the invariance of the classical keto–enol and acid dissociation constants over the entire neutralization range. Thus, within the 2.7 and 2.0% differences noted above for acetylacetone and benzoylacetone, a satisfactory correlation has been demonstrated between the enol plus enolate ion fraction determined by the Kurt Meyer procedure and that calculated from the acid enol properties. Taking the latter as a basis, it may be concluded that the Kurt Meyer bromine addition procedure described above for partially neutralized solutions furnishes results that are reliable to within the 2.7 and 2.0% deviations observed.

Summary

1. At 25°, the fraction of acetylacetone present in the enol form in dilute aqueous solution (3.3×10^{-3} *M*) is 0.170. The corresponding value for benzoylacetone in 1.7×10^{-3} *M* aqueous solution containing 7.5% ethyl alcohol by weight is 0.341. The classical acid dissociation constants of the enol forms of the above compounds at $25.0 \pm 0.1°$ are $6.88 \pm 0.15 \times 10^{-9}$ and $5.89 \pm 0.11 \times 10^{-9}$, respectively.

2. The fraction of the above compounds present in the enol plus enolate ion form at 25° has been measured as a function of the fraction neutralized in dilute aqueous solution by the Kurt Meyer bromine addition reaction. An equation expressing this relationship has been derived that is based on the dissociation constant and the keto–enol equilibrium. Values predicted by this equation are larger than the measured values for acetylacetone and benzoylacetone by 2.7 and 2.0%, respectively.

FLUSHING, NEW YORK RECEIVED AUGUST 28, 1945

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE AND THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Heat Capacity, Heat of Fusion and Entropy of 11-*n*-Decylheneicosane

BY F. B. FISCHL,[1] B. F. NAYLOR,[2] C. W. ZIEMER,[1] G. S. PARKS[2] AND J. G. ASTON[1]

This is the beginning of a series of investigations at The Pennsylvania State College, dealing with hydrocarbons of high molecular weight. A similar series of investigations has been in progress at Stanford University since 1937. The object of both series is the establishment of a relationship between structure and various thermodynamic functions. Thus it should be possible to estimate the entropy of a high-molecular weight hydrocarbon from previous systematic calorimetric data on other compounds.

This paper furnishes a comparison of data on the same compound obtained independently in the laboratories of Stanford University and The Pennsylvania State College.

Preparation and Purification of Sample.—The sample was one of the first compounds prepared by API Project 42. It was synthesized by treating decylmagnesium bromide with ethyl carbonate. The alcohol, after careful fractionation, was dehydrated to the olefin which was catalytically hydrogenated. The saturated hydrocarbon was fractionated through a 10-plate low pressure fractionation column (0.1 mm.) and passed several times through silica gel.

The Heat Capacity Measurements.—In the measurements at The Pennsylvania State College the sample was accurately weighed into calorimeter D, which was designed for the measurement of thermal data of solids and liquids. After freeing the sample from the last traces of air by repeated freezings and evacuations to 10^{-6} mm. of mercury, the calorimeter space above the compound was filled with approximately one-half atmosphere of helium.

The detailed description of this adiabatic solids calorimeter will be published shortly along with a discussion of the accuracy.[3] It is estimated that all thermal data obtained with it, above 40°K., have an accuracy of 0.2%. It is possible to reproduce the heat capacity data on the solid with a precision of better than 0.1% above 80°K.

The measurements at Stanford University were carried out as described previously.[4] In view of the accuracy of the various factors involved, the absolute error in the experimental values of the heat capacities and heat of fusion is probably less than 0.7%, except insofar as impurities in the sample of this hydrocarbon may cause premelting or otherwise influence the results. The fortuitous errors were ordinarily under 0.25%.

The *defined calorie*, taken equal to 4.1833 international joules, has been used throughout the studies in both laboratories. Temperature measurements have been on the basis: 0°C. = 273.16° K. The value 436.822 has been adopted as the molecular weight of 11-*n*-decylheneicosane. The sample of this material used in the calorimeter at The Pennsylvania State College was 0.15216 mole; that used at Stanford was 0.06905 mole.

The heat capacities measured at The Pennsylvania State College on the solid compound, uncorrected for premelting, are listed in Table IA. Here the temperature rise can be estimated from the intervals between points of a series. The results of the heat capacity measurements ob-

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(1) At The Pennsylvania State College.

(2) At Stanford University.

(3) Aston and Ziemer, to be published.

(4) Parks, THIS JOURNAL, 47, 338 (1925).

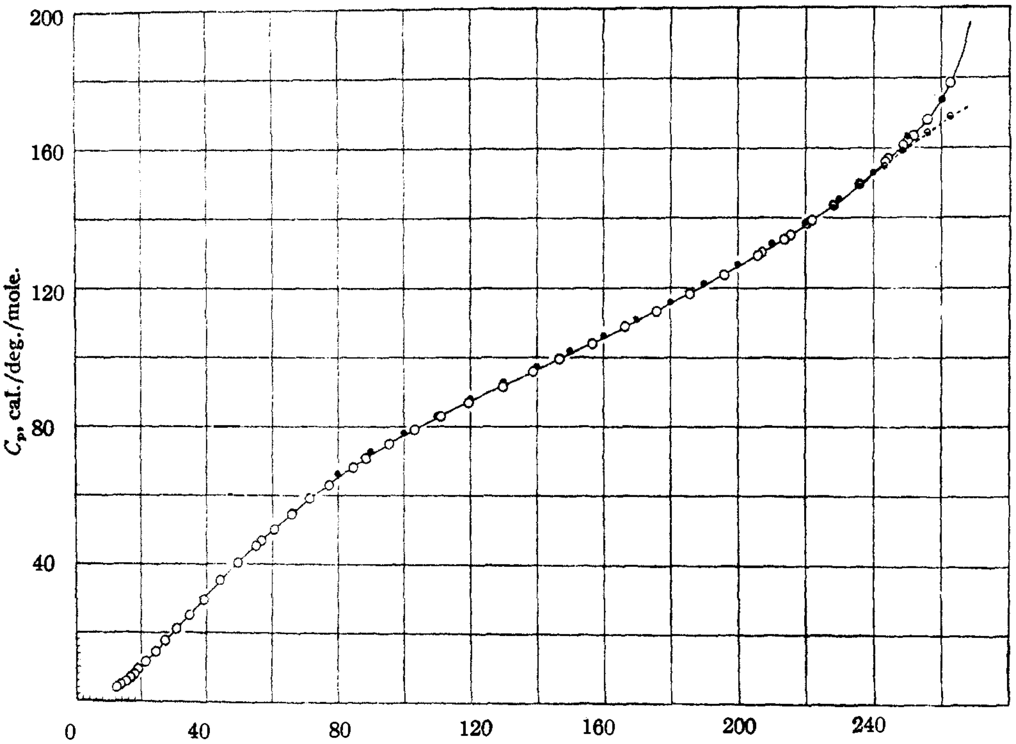

Fig. 1.—The heat capacity of solid 11-*n*-decylheneicosane at The Pennsylvania State College, without premelting correction ○; with premelting correction ⊖; at Stanford University ●.

tained at Stanford University in both the solid and liquid range are listed in Table IB. The two sets of heat capacity results for the solid phase are also represented in Fig. 1, where all the Pennsylvania State College data have been plotted together with the Stanford values which have been deduced for rounded temperatures.

Table IA

The Heat Capacity of Solid 11-*n*-Decylheneicosane

(At The Pennsylvania State College)

Temp., °K.	C_p, cal./deg./mole	Temp., °K.	C_p, cal./deg./mole	Temp., °K.	C_p, cal./deg./mole
Series I		209.22	131.66	27.53	17.679
56.73	46.54	215.34	135.18	30.89	21.175
60.94	50.21	222.02	139.49	34.78	25.16
66.27	54.69	228.49	143.86	39.18	29.76
71.66	58.92	235.92	149.66	44.17	35.20
77.33	62.94	243.46	155.80	49.61	40.30
88.66	70.56	248.67	160.39	55.26	45.28
95.70	74.80	255.91	167.93	60.75	50.07
103.28	79.03	262.63	178.25	65.92	54.37
111.22	82.91	268.43	223.62		
119.50	86.87			Series III (misc.)	
129.88	91.67	Series II		84.92	68.14
138.71	95.81	12.37	4.140	206.85	130.06
147.67	99.97	13.14	4.535	213.67	134.00
156.74	104.03	15.31	5.724	243.26	155.52
166.33	108.43	16.60	6.848	249.99	161.72
176.00	113.32	17.79	7.814		
185.96	118.40	19.21	9.385		
196.07	123.65	21.36	11.540		
205.86	129.40	24.29	14.590		

Table IB

The Heat Capacity of 11-*n*-Decylheneicosane

(At Stanford University)

Temp., °K.	C_p, cal./deg./mole	Temp., °K.	C_p, cal./deg./mole	Temp., °K.	C_p, cal./deg./mole
Crystals		185.0	118.2	250.2	162.5
80.3	66.62	195.5	124.1	255.8	168.3
82.5	67.93	201.7	127.2	259.7	173.5
83.9	69.85	206.0	130.4	264.9	182.9
89.5	72.29	213.7	134.5		
94.6	74.70	218.2	137.3	Liquid	
108.1	81.82	223.7	140.8	282.0	224.0
124.0	89.55	228.2	143.8	285.0	224.6
137.6	95.66	232.8	147.6	289.8	226.0
149.6	101.7	237.7	150.4	293.9	227.6
166.6	108.9	239.7	152.3	297.4	229.4
175.4	113.3	243.4	155.9		

The heat capacity measurements on the liquid at The Pennsylvania State College are listed in Table II and shown graphically in Fig. 2. There was definite evidence of lack of reproducibility of these liquid heat capacities. The history of the sample prior to each determination is shown below:

Series A.—The sample was cooled to 55°K., heated slowly, and melted; the heat capacity measurements were started immediately after the fusion which was in all cases within ten minutes.

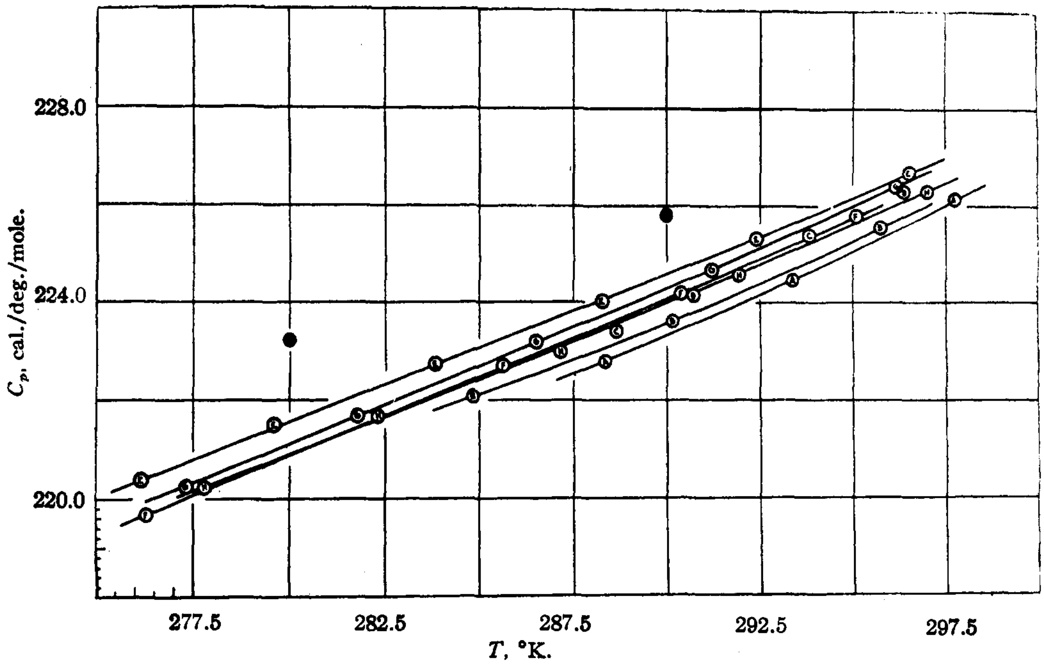

Fig. 2.—The heat capacity of liquid 11-*n*-decylheneicosane at The Pennsylvania State College ○; at Stanford University ●.

Series B.—The sample was supercooled over a period of 20 hours from 287 to 277°K.

Series C.—The sample was cooled to 11°K., heated slowly, and measurements on the liquid were taken immediately thereafter.

Series D—The sample was cooled slowly to 180°K., heated rapidly, and melted; the measurements on the liquid were begun one hour after the fusion.

Series E and F.—In both cases, the sample was treated exactly alike. The compound was supercooled in one-half hour from 297 to 274°K.

Series G.—The compound was heated to 315°K. and allowed to remain at this temperature for twenty hours. It was then supercooled in fifty minutes to 275°K.

Series H.—After heating the sample to 303°K. and allowing it to remain at this temperature for ten hours, it was supercooled to 276°K. over a period of twenty-four hours. The liquid sample was then kept between 275–276°K. for another twenty-four hours.

TABLE II

THE HEAT CAPACITY OF LIQUID 11-*n*-DECYLHENEICOSANE (At The Pennsylvania State College)

Temp., °K.	C_p, cal./deg./mole	Temp., °K.	C_p, cal./deg./mole
Series A			
288.36	222.78	292.41	225.30
293.36	224.47	296.52	226.70
297.76	226.13	Series F	
Series B		276.32	219.68
284.84	222.08	285.63	222.71
290.16	223.63	290.38	224.18
295.74	225.54	295.11	225.78
Series C		Series G	
288.65	223.41	277.32	220.26
293.81	225.39	281.78	221.68
Series D		286.50	223.21
290.72	224.15	291.20	224.66
296.36	226.29	296.15	226.39
Series E		Series H	
276.16	220.39	277.78	220.24
279.61	221.51	282.33	221.69
283.82	222.75	287.16	223.00
288.26	224.03	291.95	224.58
		297.01	226.32

Table III contains a comparison of heat capacity values at rounded temperatures as derived independently in our two laboratories. In this connection an attempt has been made to correct for premelting in the values for the solid from 250° upward. The estimates for such premelting corrections have differed considerably in magnitude in the two laboratories, although the comparative heat capacities as actually measured in the neighborhood of 260° were within 0.5%.

The Melting Point and Heat of Fusion.—The procedure at The Pennsylvania State College was the same as that described previously.[5] The melting point data thus obtained indicated 3.52 mole per cent. impurity (liquid soluble, solid insoluble) with 282.34 ± 0.05°K. as the resulting melting point, corrected to the pure state. Four determinations of the heat of fusion are summarized in Table IV. These results were corrected

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(5) Aston and Messerly, THIS JOURNAL, 58, 2354 (1936).

TABLE III

THE MOLAL HEAT CAPACITY OF 11-DECYLHENEICOSANE AT ROUNDED TEMPERATURES

C_p in cal./deg./mole

Temp., °K.	(At The Pennsylvania State College)	(At Stanford University)	Dev., %
	Solid		
12	6.15	....	....
15	8.65	....	....
20	10.13	....	....
25	15.23	....	....
30	20.27	....	....
40	30.78	....	....
50	40.65	....	....
60	49.43	....	....
70	57.60	....	....
80	64.89	66.40	+2.32
90	71.40	72.56	+1.63
100	77.21	77.97	+0.98
110	82.35	82.95	+0.73
120	87.10	87.76	+0.76
130	91.71	92.52	+0.88
140	96.35	97.11	+0.80
150	100.92	101.82	+0.89
160	105.58	106.24	+0.63
170	110.36	110.69	+0.30
180	115.38	115.63	+0.22
190	120.46	121.13	+0.56
200	125.90	126.59	+0.55
210	131.93	132.62	+0.52
220	138.18	138.69	+0.37
230	145.00	145.46	+0.32
240	152.60	152.67	+0.05
250	160.13	161.19	+0.66
260	167.50	170.36	+1.71
265	171.18	....	....
	Liquid		
280	220.92	223.2	+1.03
290	223.98	225.8	+0.81
300	227.00	230.2	+1.41

for premelting on the basis of 3.52 mole per cent. impurity.

Correspondingly, the measurements at Stanford yielded 282.2 ± 0.1°K. as the corrected melting point, with an estimate of 3.4 mole per cent. of impurity. Two determinations for the heat of fusion corrected for premelting as above were as follows: run 1, 16,984 cal./mole; run 2, 16,975 cal./mole; mean, 16,980 cal./mole. Thus the deviation of the heats of fusion as measured in our two laboratories is 0.22%.

TABLE IV

MOLAL HEAT OF FUSION OF 11-*n*-DECYLHENEICOSANE

(At The Pennsylvania State College)

Temp. interval, °K.	Cor. heat input, cal./mole	$\int C_p\, dT$, cal./mole	Pre-melting effect, cal./mole	ΔH fusion, cal./mole
271.121–285.996	19479.34	2808.85	349.89	17020.4
257.058–286.065	22208.29	5207.83	22.88	17023.3
254.751–287.432	22891.37	5890.10	14.79	17015.7
255.241–289.153[a]	23207.96	6212.80	16.05	17011.2
			Av.	17017.7 ± 6.0

[a] This heat of fusion was found by summarizing the energy inputs required for the determination of the melting point.

The Entropy from Thermal Data.—Tables VA and VB summarize the calculation of the entropy at 25°C. from calorimetric data. The difference between the two laboratories in molal entropy change from 80–298.16°K. is 1.48 e. u. (0.71%) which is within the experimental error of both laboratories.

The molal entropy of the liquid at 298.16°K., based entirely on the data at The Pennsylvania State College and including an extrapolation from 0–15°K. using the Debye theory with six degrees of freedom, is 259.60 (±0.5) e. u.

As the heat capacity measurements at Stanford University did not go below 80°K., the entropy increment from 0–80°K. has also been estimated by the application of the extrapolation method of Kelley, Parks and Huffman[6] to the Stanford data at 80 and 110°. Thereby the increment has been computed as 52.1 (±1.5) e. u. Combination

TABLE VA

MOLAL ENTROPY OF 11-*n*-DECYLHENEICOSANE FROM THERMAL DATA AT 80°K.

(The Pennsylvania State College Measurements)

0–15.00°K., Debye extrapolation (6 degrees of freedom, $\theta = 64.303$)	2.710
15–80°K. graphical, $\int C_p\, d \ln T$	48.004 ± 0.1
Molal entropy at 80°K.	50.714 ± 0.1 e. u.

TABLE VB

MOLAL ENTROPY CHANGE OF 11-*n*-DECYLHENEICOSANE FROM THERMAL DATA FROM 80 TO 298.16°K.

(At Stanford University)		(At The Pennsylvania State College)	
80–282.2°K. graphical, $\int C_p\, d \ln T$	137.78 ± 0.7	80–282.34°K. graphical, $\int C_p\, d \ln T$	136.390 ± 0.3
Fusion, 16980/282.2	60.17 ± 0.3	Fusion, 17018/282.34	60.27 ± 0.1
282.2–298.16°K. graphical, $\int C_p\, d \ln T$ (liquid)	12.45 ± 0.1	282.34–298.16°K. graphical, $\int C_p\, d \ln T$ (liquid)	12.220 ± 0.02
Total (80°K.–298.16°K.)	210.40 ± 1.1 e. u.	Total (80°K.–298.16°K.)	208.884 ± 0.4 e. u.

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(6) Kelley, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929). The constants for Class I (*i. e.*, aliphatic) compounds have been used in obtaining the present estimate. Recent tests have shown that the extrapolation method with these constants is valid to within 2 or 3% for aliphatic compounds that are straight-chained or involve no more than one branch on what may be termed the main chain. However, the estimate so computed is rather sensitive to the choice of the heat capacity data for 80 and 110°. Thus in the present case, the application of the method to The Pennsylvania State College data yields S_{80} = 50.03 e. u. as compared with the corresponding experimental result of 50.71 in Table VA.

of this value with the corresponding increment from 80 to 298.16° yields for the molal entropy of the liquid $S^\circ_{298.16}$ = 262.5 (±2.6) e. u. from the study at Stanford.

Discussion

As shown in Fig. 2, the heat capacity measurements on liquid 11-*n*-decylheneicosane at The Pennsylvania State College are not reproducible. A similar phenomenon has been observed in The Pennsylvania State College laboratory in the case of liquid isopentane[7] and questioned by Guthrie and Huffman,[8] who obtained perfect reproducibility on the same sample. No adequate explanation of this situation has yet been found and the results obtained at The Pennsylvania State College are still believed to be valid.[9] The lack of reproducibility in the case of 11-*n*-decylheneicosane is 0.6%, which is several times the estimated accuracy of the determination. In view of the complicated nature of the compound and the large amount of impurity present, it is useless to speculate on the cause of the phenomenon.

This lack of reproducibility in the liquid region was not observed at the Stanford Laboratory as is to be expected since the accuracy is only 0.7%. If the lack of reproducibility in The Pennsylvania State College data is due to calorimetric errors, no reasonable cause for such errors has been discovered.

Acknowledgment.—We wish to thank Project 42 of the American Petroleum Institute for supplying the sample and for aiding financially the work of The Pennsylvania State College.

Summary

1. The heat capacity of solid and liquid 11-*n*-decylheneicosane has been measured from 12.27 to 295.74°K. at The Pennsylvania State College, and from 80.3 to 297.4°K. at Stanford University.

2. The results at The Pennsylvania State College indicated that the liquid heat capacities are not reproducible.

3. The equilibrium temperatures of the fusion, together with the heat of fusion, have been determined in both laboratories.

4. From The Pennsylvania State College measurements the mole per cent. impurity, on the basis of the melting point lowering from 50–100% was calculated to be 3.52% and the melting point of the *pure* material to be 282.34 ± 0.05°K. The corresponding Stanford data were 3.4% impurity and a melting point of 282.2 ± 0.1°K.

5. The molal entropy of the liquid at 298.16°K. as determined from the thermal data at The Pennsylvania State College is 259.60 e. u. The data at Stanford yield a corresponding value of 262.5 e. u., based on the use of an approximate extrapolation method below 80°K.

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[7] Aston and Schuman, THIS JOURNAL, **64**, 1034 (1942).

[8] Guthrie and Huffman, *ibid.*, **65**, 1139 (1943).

[9] Aston, *ibid.*, **65**, 2041 (1943).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF HOFFMANN-LA ROCHE, INC.]

A Simple Synthesis of *dl*-Desthiobiotin and Related Substances

BY ROBERT DUSCHINSKY AND L. ALLEN DOLAN

Imidazolone derivatives carrying appropriate substituents in the 4- and 5-positions of the nucleus were believed to be promising starting materials for the synthesis of biotin and related substances. The present paper describes, as a first step toward this goal, a general method of introducing side chains into the 5-position of 4-methylimidazolone-2 (II), as well as the hydrogenation of the obtained imidazolone derivatives. The new method is illustrated by the formulas I–VIII, which represent the synthesis of the biologically important 4-methyl-5-(ω-carboxyamyl)-imidazolidone-2 or *dl*-desthiobiotin (VI).

A synthesis of desthiobiotin has already been reported by Wood and du Vigneaud.[1] Our synthesis is quite different in approach, and was completed prior to this publication. It is based on the observation that 4-methylimidazolone-2 (II) undergoes Friedel–Crafts condensations, the acyl group being introduced in position 5.

The hitherto unknown 4-methylimidazolone-2 (II) became accessible by alternative methods from ethyl acetoacetate, *i. e.*, *via* oximinoacetone (I) or *via* ethyl α-oximinoacetoacetate (VII). The oximino compounds were converted by hydrogenation to the corresponding amino compounds, which were not isolated but directly condensed with cyanic acid. When the ester (VIII), first described by Gabriel and Posner,[2] was saponified by alkaline reagents, the decarboxylated substance II was isolated instead of the expected free acid. Like all imidazolone derivatives, the substances VIII and II give a deep red ferric chloride reaction, indicating the presence of an enolic hydroxy group. This reaction is suppressed when one or two acetyl groups are introduced into the nucleus by treatment with acetic anhydride.

4-Carboxy-imidazolone-2[3] and 4-methyl-5-car-

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[1] Wood and du Vigneaud, THIS JOURNAL, **67**, 210 (1945).

[2] Gabriel and Posner, *Ber.*, **27**, 1144 (1894).

[3] Hilbert, THIS JOURNAL, **54**, 3414 (1932).