

prepare extremely pure samples of that hydrocarbon. The Grignard reaction of tertiary butyl chloride with methylmagnesium chloride was used to produce the neopentane. The product was washed with 85 and 95% sulfuric acid and then photobrominated to ensure the complete removal of unsaturates, since isobutene is the most likely impurity. The residual bromine and any hydrogen bromide formed were removed by distilling the mixture through 40% potassium hydroxide (aqueous) and over solid potassium hydroxide. The resulting neopentane was finally purified by low temperature distillation in a column of conventional design. The distillate was assumed to be pure when the temperature remained constant at 9.6° for thirty to sixty minutes under total reflux. This "pure" neopentane was taken off in four consecutive fractions, the purity of which was checked by determining the vapor pressure-temperature relations of large samples over a wide range of temperature. No indications of impurity could be detected.

Preliminary experiments showed that the rates of the mercury photosensitized reaction of different samples, though surprisingly low, were very variable. Samples of the unreacted and of the "partially decomposed" neopentane were analyzed by the mass spectrometer with the following results:

Sample	Percentages					
	A	B	C	D	E	F
Neopentane	96.4	99.6	99.9	100	100	100
<i>n</i> -Pentane	1.1
Dimethylcyclopropane	1.6	0.4	trace
C ₆ hydrocarbons	1

in which Sample A was the "pure" unreacted neopentane and B to F were "partially decomposed" samples. It was stated by the analyst that samples D, E and F were "apparently of the same purity as the neopentane used for calibrating as obtained from Dr. F. D. Rossini, National Bureau of Standards, Standard Sample No. 299-5s. It is certified to be 99.96% pure; impurity 0.04 = 0.02%."

Accordingly a large sample of crude (undistilled) neopentane (about 30 liters of gas) was subjected to prolonged mercury sensitization by circulating a mixture of gaseous neopentane and mercury through a quartz vessel illuminated by a low pressure mercury lamp, the radiation from which consisted largely of the unreversed 2537 Å. line, for seventy to eighty hours, roughly distilled into 5 fractions and analyzed on the mass spectrometer. The results were:

Fraction no.	Percentages				
	1	2	3	4	5
Neopentane	99 (8) ^a	99 (7) ^a	99 (6) ^a	99 (4) ^a	99 (0) ^a
Hexane	0.2	0.3	0.4	0.6	1.0

^a The figures in parentheses are uncertain.

Hence, in the absence of very efficient fractionation, mercury photosensitization is an efficient

method of obtaining neopentane of high purity. This method of purification is possible only because neopentane is remarkably resistant to attack by Hg(³P₁) atoms whereas the impurities react readily to give, ultimately, heavy polymers and non-condensable gases (hydrogen and methane) which are easily separated from the unreacted neopentane.

The Grignard reaction was carried out by Dr. A. Cambron and Mr. R. A. B. Bannard of these laboratories, and the mass spectrometer analyses by Dr. Fred L. Mohler of the National Bureau of Standards, Washington, D. C., to whom our thanks are due. The laboratory assistance of Mr. J. R. Pilon is gratefully acknowledged.

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The Reduction of *p*-Hydroxyformanilide by Lithium Aluminum Hydride to *N*-Methyl-*p*-aminophenol

BY JACOB EHRLICH

This reduction of an anilide to a secondary amine proceeds smoothly in tetrahydrofuran as solvent. The method is applicable to various amides using diethyl ether or tetrahydrofuran as solvent, to be reported in a later communication.

Experimental

A solution of 1.9 g. (0.05 mole)¹ of lithium aluminum hydride in 36 cc. of anhydrous tetrahydrofuran² was prepared in a 3-neck conical flask provided with sealed stirrer, thermometer, reflux condenser, hopper³ and calcium chloride guard-tube.⁴ The solution was brought to 20–25° and 2.75 g. (0.02 mole) of *p*-hydroxyformanilide was added in small portions during thirty minutes, cooling externally with ice-water to maintain this temperature. The hopper was flushed with 4 cc. of tetrahydrofuran and the charge stirred twenty minutes more at 20–25°. Dur-

(1) Assuming only one labile hydrogen (phenolic) in 1 mole of *p*-hydroxyformanilide, then 0.25 mole of LiAlH₄ would be destroyed prior to any reduction. The reduction of the formyl radical would consume a further 0.5 mole of LiAlH₄, making a 4:3 molar ratio of anilide:LiAlH₄. If the amido hydrogen is also labile, the ratio becomes 1:1. If the formyl hydrogen is labile, the ratio becomes 4:5. However, these calculations are only of academic interest, for the 0.02:0.05 molar ratio was arrived at empirically. If less LiAlH₄ is employed, the yield drops proportionally.

(2) The tetrahydrofuran was obtained from E. I. du Pont de Nemours and Co. This was rendered water and peroxide free by storing 500 cc. in an amber bottle over 75 g. of flake sodium hydroxide for two weeks, occasionally shaking. The clear, colorless supernatant liquor was decanted (from now discolored solids) for use in the reductions without further purification. On dissolving the LiAlH₄ in the tetrahydrofuran the heat of solution will raise the temperature to about 50°.

(3) Similar in construction (but smaller capacity) to that described by Swift and Billman, *Ind. Eng. Chem., Anal. Ed.*, **17**, 600 (1945). However, this may be omitted and the same results obtained by using a removable rubber stopper.

(4) In various reductions no special precautions, except the exclusion of atmospheric moisture, were employed, and no uncontrolled or explosive reaction was observed. However, as an added precaution, it would be desirable to conduct the reaction under an atmosphere of dry nitrogen.

ing this period a thin slush formed. The temperature was then raised to 63–66° and maintained for ten minutes. The pale pink slurry was then chilled to 20–25°, 77 cc.⁵ of 3 *N* hydrochloric acid added *cautiously* from a dropping funnel (ice-water cooling as required), resulting in a pale slightly cloudy solution.

The charge then was steam-distilled (about 90 cc. distillate) to remove the solvent, digested while hot with 0.3 g. of Norit and 0.2 g. of Filter-Cel and filtered with suction. The colorless filtrate was cooled to 0–5°, 10 cc. of concentrated hydrochloric acid added, then titrated at this temperature with molar sodium nitrite solution to a strong blue streak (ten minutes end-point) on starch-iodide paper. Almost the theoretical amount was required. During the titration pale yellow nitrosamine needles separated. The crystals were filtered with suction, washed with water and dried at 55°; yield 2.66 g., m. p. 134–135°. The filtrate, on extraction with ether, yielded an additional 0.12 g.; total yield 92%.

On recrystallizing the combined crops from 10% ethanol, in the presence of a little Norit, the m. p. was raised to 135.5°, identical with purified *N*-nitroso-*N*-methyl-*p*-aminophenol prepared from photographic Metol as shown by mixed m. p.

(5) The first 20 cc. of 3 *N* hydrochloric acid must be fed very slowly, dropwise. During this period the main heat effect is evident and the bulk of the hydrogen gas evolved (by decomposition of the excess lithium aluminum hydride). Thereafter the balance may be added faster. Prior to the acid addition the calcium chloride tube is removed (*versus* any back pressure) and the flask vented to the hood.

CONTRIBUTION FROM THE
EHRlich LABORATORY

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The Constitution of Citrinin

By T. S. GORE, T. B. PANSE AND K. VENKATARAMAN

The structures originally assigned¹ to citrinin (I) and its degradation products (II) and (III) are untenable in the light of their behavior towards diazonium salts.² Cram³ has now shown by synthesis and direct comparison that (III) is 4-methyl-5-ethylresorcinol, a conclusion at which we had arrived by circumstantial evidence. The 2,4 and 4,6-compounds were ruled out by the ability of (III) to form disazo dyes. Comparison of the absorption spectra and the color reactions of the bis-benzeneazo derivative of (III) with those of 2,4- and 4,6-bis-benzeneazoresorcinol and a series of analogous dyes showed that (III) is 5-methyl-4-ethylresorcinol (IV) or 4-methyl-5-ethylresorcinol (V). The absorption curves for 2,4-bis-benzeneazoresorcinol, 2,6-bis-benzeneazo-5-methyl-4-ethyl resorcinol and the bis-benzeneazo derivative of (III) had a well-defined, high intensity band in the visible region ($\lambda_{\max.} \sim 415 \mu\mu$; $\epsilon_{\max.} \sim 60,000$). 4,6-bis-Benzeneazoresorcinol and 4,6-bis-benzeneazo-2-ethylresorcinol exhibited a band of relatively low intensity in the visible region ($\lambda_{\max.} \sim 415 \mu\mu$; $\epsilon_{\max.} \sim 20,000$) and absorption maxima in the near ultraviolet ($\lambda_{\max.} \sim 340 \mu\mu$; $\epsilon_{\max.} 36,000$).

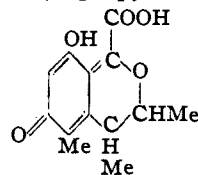
(1) Raistrick, Robinson, *et al.*, *Phil. Trans. Roy. Soc.*, **B220**, 269, 297 (1931).

(2) Gore, *et al.*, *Nature*, **167**, 333 (1946).

(3) Cram, *THIS JOURNAL*, **70**, 440 (1948).

Shah and Robinson's synthesis⁴ of (IV) was repeated, and it was found to melt at 79–82° (Shah and Robinson, m. p. 75–80°), while (III) as a monohydrate melts at 68–69°, and after dehydration at 98–99°; the m. p. of (III) was considerably depressed by admixture with (IV). Cram³ has quoted us erroneously as reporting a m. p. of 65–70° for (III). The bis-benzeneazo derivatives of (III) and (IV) melted, respectively, at 171° and 188°, and the mixed m. p. was lower. It followed therefore that (III) is 4-methyl-5-ethylresorcinol. However, this is in conflict with the observation of Hetherington and Raistrick¹ that neither of the acids obtained by oxidation of the dimethyl ether of (III) gave the anthrachryson reaction. We prepared 3,5-dimethoxy-2-methylbenzoic acid (VII) by the methylation of the corresponding α -resorcylic acid,⁵ and found that it readily gave a bordeaux-red color on warming with sulfuric acid (the anthrachryson reaction); Cram has recorded that the acid (VI) synthesized by him corresponds in its properties to one of Hetherington and Raistrick's acids. The m. p. (157–158°) reported for (VI) by Cram is in agreement with ours, while Hetherington and Raistrick's two acids melted at 142–146° and 98–99°.

From the formulation of (III) as 4-methyl-5-ethylresorcinol, the properties of (II), including the formation of (III) from (II) by alkali fusion, are fully explained by the structure 4-methyl-5-(1-methyl-2-hydroxy)-propyl-resorcinol, proposed



by Cram. The experimental results of Hetherington and Raistrick¹ and the behaviour of citrinin towards diazonium salts² would then agree with the above constitution for citrinin.

(4) Shah and Robinson, *J. Chem. Soc.*, 1491 (1934).

(5) Woodward and Reed, *THIS JOURNAL*, **65**, 1569 (1943).

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The Employment of Sodium Hydride as a Condensing Agent

By NATHAN GREEN AND F. B. LAForge

Sodium hydride is now being produced on a large scale, and its advantages as a catalyst in various organic reactions have been indicated by Hansley and Carlisle.¹ Its use in this Laboratory in the preparation of ethyl β -oxocaprylate, ethyl β -carbethoxy- α -oxo-enanthate, and 5-carbethoxy-dihydrocinerone has been described in previous articles.^{2,3} We have since employed this reagent in

(1) Hansley and Carlisle, *Chem. Eng. News*, **23**, 1332 (1945).

(2) Soloway and LaForge, *THIS JOURNAL*, **69**, 2677 (1947).

(3) LaForge and Soloway, *ibid.*, **69**, 2932 (1947).