TABLE I

A. HYDROGENATION OF MALEIC ACID

Hydrogen absorbed, cc.	Total time, seconds Catalyst I (original method)	Catalyst II (modified method)
100	78	60
200	123	98
300	166	135
400	208	173
500	249	213
600	288	253
B. HYDROGENATION OF BENZALDEHYDE[4]		
100	70	152
200	125	239
300	181	314
400	240	388
500	304	465
600	372	545

These results show that the catalyst prepared by the modified procedure was in this case somewhat better for the hydrogenation of maleic acid than that made in the usual way, while the reverse is true for the hydrogenation of benzaldehyde. Reference to the previous study of rates of hydrogenation by this same technique[2] shows that the catalysts reported here are even more active than those in the earlier work.

[4] The addition of a trace of $FeSO_4$ sometimes promoted the reaction and sometimes poisoned it.

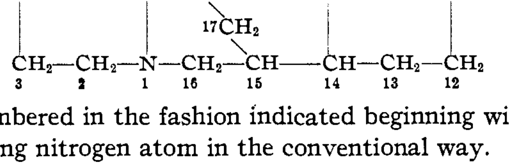
DEPARTMENT OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, NEW YORK

RECEIVED MARCH 5, 1936

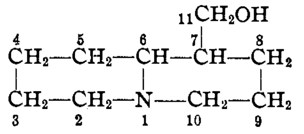
The Numbering of the Sparteine Molecule and its Derivatives

BY JAMES FITTON COUCH

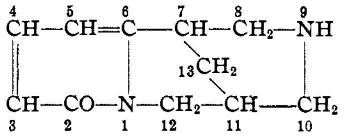
The constitution of sparteine as modified by Clemo and Raper [*J. Chem. Soc.*, 644–645 (1933)] from the structure suggested by Ing [*ibid.*, 504–510 (1933)] may be rearranged to the following form, and the component atoms may then be



numbered in the fashion indicated beginning with a ring nitrogen atom in the conventional way. It would be more convenient in this particular case to start with carbon atom number 16 but it is better to adhere to the established rule. This arrangement of the sparteine formula which has been accepted by Prof. Clemo [personal communication] shows at once its symmetrical character and relationship to other lupine alkaloids and to cytisine and anagyrine. Lupanine becomes 2-keto-sparteine, hydroxylupanine tentatively its 10-hydroxy derivative and anagyrine is 3,4,5,6-tetradehydro-2-keto-sparteine. Lupinine may be formulated as



and cytisine



indicating a close relationship between these alkaloids since cytisine may be derived from (hypothetical) tetradehydro-2-keto-lupinine by condensation of methylamine across atoms 9 and 11 of the lupinine skeleton, atom 8 becoming atom 13 of cytisine. Sparteine may be theoretically derived from lupinine by condensation with piperidine in an analogous manner.

BUREAU OF ANIMAL INDUSTRY
WASHINGTON, D. C.

RECEIVED MARCH 2, 1936

Amino Alcohols Derived from 1,2,3,4-Tetrahydrodibenzofuran

BY RICHARD A. ROBINSON AND ERICH MOSETTIG

In logical connection with a study of derivatives of 4,5-phenanthylene oxide [Mosettig and Meitzner, THIS JOURNAL, **56**, 2738 (1934)] the investigation of dibenzofuran derivatives was begun in this Laboratory in 1932 with the hope of finding in this series compounds resembling, particularly in their analgesic action, morphine. In our first paper dealing with dibenzofuran derivatives [Mosettig and Robinson, *ibid.*, **57**, 902 (1935)] we outlined in some detail the direction in which our further synthetic experiments were to proceed. In the meantime other research groups [Kirkpatrick and Parker, *ibid.*, **57**, 1123 (1935); Gilman, Smith, and Cheney, *ibid.*, **57**, 2095 (1935)] have approached the synthesis of possibly analgesic and hypnotic substances in the dibenzofuran series in a way which is in part similar to ours; previous publications from these investigators had not indicated any intention of seeking morphine-like substances. In order to avoid unnecessary duplication of effort, some of our recent experimental results are submitted in this preliminary form.

1,2,3,4-TETRAHYDRODIBENZOFURAN DERIVATIVES

Substance	M. p., °C. (corr.)	Formula	Analyses, % Calcd.	Analyses, % Found
7-ω-Bromoacetyl-	81–82	$C_{14}H_{13}O_2Br$	Br, 27.27	27.72
7-[2-(Dimethylamino)-1-oxo-ethyl]-hydrochloride	244–247	$C_{16}H_{20}O_2NCl$	Cl, 12.07	12.06
			N, 4.77	4.73
7-[2-(Diethylamino)-1-oxo-ethyl]-hydrochloride	202–210	$C_{18}H_{24}O_2NCl$	Cl, 11.03	11.11
			N, 4.35	4.19
7-[2-Piperidino)-1-oxo-ethyl]-hydrochloride	235–239	$C_{19}H_{24}O_2NCl$	Cl, 10.63	10.65
			N, 4.20	4.59
7-[2-(1,2,3,4-Tetrahydroisoquinolino)-1-oxo-ethyl]-hydrochloride	260–264	$C_{23}H_{24}O_2NCl$	N, 3.67	3.64
7-[2-(Dimethylamino)-1-hydroxy-ethyl]-hydrochloride	220–222	$C_{16}H_{22}O_2NCl$	C, 64.95	65.40
			H, 7.50	7.68
			Cl, 12.00	12.08
7-[2-(Piperidino)-1-hydroxy-ethyl]-hydrochloride	230–232	$C_{19}H_{26}O_2NCl$	C, 67.93	67.63
			H, 7.81	7.72
			Cl, 10.56	10.67
7-[2-(1,2,3,4-Tetrahydroisoquinolino)-1-hydroxy-ethyl]-hydrochloride	197–200	$C_{23}H_{26}O_2NCl$	C, 71.94	71.85
			H, 6.83	6.94

The amino alcohols derived from 1,2,3,4-tetrahydrodibenzofuran which carry the alkamine side chain in position-7 were prepared by a method described in principle previously for the synthesis of their analogs in the dibenzofuran series itself [Mosettig and Robinson, *ibid.*, **57**, 2186 (1935)]. The constitutional proof for the starting material, 1,2,3,4-tetrahydro-7-acetyl-dibenzofuran, has been offered recently by Gilman, Smith, and Cheney (*l. c.*). Considerable difficulties have been encountered in the catalytic reduction of the amino ketones to the corresponding amino alcohols.

COBB CHEMICAL LABORATORY
UNIVERSITY OF VIRGINIA
UNIVERSITY, VA.

RECEIVED FEBRUARY 19, 1936

A Note on Some Color Reactions of Hydroquinone in the Solid State

BY SIDNEY J. FRENCH AND DONALD J. SAUNDERS

J. Maldiney in 1914[1] reported briefly that colors of blue and gray were obtained when solid hydroquinone was mixed with solid alkali carbonates. He attributed the effect to the action of light and to a slight oxidation of the hydroquinone.

Further investigation of these color reactions by the writers has shown that they are dependent on the presence of small amounts of moisture, for the anhydrous salts give no color while the presence of an excess of water gives a yellow solution. A number of salts were used and it was noted (1) that only the more alkaline salts give colors and (2) the colors ranged from gray through blue and green to black, being roughly proportional to the increasing alkalinity of the compound used. Thus, trisodium arsenate and sodium tetraborate gave blue gray colors; sodium silicate and sodium cyanide, blue; sodium phosphate and sodium carbonate, blue green; and sodium hydroxide, black. Less alkaline salts such as sodium bicarbonate and disodium phosphate gave no colors. Salts showing colors were salts of acids having smaller ionization constants than that of hydroquinone in its primary ionization stage, while salts showing no color were those of acids having higher ionization constants than that of hydroquinone.

Dry buffer mixtures were prepared as indicated in Table I. The *p*H of the solution of each buffer mixture is shown together with the color produced when each dry buffer is mixed with an equal quantity of hydroquinone and placed in a desiccator over water. The results indicate the change in color with increasing alkalinity of the mixture and indicate the possibility of determining the approximate alkalinity of a substance in the solid state. Colors corresponding to various *p*H solution ranges would be as follows.

TABLE I

BUFFER MIXTURE COMPOSITIONS

	Parts by weight Compound	Parts by weight NaOH	*p*H of soln.	Color with hydroquinone
Glycine	5.5	4.5	10.4	No color
$Na_2HPO_4 \cdot 12H_2O$	2.69	0.060	10.97	Faint gray
$Na_2HPO_4 \cdot 12H_2O$	2.69	.100	11.29	Gray
$Na_2HPO_4 \cdot 12H_2O$	2.69	.200	11.77	Blue gray
$Na_2HPO_4 \cdot 12H_2O$	2.69	.300	12.06	Blue
Glycine	3.0	7.0	12.50	Blue green
Glycine	1.0	9.0	12.8–12.9	Green
None	...	solid	....	Black

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[1] J. Maldiney, *Compt. rend.*, **158**, 1782 (1914).