When the amine was boiled twelve hours in ethanol the recovery of material was quantitative and its chloroplatinate contained 29% of platinum.

CHEMICAL LABORATORY
UNIVERSITY OF TORONTO
TORONTO, ONTARIO

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3-Benzyl-5,5-dimethylhydantoin

BY T. EARL JORDAN AND SARA GINSBURG[1]

3-Benzyl-5,5-dimethylhydantoin was prepared by treating benzyl chloride with 5,5-dimethylhydantoin. It was found that this compound would neither hydrolyze to the corresponding amino acid nor react with acetic anhydride under conditions which usually effect such reactions of substituted hydantoins. This stabilizing effect of the benzyl group was unexpected.[1a,2,3]

Experimental

The 5,5-dimethylhydantoin was prepared by a modification of the method of Bucherer and Libe.[4] A mixture of acetone, sodium cyanide and ammonium hydroxide (mole ratio of 1:1.2:1.35) was agitated with carbon dioxide in an autoclave at 150–200 lb. gage pressure and 80 ± 5° until adsorption ceased. The solvent medium was 50% ethanol–water solution sufficient to equal two and one-half times the weight of the reactants. The by-product sodium bicarbonate was filtered off, washed with alcohol; the filtrate and washings were combined, distilled until practically free of alcohol; the residue was treated with hydrogen peroxide to destroy any unreacted sodium cyanide, neutralized with dilute sulfuric acid and cooled. 5,5-Dimethylhydantoin was filtered off and recrystallized from water; yield, 82%; colorless needles, m. p. 175°.

3-Benzyl-5,5-dimethylhydantoin was obtained by treating 5,5-dimethylhydantoin with benzyl chloride in the presence of sodium bicarbonate (mole ratios of 1:1.3:1.4). Three hours were required for the addition of benzyl chloride; the refluxing and agitation were continued for five hours longer. On cooling, an oily solid precipitated. This was neutralized, filtered and recrystallized from 30% alcohol; yield, 80%; white needles, m. p. 106° (cor.).

Anal. Calcd.: C, 66.06; H, 6.42; N, 12.84. Found: C, 65.9; H, 6.6; N, 12.7. Solubility in H_2O: at 20°, 0.35 g. in 100 ml.; at 100°, 1.37 g. in 100 ml.; in boiling 50% alcohol, 100 g. in 100 g.; in boiling 30% alcohol, 20 g. in 100 g.

Attempts to hydrolyze the 3-benzyl-5,5-dimethylhydantoin with 60% sulfuric acid by refluxing for twenty-three hours resulted in practically no reaction. Refluxing with 80% sulfuric acid for ten hours resulted in a tar only.

Refluxing 3-benzyl-5,5-dimethylhydantoin for four hours with a large excess of acetic anhydride and a trace of concentrated sulfuric acid resulted in no reaction.

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[1] Present address: Physicians Drug & Supply Co., Philadelphia, Pa.

[1a] H. L. Dakin, *J. Biol. Chem.*, **44**, 518 (1920).

[2] W. Robson, *ibid.*, **62**, 495 (1924).

[3] H. L. Wheeler and C. Hoffman, *Am. Chem. J.*, **45**, 368 (1911).

[4] H. T. Bucherer and V. P. Libe, *J. prakt. Chem.*, **141**, 5 (1934).

CHEMICAL RESEARCH LABORATORY
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The Relative Efficiency of Various Surfaces for the Recombination of Hydrogen Atoms

BY SIDNEY KATZ, G. B. KISTIAKOWSKY AND ROBERT FRANK STEINER

An investigation has been made of the relative efficiency of various metallic surfaces in promoting the recombination of hydrogen atoms.

The steady-state temperature rise produced in the catalyst by the heat of recombination was taken as a measure of the relative effectiveness. Atomic hydrogen was produced by a 5000-volt a. c. discharge. A flow system was utilized, with hydrogen from a high pressure cylinder diffusing into the discharge tube through a long glass capillary. The pressure of hydrogen at one end of the capillary was maintained effectively constant by means of a mercury overflow bottle. Prior to entering the capillary, the hydrogen was bubbled through a dilute solution of sulfuric acid, to ensure the presence of sufficient moisture to inhibit atomic recombination on the walls.

Hydrogen, after leaving the discharge tube, streamed by the catalyst cone, which fitted over a glass thermocouple well, blown into the wall of the system and projecting into the center of hydrogen flow. Temperature rise was recorded by means of a copper–constantan thermocouple, one junction of which was inserted in the thermocouple well and the other immersed in an ice-water-bath. Measurements were made with a Leeds and Northrop student potentiometer. All readings were recorded in microvolts.

The catalyst cones were introduced into a separately evacuable chamber, placed above the thermocouple well, which was then closed and evacuated. It was separated from the hydrogen flow system by a large bore stopcock. The cones, suspended by threads, were lowered by means of a winch upon the thermocouple well, through the bore of the large stopcock. This arrangement permitted an interchange of catalyst cones without interruption of hydrogen flow or the electric discharge. The cones were turned from

TABLE I

Surface	$V_{\text{final}} - V_{\text{initial}} =$ ΔV (microvolts) (average values)	$-\Delta V/\Delta V_{\text{cobalt}}$
	Run I	
Cobalt	1041	1.00
Nickel	950	0.91
Copper	767	.74
Chromium	735	.71
Brass	756	.73
Zinc	342	.33
Tin	90	.09
Cadmium	698	.67
Paraffin	240	.23
	Run II	
Cobalt	447	1.00
Nickel	410	0.92
Copper	312	.70
Zinc	146	.33
Brass	280	.63
	Run III	
Cobalt	696	1.00
Platinum	710	1.02
Iron	578	0.83

brass and coated by electrodeposition with the various metals.

The system was evacuated with a mercury diffusion pump in series with a rotary oil pump. A hydrogen pressure of approximately 0.5 mm. was maintained constant during each run as indicated by a McLeod gage.

In our measurements, the rise in temperature with time was recorded and the final steady-state temperature used in calculating results. Cobalt was chosen as the standard because of its high efficiency and resistance to poisoning. In each group of runs, the discharge was left on continuously and the cobalt cone and the others with which it was compared were introduced successively, each cone being introduced several times. The temperature rise relative to cobalt was thus obtained for each surface. Our results are summarized in Table I.

Freshly electroplated cones were used for each run. Although the absolute magnitude of ΔV varied from run to run, the values relative to cobalt remained quite reproducible. On the basis of the preceding results, the surfaces investigated may be assigned an order of activity as follows

$$\begin{array}{lllllll} \text{Pt} & & \text{Cu} & & \text{Zn} & & \\ \text{Co} & > & \text{brass} & > & \text{paraffin} & > & \text{Sn} \\ \text{Ni} & & \text{Fe} & & & & \\ & & \text{Cr} & & & & \\ & & \text{Cd} & & & & \end{array}$$

It was observed that the activity of a given cone tended to decline with time. This is probably attributable to progressive poisoning. The results were so reproducible that we believe the above relative efficiencies to be more accurate than those previously determined.[1,2,3]

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(1) E. Boehm and K. F. Bonhoeffer, *Z. physik. Chem.*, **119**, 385 (1926).

(2) H. S. Taylor and G. I. Lavin, THIS JOURNAL, **52**, 1910 (1930).

(3) G. I. Lavin and W. F. Jackson, *ibid.*, **53**, 3189 (1931).

GIBBS CHEMICAL LABORATORY
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Dinitration of *p*-Bromotoluene

BY RICHARD D. KLEENE

The simple nitration of *p*-bromotoluene has been studied in detail[1] but more vigorous nitration leading to the introduction of two nitro groups has not been hitherto reported. In the present study, the only product succcessfully isolated was 2,3-dinitro-4-bromotoluene, which was synthesized independently from 2,3-dinitro-4-aminotoluene. The 2,5-dinitro isomer was also prepared, but from 2,5-dinitro-4-aminotoluene. Both isomers and also the 3,5-dinitro isomer were reduced to the amines and acetylated.[2]

Experimental

The melting points given are uncorrected.

2,3-Dinitro-4-bromotoluene.—One ml. of *p*-bromotoluene was added dropwise to a vigorously shaken mixture of 4 ml. of 98% sulfuric acid and 2 ml. of 70% nitric acid, the temperature rising to 90° and then subsiding. The semi-solid product was washed free of acid and crystallized from alcohol. About 200 mg. of colorless needles was obtained which melted at 129–130° after recrystallization from alcohol and which showed no depression in a mixed melting point determination with a sample prepared independently by the method described in the next paragraph.

One gram of 2,3-dinitro-4-aminotoluene[3] was slurried in 5 ml. of 98% sulfuric acid, cooled externally with ice, and 1 g. of sodium nitrite dissolved in 3 ml. of sulfuric acid was added slowly. The resulting slurry was stirred for one hour and a few crystals of sulfamic acid were then added. The slurry was added to a mixture of 25 ml. of 48% hydrobromic acid, 5 g. of cuprous bromide and 100 g. of ice. The mixture was allowed to stand in the cold for two days and was then poured into excess ice and filtered. The filter cake was leached with 50 ml. of hot alcohol, filtered and the filtrate evaporated to dryness. The residue was warmed on a steam-bath with 10 ml. of 70% nitric acid in which it dissolved. As soon as the evolution of nitric oxide ceased, the solution was diluted with a few ml. of water and cooled. The product formed colorless needles which when recrystallized from alcohol melted at 129°. The yield was about 200 mg.

Anal. Calcd. for $C_7H_5O_4N_2Br$: C, 32.2; H, 1.92; N, 10.72; Br, 30.6. Found: C, 32.0; H, 2.06; N, 11.0; Br, 30.6.

2,5-Dinitro-4-bromotoluene was prepared from 2,5-dinitro-4-aminotoluene[3] by the method described above. After two recrystallizations from alcohol it was obtained as straw-colored needles which melted at 111°.

Anal. Calcd. for $C_7H_5O_4N_2Br$: N, 10.72. Found: N, 10.9.

2,5-Diacetamino-4-bromotoluene was prepared by reducing the dinitro compound with tin and hydrochloric acid, followed by acetylation with acetic anhydride.[2] The product was twice recrystallized from alcohol and formed colorless needles which melted at 284°.

Anal. Calcd. for $C_{11}H_{13}O_2N_2Br$: C, 46.3; H, 4.56; N, 9.83; Br, 28.1. Found: C, 46.5; H, 4.70; N, 9.65; Br, 28.1.

2,3-Dinitro-4-bromotoluene failed to yield a crystalline derivative by this method.

3,5-Diacetamino-4-bromotoluene was prepared from 3,5-dinitro-4-bromotoluene[4] by the foregoing method. The product, recrystallized from alcohol, formed colorless needles which melted at 244.5–245°.

Anal. Calcd. for $C_{11}H_{13}O_2N_2Br$: C, 46.3; H, 4.56; N, 9.83; Br, 28.1. Found: C, 46.2; H, 4.64; N, 9.86, Br, 28.3.

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(1) (a) Shaw and Turner, *J. Chem. Soc.*, 1884 (1932); (b) Holleman, *Rec. trav. chim.*, **34**, 283 (1915).

(2) Ipatieff and Schmerling, THIS JOURNAL, **59**, 1056 (1937).

(3) Page and Heasman, *J. Chem. Soc.*, **123**, 3235 (1923).

(4) Jackson and Ittner, *Am. Chem. J.*, **19**, 7 (1897).

CHICAGO, ILLINOIS

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meso-2,5-Dibromohexane

BY NATHAN KORNBLUM AND JOHN H. EICHER

The conversion of 2,5-hexanediol to 2,5-dibromohexane in 70–90% yields has previously been accomplished by treatment with fuming hydrobromic acid.[1,2,3] A distinctly more convenient procedure, which routinely gives better than 90% yields of 2,5-dibromohexane, involves treating the

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(1) Duden and Lemme, *Ber.*, **35**, 1335 (1902).

(2) Pace, *Arch. farmacol. sper.*, **42**, 167 (1926); *C. A.*, **21**, 1964 (1927).

(3) W. H. Florsheim, Ph.D. Thesis, University of California at Los Angeles, May, 1948.