TABLE B

STRONGEST ARC LINES OF ELEMENT 61 IN THE 3000–3450 Å. REGION

Wave length, Å.	Relative intensity
3366.05 ± 0.03	Weak
3377.64 ± .03	Weak
3391.25 ± .03	Medium
3418.67 ± .03	Weak
3427.42 ± .03	Strong
3441.09 ± .03	Weak
3449.81 ± .03	Medium

Unfortunately, it was impossible to compare these (arc) spectra with the (spark) spectrum observed by Timma.[5] His observations covered the 3630–4400 Å. region; aside from the fact that the methods of excitation used were different, his principal lines could not be looked for in the present arc spectrum with any hope of success because of interference by C_2 and CN bands. However, the spark lines he mentioned as due to element 61 were observed in the spectrum of aliquots of samples 1, 2 and 3 when excited by the copper spark technique.

(5) D. Timma, MonC-166 (U. S. Atomic Energy Commission).

OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENN.
RECEIVED JANUARY 26, 1949

A Convenient Synthesis of Phenaceturic Acid[1]

BY JARED H. FORD

Phenaceturic acid was required as a starting material in numerous experiments directed toward the synthesis of benzylpenicillin.[2] The following method which employs methyl phenylacetate as the starting material was found to be more convenient than the literature method[3] in which phenylacetyl chloride was used.

Experimental

Glycine (75.1 g.) was added to a solution of 23 g. of sodium in 850 ml. of anhydrous methanol, and the mixture was boiled under reflux a few minutes to obtain a clear solution. One hundred fifty grams of methyl phenylacetate was then added and the solution was boiled under reflux for three days. The methanol was distilled off and the residue was dissolved in 400 ml. of cold water which contained 20 g. of sodium bicarbonate. The resulting solution was twice extracted with ether to remove unchanged methyl phenylacetate, and then acidified to *p*H 2 with concentrated hydrochloric acid. After standing overnight in a refrigerator, the product was filtered, washed with cold water and dried in a vacuum oven. The resulting white crystals melted at 139–141° (lit.,[3] 143°); yield, 122.6 g. (63.5%). One recrystallization from hot water (400 ml.) gave 114.2 g. of product which melted at 143–144°. From the ether extracts were obtained 42.1 g. (28%) of methyl phenylacetate; b. p. 96–98° (14 mm.).

A longer period of heating did not increase the yield and it appears likely that an equilibrium is involved

$$C_6H_5CH_2COOCH_3 + NH_2CH_2COONa \rightleftarrows C_6H_5CH_2CONHCH_2COONa + CH_3OH$$

ANTIBIOTICS RESEARCH DEPARTMENT
THE UPJOHN COMPANY
KALAMAZOO 99, MICHIGAN
RECEIVED MAY 5, 1949

(1) This work was done under contract between the Office of Scientific Research and Development and The Upjohn Company (Contract OSRD-cmr-399).

(2) Clarke, Johnson and Robinson, "The Chemistry of Penicillin." Princeton University Press, Princeton, N. J., 1949.

(3) Hotter, *J. prakt. Chem.*, [2] **38**, 98 (1888).

Alkyl Derivatives of Ethylenediamine

BY ALBERT E. FROST, JR., STANLEY CHABEREK, JR., AND ARTHUR E. MARTELL

In the course of other work a number of symmetrical dialkyl ethylenediamines have recently been prepared and characterized. A number of other amines, containing a smaller or larger number of alkyl groups, and a few dialkyl piperazines were obtained as by-products. The by-products not previously reported for this method and their properties are listed in Table I. The method of preparation, which involved the reaction of ethylene dichloride with an excess of primary amine, has been described by others.[1,2,3,4,5] The main products were characterized as the dipicrates and as the phenylureas, which are listed in Table II. Attempts to prepare the phenylurea from tribenzylethylenediamine were unsuccessful, and it was found that picrates could not be formed readily from dioctylpiperazine, tetraoctylethylenediamine, didodecylpiperazine and tribenzylethylenediamine. The picrate obtained with dibenzylethylenediamine was shown by analysis to be the monopicrate. Repeated recrystallization from various solvents did not change the melting point or the analysis.

TABLE I

BY-PRODUCTS

Amine	B. p., °C.	B. p., Mm.	M. p., °C.	N, % Calcd.	N, % Found
N,N′-Dioctylpiperazine	187–190	1	53–55	9.02	9.09
N,N,N′,N′-Tetraoctylethylenediamine	.....		130–133	5.51	5.29
N,N′-Didodecylpiperazine	265–275	8	54–56	6.63	6.34
N-Monobenzylethylenediamine	155–160	5	.....	18.65	18.72
N,N,N′-Tribenzylethylenediamine	225–235	4	99–100	8.48	8.64
Trioctyldiethylenetriamine[a]	213–215	2	.....	9.55	9.28

[a] *Anal.* Calcd. for $C_{28}H_{61}N_3$: C, 76.5; H, 14.0. Found: C, 76.4; H, 14.0.

For this method of preparation, it was found that the separation of the insoluble crystalline monohydrate obtained by treating the reaction product with a dilute aqueous solution of strong base provided the most convenient method of

(1) Sebrell and Clifford, U. S. Patent 1,948,317 (Feb. 20, 1934).

(2) Kyrides, U. S. Patent 2,126,560 (Aug. 9, 1938); U. S. Patent 2,267,685 (Dec. 23, 1941).

(3) Zienty and Thielke, THIS JOURNAL, **67**, 1040 (1945).

(4) Zienty, *ibid.*, **68**, 1388 (1946).

(5) Clifford, U. S. Patent 2,216,620 (Aug. 9, 1938).

TABLE II

Amine	Derivatives Dipicrate M. p., °C.	N, % Calcd.	 Found	 Phenylurea M. p., °C.	N, % Calcd.	 Found
N,N'-Dibutylethylenediamine	148–149.5^{a,6}	17.78	17.43	174–174.5	13.65	13.31
N,N'-Dioctylethylenediamine	158–159.5^{b,7}	15.09	14.73	129.5–130	10.72	10.30
N,N'-Didodecylethylenediamine	152–154.5^{c,7}	13.11	13.11	235 (subl.)	8.83	8.64
N,N'-Dicyclohexylethylenediamine	210 (dec.)	16.42	16.04	206	12.11	12.45
N,N'-Dibenzylethylenediamine	208–210^{d} (dec.)	14.93	14.71	182^{8}	11.71	11.73
N,N'-Dibutylpiperazine	155–156	17.07	16.89	....	...	...

[a] King and McMillan reported 188°. [b] Linsker and Evans reported 108°. [c] Linsker and Evans reported 112°. [d] Monopicrate.

isolation. This was not possible in the case of dibenzylethylenediamine, which did not form a solid monohydrate under the conditions employed. The by-products listed in Table I were obtained by fractional distillation of the dialkyl ethylenediamines.

Acknowledgment.—The authors are indebted to F. C. Bersworth, of the Bersworth Laboratories, Framingham, Massachusetts, for financial support for this research.

---

(6) King and McMillan, THIS JOURNAL, **68**, 1776 (1946).

(7) Linsker and Evans, *ibid.*, **68**, 1432 (1946).

(8) Van Alphen, *Rec. trav. chim.*, **54**, 93 (1935).

DEPARTMENT OF CHEMISTRY
CLARK UNIVERSITY
WORCESTER, MASSACHUSETTS
RECEIVED JUNE 17, 1949

Acetyldesoxycellulose Quaternary Salts

BY F. N. HAYES AND CHAO-HAN LIN

A cellulose acetate tosylate was prepared by the method of Malm, Tanghe and Laird.[1] Separate portions of it were heated with pyridine, 3-picoline and isoquinoline to give quaternary salts, resulting from displacement of tosylate ions. Similar reactions of *p*-toluenesulfonate esters with tertiary amines are well known.[2,3] Table I gives analytical data and the calculated values for free hydroxyls, unreacted tosylate ester groups, and quaternary salt groups per glucose unit for each of the three products.

The average over-all percentage conversion of the original hydroxyl groups to quaternary salt groups may be used as an estimate of the per cent. primary free hydroxyl in the original cellulose acetate. Our value of 28% compares favorably with a reported value of 25% on a similar sample,[1] determined by the method of tosylation and iodination.

TABLE I

Sample	Percentage N^{a}	 S^{a}	Amount per g. u. Free^{b} OH	 Tos.^{b} ester	 Quat.^{b} salts	Percentage Tos. re-placed	Conv. of OH to quat. salt
I	..	6.85	0.96	0.69	..	..	..
II	1.93	5.81	1.02	.14	0.49	71	30
III	1.77	5.96	0.97	.26	.42	61	26
IV	1.72	5.74	0.96	.22	.47	68	29

[a] Analyses by Micro-Tech Laboratories, Skokie, Ill. [b] Calculated from the analyses, assuming that the acetyl content remains unchanged.

A sample of cellulose acetate, EK-102893,[4] was tosylated[1] and the product (I) was reprecipitated from acetone by alcohol. Pyridine, 3-picoline and isoquinoline were dried and redistilled.

A solution of 6.0 g. of cellulose acetate tosylate in 60 ml. of pyridine was heated on a steam-bath for twenty-four hours, at the end of which time, it was diluted with 40 ml. of acetone and treated with just enough water to obtain a homogeneous solution. This was slowly poured into excess acetone with good stirring. The precipitated product was filtered, washed with acetone and twice reprecipitated from hot alcohol by ether. The yield of the purified product (II) was 5.5 g.

In a similar manner, 3.0 g. of the tosyl ester gave 2.8 g. of a 3-picolinium salt (III) and 8.0 g. yielded 7.8 g. of an isoquinolinium salt (IV).

---

(1) Malm, Tanghe and Laird, THIS JOURNAL, **70**, 2740 (1948).

(2) Cary, Vitcha and Shriner, *J. Org. Chem.*, **1**, 280 (1936).

(3) King, Dodson and Subluskey, THIS JOURNAL, **70**, 1176 (1948).

(4) Kindly supplied for this project by Eastman Kodak Company, with analysis: 1.35 acetyls per glucose unit.

DEPARTMENT OF CHEMISTRY
ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO, ILLINOIS
RECEIVED JUNE 30, 1949

Separation of Hafnium and Zirconium by a Fractional Distillational Procedure

BY D. M. GRUEN AND J. J. KATZ

In view of current interest in hafnium–zirconium separations,[1] we have investigated a separation method first reported by van Arkel and De Boer.[2] This method involves fractional distillation at atmospheric pressure of the volatile complex compounds formed by reaction of zirconium and hafnium tetrachlorides with either phosphorus pentachloride or phosphorus oxychloride. Although van Arkel and De Boer showed that distillation resulted in considerable separation of hafnium and zirconium they gave no quantitative data on the relative volatilities of the zirconium and hafnium compounds.

The present work is concerned chiefly with the phosphorus oxychloride complexes, since these have lower boiling points and greater thermal stability than the corresponding phosphorus

---

(1) K. Street and G. T. Seaborg, THIS JOURNAL, **70**, 4268 (1948).

(2) A. E. van Arkel and J. H. De Boer, *Z. anorg. Chem.*, **141**, 289–296 (1924).