tetranitrate of 4,4′-*bis*-(β,γ-dihydroxypropoxy)-3,3′-dinitroarsenobenzene were prepared from the corresponding arsonic acids by reduction with hypophosphorous acid.

6. 4-β,γ-Dihydroxy-*n*-propoxyphenylarsenious oxide, 3-nitro-4-β,γ-dihydroxy-*n*-propoxyphenylarsenious oxide and 3-amino-4-β,γ-dihydroxy-*n*-propoxyphenylarsenious oxide were prepared from the corresponding arsonic acids by reduction with sulfurous acid employing hydriodic acid as a catalyst.

LINCOLN, NEBRASKA RECEIVED AUGUST 2, 1937

[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE UNIVERSITY OF FLORIDA]

Derivatives of Piperazine. XII. Alpha Amino Ketones Derived from N-Phenylpiperazine and Derivatives

BY BURT L. HAMPTON AND C. B. POLLARD

Four new α-amino ketones (Table I) derived from N-phenylpiperazine have been prepared with the object of studying the effects of various reducing agents on these ketones. It was hoped that secondary alcohols, similar in structure to ephedrine and related compounds, could be prepared which would possess useful physiological properties. The effect of various reducing agents on the ketones prepared will be reported in a subsequent publication.

The syntheses may be effected in two ways:

A. Since N-phenylpiperazine is a much stronger base than the products obtained, two moles of it in ether solution in the cold may be mixed with one mole of the phenacyl halide and the solution allowed to stand for several hours or overnight. A portion of the free ketone obtained separates out together with the hydrochloride of N-phenylpiperazine which may be removed by washing with water. The remainder of the product is obtained by evaporating off the ether and washing the residue with a small portion of cold alcohol. The whole is then recrystallized from alcohol. In the case of the reaction between N-phenylpiperazine and *p*-chlorophenacyl bromide alcohol was used as the solvent, the product being obtained by evaporating the alcohol to a small volume, cooling, filtering the precipitate, washing with water and then recrystallizing from alcohol.

B. The same products may be obtained by refluxing for thirty minutes in alcoholic solution one mole of the phenacyl halide and one mole of N-phenylpiperazine together with a slight excess of sodium carbonate. The alcoholic solution is evaporated to a small volume, cooled, the precipitate filtered off, washed with water and then recrystallized from alcohol. The yields are from 80 to 85%, method B giving better results.

The ketones are slightly soluble in alcohol and ether, soluble in chloroform and insoluble in water. They do not show a sharp melting point, but melt over a 2° range.

All of the ketones readily form oximes by refluxing them in alcoholic solution with molecular proportions of hydroxylamine. The oximes are not very soluble in alcohol, and are, therefore, very readily isolated. In contrast to the ketones the oximes melt over a range of 1°. The yields of the oximes are from 80 to 85%.

The hydrochlorides of the ketones are prepared

TABLE I

	Compound	M. p. (corr.), °C.	Formula	Recryst. from	N, %		Cl, %	
					Found	Calcd.	Found	Calcd.
1	N-phenyl-N′-phenacylpiperazine	106–108	$C_{18}H_{20}ON_2$	EtOH	9.96	9.99		
2	N-phenyl-N′-*p*-methylphenacylpiperazine	136–138	$C_{19}H_{22}ON_2$	EtOH	9.57	9.52		
3	N-phenyl-N′-*p*-methoxyphenacylpiperazine	145–147	$C_{19}H_{22}O_2N_2$	EtOH	9.17	9.03		
4	N-phenyl-N′-*p*-chlorophenacylpiperazine	131–133	$C_{18}H_{19}ON_2Cl$	EtOH	8.95	8.90		
5	Oxime of 1	157–158	$C_{18}H_{21}ON_3$	EtOH	14.36	14.23		
6	Oxime of 2	184–185	$C_{19}H_{23}ON_3$	BuOH	13.66	13.59		
7	Oxime of 3	182–183	$C_{19}H_{23}O_2N_3$	BuOH	12.84	12.92		
8	Oxime of 4	169–170	$C_{18}H_{20}ON_3Cl$	BuOH	12.63	12.74		
9	Monohydrochloride of 1	210–212	$C_{18}H_{21}ON_2Cl$	Abs. EtOH	8.70	8.84	11.02	11.19
10	Monohydrochloride of 2	235–237	$C_{19}H_{23}ON_2Cl$	Abs. EtOH	8.53	8.47	11.12	10.72
11	Monohydrochloride of 3	227–229	$C_{19}H_{23}O_2N_2Cl$	EtOH	8.10	8.08	10.51	10.23
12	Monohydrochloride of 4	225–227	$C_{18}H_{20}ON_2Cl_2$	EtOH	7.71	7.98	10.33	10.09

by dissolving 3 g. of the ketone in alcohol and adding an excess of concentrated hydrochloric acid. The product is precipitated by the addition of ether and recrystallized from alcohol. The ketones do not readily form dihydrochlorides, evidenced by the fact that all the salts prepared in the above way were the monohydrochlorides. These salts are only very slightly soluble in water.

The physical data of these compounds are shown in the accompanying table.

Summary

1. Certain α-amino ketones and derivatives related to N-phenylpiperazine have been prepared and studied.

2. The action of various reducing agents on these ketones will form the basis of a subsequent publication.

GAINESVILLE, FLORIDA RECEIVED SEPTEMBER 13, 1937

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

Studies on Lignin and Related Compounds. XXXII. The Guaiacyl and Syringyl Groups in Various Woods

BY W. LINCOLN HAWKINS, GEORGE F. WRIGHT AND HAROLD HIBBERT

In two recent communications of this series[1] it was shown that treatment of spruce lignin sulfonic acid with alkali gives a 6–7% yield of vanillin, the higher percentage being obtained from the β-lignin sulfonic acid, fractionated with quinoline. This finding has been confirmed by application of the method to various other species of wood and to straw.[2] In the present investigation comparable yields of vanillin have been obtained from other soft woods (balsam and Eastern hemlock), but the hard woods, such as birch, oak, aspen and maple, have been found to yield both vanillin and syringaldehyde in approximately equal amounts (2.8% of each, Table I).

Although there was little doubt but that these aldehydes originated in the lignin, and not in some other part of the woody substance, the latter contingency has been eliminated by actual isolation of 2.3% of vanillin and 2.3% of syringaldehyde by treatment of the lignin sulfonic acid recently prepared from oak lignin[3] with alkali. Since this oak lignin, prepared by acetolysis of wood and subsequently purified by saponification, had been separated from the non-ligneous constituents it is evident that the aromatic aldehydes represent fission products of the lignin structure. The approximately equal yield of both aldehydes suggests either that they are incorporated in the same complex or, alternatively, that two closely related lignins exist in equal quantities in the same wood. These two possibilities which may have some bearing on the mode of formation of lignin in wood will be discussed in a forthcoming communication. For the present it is to be noted that the age of the woody tissue seems to have no connection with aromatic type since the heart and sap wood of maple were found to give approximately identical amounts of the mixed aldehydes. This conclusion regarding relation of age to vanillin formation is also in harmony with the production of vanillin from straw lignin sulfonic acid,[2] in other words, the synthesis of aromatic groups formed as the result of a short, seasonal plant metabolism.

Experimental

Isolation of Vanillin and Syringaldehyde from Yellow Birch Sulfite Liquors.—The liquors, obtained by cooking 13.5 kg. of yellow birch chips with 60 liters of sodium bisulfite cooking liquor (6.0% "total" and 1.1% "combined" sulfur dioxide) at a maximum temperature of 125° for eight hours, were heated in 12-liter batches with 9% sodium hydroxide solution at 160° (90 lb./sq. in. (6 atm.)) for four hours. The combined cooks were treated with carbon dioxide until barely alkaline and the solution then heated to 90°. After cooling, the supernatant liquor was decanted from solid material and extracted continuously with benzene. This extract was concentrated to 3 liters and extracted with 1.3 liters of 21% sodium bisulfite. The resulting bisulfite addition compound was decomposed with excess sulfuric acid and the aldehydes extracted with ether. This extract, upon evaporation, yielded 73.5 g. of a brown viscous oil, 4.5 g. of which was distilled at 140–145° (0.014 mm.). The crystalline distillate (3.5 g.) was fractionally crystallized from benzene–petroleum ether (b. p. 30–50°). The more soluble fraction (0.62 g.) after two recrystallizations from water melted at 111.5–112°; a mixed melting point with synthetic syringaldehyde[4] (m. p. 110–112°) was not lowered. The compound was further

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[1] Tomlinson and Hibbert, THIS JOURNAL, **58**, 345, 348 (1936).

[2] Alvfeldt and Hägglund, *Svensk Pappers-Tidn.*, **40**, 236 (1937).

[3] Hibbert and Steeves, THIS JOURNAL, **59**, 1768 (1937).

[4] Graebe and Martz, *Ber.*, **36**, 1032 (1903).