+) but no evidence for their presence was obtained. Fe^{53} could not have been detected under the experimental conditions used if its relative yield was of the same order of magnitude as Fe^{52}. However, Mn^{52m} and especially Mn^{51} would have been observed if formed in about the same yield as Mn^{52}. The Cr fractions gave no indication of an activity of longer half-life than the 44-minute Cr^{49} observed. Calculations showed that had the 26.5-day Cr^{51} been formed in approximately the same yield as Cr^{49}, it would have escaped detection.

Nuclides of half-life greater than 100 days formed in low yield also would not have been observed. Even if produced in relatively fair yield 270-day Co^{57}, 2.9-year Fe^{55} and 310-day Mn^{54} would have been extremely difficult to detect with the usual counters because of the nature of their radiations and their long half-lives. It is possible that 6-day Ca^{47} and 16-day V^{48} were present but it was not possible to make specific assignments since the chemical procedures were longer than for the majority of the elements, the chemical yields were low and the activities low.

The nuclide yields, shown in Table I, were calculated relative to Co^{55} formed in each bombardment on the basis of (1) measured activities cal-

culated to infinite bombardment time and 100% chemical yield, (2) counter efficiencies for the various radiations and (3) the probable decay scheme. Each value represents an average of the results of several bombardments. However, they are only a rough approximation because of errors due to (1) self and air absorption, (2) scattering, (3) uncertainties in counter efficiencies and (4) uncertainties in the decay schemes for some of the nuclides.

TABLE I

YIELDS RELATIVE TO Co^{55}

Mass No.	Ni	Co	Fe	Mn	Cr	Mass No.	Sc	K	Cl
58		40				44m	1		
57	0.16					44	0.4		
56		5		1.5		43	1		
55		1.0				42		0.2	
52			0.13	3.5		39			0.01
49					1	38			.02

An inspection of the relative yields with decreasing atomic number reveals an alternation in magnitude superimposed on a steady decrease in yield. The yield of Co is large, of Fe small, of Mn large, of Cr small. In the case of mass number 52, the yield of Mn is 20 to 30 times as great as that of Fe. These observations are similar to those reported[3] for the spallation of copper by 190 Mev. deuterons. As was suggested for copper, the present results may be accounted for by assuming that the incident proton, according to the theory of Serber,[4] leaves the struck Co^{59} nucleus in an excited state which then emits one α-particle plus three neutrons to form Mn^{52} while formation of Fe^{52} would require the ejection of a larger number of particles less firmly bound to each other. Since Mn^{56} cannot be produced from Co^{59} by emission of an α-particle, its yield might be less than that of Mn^{52}. There is evidence that α-particles[5] and even heavier nuclei[6,7] are emitted in spallation reactions.

If α-particles are a product of spallation, they in turn could produce nuclides of atomic number two greater than the target element. Pure copper was bombarded with 250 Mev. protons, the target dissolved, gallium carrier added and gallium separated chemically. The gallium fraction showed two positron activities of half-life 9.3 hours and 69 minutes, corresponding to Ga^{66} and Ga^{68}, respectively. In addition, a longer activity, too weak to characterize, of half-life about 5 days was also present. While Ga^{66} might be formed from Cu^{65} by a (p,π^-) reaction, such a reaction cannot account for Ga^{68}. It would appear, therefore, that Ga^{66} and Ga^{68} were produced by secondary (α, n) reactions on natural Cu^{63} and Cu^{65}.

(1) As listed in "Tables of Isotopes," G. T. Seaborg and I. Perlman, *Rev. Modern Phys.*, **20**, 585 (1948).

(2) W. M. Good, D. Peaslee and M. Deutsch, *Phys. Rev.*, **69**, 313 (1946); L. G. Elliot and M. Deutsch, *ibid.*, **64**, 321 (1943).

(3) F. O. Bartell, A. C. Helmholtz, S. D. Softky and D. B. Stewart, *ibid.*, **80**, 1006 (1950).

(4) R. Serber, *ibid.*, **72**, 1114 (1947).

(5) N. A. Bonner and W. C. Orr, *ibid.*, **76**, 140 (1949).

(6) S. C. Wright, *ibid.*, **79**, 838 (1950).

(7) L. Marquez and I. Perlman, *ibid.*, **81**, 953 (1951).

Analytical

The cobalt targets were dissolved in the minimum amount of concentrated nitric acid and known milligram quantities of inert carriers added. It was necessary to use yttrium as the carrier for radioscandium. Separations were carried out from this solution by the procedures[8] indicated below, with extensive use being made of holdback carriers and scavengers to ensure purity. These chemical procedures were adapted to fit the particular order of removal of the various ions from the solutions of the different target samples. Chemical yields were determined by quantitative methods, usually gravimetric.

Chlorine was distilled as Cl_2 while the target, to which carrier had been added, was being dissolved in concentrated nitric acid and precipitated as AgCl. Potassium was precipitated as $KClO_4$ and as K_2PtCl_6. Calcium was precipitated as CaC_2O_4. Scandium was carried by precipitated YF_3 and $Y(OH)_3$. Vanadium was separated by the Berkeley procedures. Chromium as peroxychromic acid was extracted into ethyl ether following removal of insoluble hydroxides with sodium hydroxide and hydrogen peroxide. Manganese was precipitated as MnO_2 from acid solution on addition of bromate. Iron was extracted into ethyl ether as $FeCl_3$ and precipitated as $Fe(OH)_3$ with aqueous ammonia. Cobalt was precipitated as $K_3Co(NO_2)_6$ after separation as the sulfide from aqueous ammonia. Nickel was precipitated with dimethylglyoxime from neutral solution.

(8) A. A. Noyes and W. C. Bray, "A System of Qualitative Analysis for the Rare Elements," The Macmillan Co., New York, N. Y., 1948; W. W. Meinke, "Chemical Procedures Used in Bombardment Work at Berkeley," AECD-2738 (UCRL-432), Technical Information Division, Oak Ridge, Tenn., 1949.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER, N. Y.   RECEIVED AUGUST 27, 1951

The Composition of W-6 Raney Nickel[1]

BY GEORGE W. WATT AND SIDNEY G. PARKER[2]

In a recent note, Ipatieff and Pines[3] published data on the composition of W-6 Raney nickel that differ markedly from results given earlier by Adkins and Billica[4] and from data obtained by the present authors prior to the appearance of the note by Ipatieff and Pines. The latter authors *assumed* that a nitric acid-insoluble residue obtained during the preparation of samples for analysis consisted of aluminum(III) oxide and that sodium was present as a sodium aluminate. Of the total aluminum found, one fraction was calculated as sodium aluminate on the basis of sodium found by analysis, another small fraction was attributed to elemental aluminum, while the major portion was interpreted as being present as aluminum(III) oxide, presumably in order that the sum of the various constituents be made exactly equal to 100%. No consideration was given to the presence of minor constituents other than sodium, and Ipatieff and Pines concluded that the aluminum(III) oxide is present in the catalyst formed by the method of Adkins and Billica[4] and influences the activity of the catalyst.

Following publication of the note by Ipatieff and Pines, we repeated most of our experiments and confirmed the results obtained earlier. The catalysts used in our work were prepared exactly as described by Adkins and Billica; with one exception, the

method of preparation of samples for analysis and the analytical procedures for the determination of nickel and aluminum were identical with those specified by Ipatieff and Pines. In contrast to the work of the latter authors, however, the nitric acid-insoluble residue was separated by filtration, washed with water, dried, and weighed; the filtrates were analyzed for aluminum.[5] Whereas Ipatieff and Pines describe the nitric acid-insoluble residue as a dense white solid, we found a grayish-white residue sufficient only to impart a pronounced turbidity to the nitric acid solution. Data relative to the aluminum content of these catalysts are given in Table I; the identity of the nitric acid-insoluble residue as $Al_2O_3 \cdot 3H_2O$ is established by the X-ray diffraction data given in Table II.

TABLE I

ALUMINUM CONTENT OF W-6 RANEY NICKEL

[a]HNO_3, %	$Al_2O_3 \cdot 3H_2O$, %	Al, %
5	1.0	12.2
10	1.0	12.5
30	0.4	12.9
60	0.5	13.0

[a] Concentration of acid used to dissolve samples for analysis.

TABLE II

X-RAY DIFFRACTION DATA FOR ALUMINUM(III) OXIDE 3-HYDRATE[a]

[b]HNO_3-insol. residue		[c]α-$Al_2O_3 \cdot 3H_2O$	
D, Å.	I/I_1	D, Å.	I/I_1
4.73	0.9	4.85	1.00
4.40	.7	4.37	.84
3.22	.5	..	..
..	..	2.46	.59
2.07	1.0	2.38	.59
..	0.2	2.05	.41
1.71	.7	1.75	.41
1.60	.2	1.69	.41
1.45	.2	1.46	.41
1.39	.2	1.41	.31

[a] Although more complete data are available, only the ten most intense diffraction maxima are included here. [b] Data obtained using Cu $K\alpha$ radiation, Ni filter, 2–3 hr. exposure at 30 kv. and 15 ma.; samples mounted in cellulose acetate capillary tubes. [c] Data from A.S.T.M. Index of X-Ray Diffraction Patterns.

Spectrographic analysis of nitric acid solutions of independent samples of W-6 Raney nickel[6] for minor constituents gave the following results (in per cent.): Na (0.5); Fe, Cu (0.2); Ca (0.1); Mg (0.005); <2: Ce, Hg; <0.2: Ba, Cd, Co, Cr, In, La, Li, Mn, Pb, Sr, Ti, Zn, Zr. Elements not detected include Ag, As, Au, Bi, Ga, K, Mo, P, Pt, Sb, Sn, Th, Tl, U, V, and W; C was not detected owing to interference.[7] The elements detected spectrographically, together with hydrogen and oxygen, presumably account for that fraction