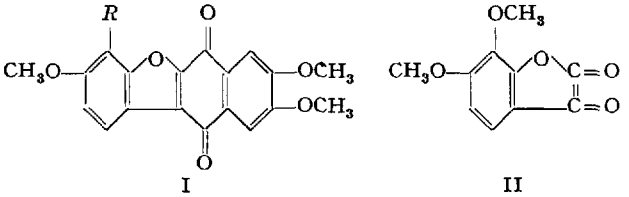
scheint die Bande der Karbonylgruppe. Ajmalin wurde durch Abbau mit Selen in Ind-N-methyl-harman übergeführt. Durch Kalischmelze lässt sich Ajmalin in eine kristalline Base (in kleiner Menge), eine stickstoffreie Säure und Indol-2-Karbonsäure aufspalten. Auf Grund dieser Spaltstücke wurde eine mögliche Strukturformel für Ajmalin diskutiert.

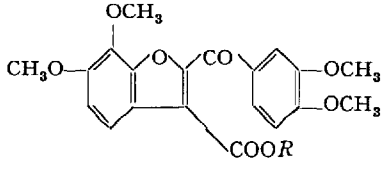
Synthesis of 3:8:9-Trimethoxy- and 3:4:8:9-Tetramethoxy-β-Brazanquinone

KOSTANECKI and his coworkers prepared 3:8:9-trimethoxy-β-brazanquinone (I, R = H, m.p. 260°C)[1] and 3:4:8:9-tetramethoxy-β-brazanquinone (I, R = OCH_3, m.p. 264°C)[2] by the oxidation of 3:8:9-trimethoxy-6-hydroxy- and 3:4:8:9-tetramethoxy-6-hydroxy-β-brazan respectively with chromic acid. In an earlier communication, a synthesis of (I, R = H) was described[3]. An independent method of synthesis of the two abovementioned quinones is now reported.



I

II



III

6:7-dimethoxycoumaranone[4] was converted into 6:7-dimethoxy-2-oximinocoumaranone (m.p. 194°) and then hydrolized to 2-hydroxy-3:4:dimethoxyphenylglyoxalic acid (m.p. 178°C; methyl ester, m.p. 99–100°C). The latter on treatment with acetic anhydride gave 6:7-dimethoxycoumarandione (II, m.p. 153°C). On interaction with ω-bromoacetoveratrone in presence of sodium ethoxide this afforded ethyl 6:7-dimethoxy-2-veratroylcoumarone-3-carboxylate (III, R=C_2H_5, m.p. 99–101°C). The corresponding acid (III, R = H, m.p. 205°C) on cyclisation through the acid chloride furnished (I, R = OCH_3, m.p. 265°C) purified by sublimation in vacuum. The identity was confirmed by colour reaction and by reductive acetylation to 3:4:8:9-tetramethoxy-6:11-diacetoxy-β-brazan (m.p. 235°C)[2].

Analogously, 6-methoxycoumarandione[5] was converted into ethyl 6-methoxy-2-veratroylcoumarone-3-carboxylate (m.p. 127–128°C). The related acid (m.p. 208°C) on cyclisation gave (I, R = H, m.p. 262°C) identical with the specimen synthesized earlier.

J. N. CHATTERJEA

Chemical Laboratory, Science College, Patna, India, February 19, 1953.

[1] V. KOSTANECKI and L. LLOYD, Ber. dtsch. chem. Ges. *36*, 2200 (1903).

[2] V. KOSTANECKI and A. ROST, Ber. dtsch. chem. Ges. *36*, 2205 (1903).

[3] J. N. CHATTERJEA, Exper. *7*, 374 (1951).

[4] A. FELIX and P. FRIEDLANDER, Mh. Chem. *31*, 55 (1910).

[5] K. FRIES and K. SAFTIEN, Ann. Chem. *442*, 291 (1925).

Résumé

Cet article décrit une méthode sans ambiguïté pour la synthèse des 3:4:8:9-tétraméthoxy- et 3:8:9-triméthoxy-β-brazanquinone.

The Stereochemistry of the Reaction of Nitrous Acid with Cyclohexylamines

BARTON and ROSENFELDER[1] have observed that ionic elimination reactions involving substituents on adjacent carbon atoms in a cyclohexane derivative proceed most readily when the two substituents form polar bonds (that is the two carbon atoms and the two substituents involved are in one plane). They have also pointed out that the formation of olefines by the action of nitrous acid on primary amines shows the same geometric specificity and cited menthylamines as examples.

We have found that, on the basis of the concept of polar and equatorial bonds, the behaviour of cyclohexylamines with nitrous acid can be correlated as follows:

When the amino group forms an equatorial bond the main reaction product is the corresponding alcohol with the hydroxy group equatorial (that is no WALDEN inversion takes place).

When the amino group is linked by a polar bond, considerable amounts of cyclohexenes are formed along with a mixture of both epimeric forms of the alcohol (that is WALDEN inversion occurs).

We have tested these rules for a number of cyclohexylamines (Table I, II). The conformation of cyclohexylamines and cyclohexanols was determined in most cases on the basis of the observation that sodium and alcohol reduction of a ketone or an oxime leads predominantly to the thermodynamically more stable epimer of the corresponding alcohol or amine[2]. Cyclohexanols and cyclohexylamines produced by such reduction should therefore in general have their hydroxy and amino groups equatorially bonded, while catalytic reduction in presence of platinum in acid media should mainly afford epimers in which the hydroxy and the amino groups will be polar linked.

HÜCKEL and coworkers[3] have carried out epimerization experiments with decalols. On the basis of their work the equatorial position can be assigned to the hydroxy and the amino groups in the following compounds: trans-α-decalol, m.p. 63°, trans-α-decalylamine, m.p. – 1°, trans-β-decalol, m.p. 75°, trans-β-decalylamine, m.p. 15°.

The data presented in tables I and II testify to the validity of the rules postulated by us. As the result of their studies on the action of nitrous acid on decalylamines HÜCKEL and coworkers found that those trans-decalylamines that are obtained by the sodium and alcohol reduction of oximes react with nitrous acid to afford decalols that are predominantly produced by the sodium and alcohol reduction of decalones[3]. It should be noted that this rule is the same as the rule described above in terms of polar and equatorial bonds.

[1] D. H. R. BARTON and W. J. ROSENFELDER, J. Chem. Soc. *1951*, 1048.

[2] G. VAVON, Bull. Soc. chim. *49*, 937 (1931). – W. HÜCKEL, Ann. Chem. *533*, 1 (1938).

[3] W. HÜCKEL, Ann. Chem. *533*, 1 (1938).

Table I

Cyclohexylamine (NH_2 equatorial)	Composition of product		Cyclohexanol produced (OH equatorial)	Ref.
	Cyclohexene	Cyclohexanol		
"trans"-3-Methylcyclohexylamine[1,2]			cis-3-Methylcyclohexanol[6]	2
trans-4-Methylcyclohexylamine[2]			trans-4-Methylcyclohexanol[2] 60% yield	3
trans-4-Phenylcyclohexylamine[3]			trans-4-Phenylcyclohexanol[3] 53% yield	3
trans-4-Cyclohexylcyclohexylamine[3]			trans-4-Cyclohexylcyclohexanol 49% yield	3
trans-4-t-Butylcyclohexylamine[3]			trans-4-t-Butylcyclohexanol[3] 55% yield	3
Menthylamine	Little	Mostly	Menthol[7]	8
iso-Menthylamine	Little	Mostly	iso-Menthol[7]	8
Carvomenthylamine[4]	15%	85%	Carvomenthol[4]	9
trans-α-Decalylamine[5], m.p. – 1°	nil	100%	trans-α-Decalol[5], m.p. 63°	5
trans-β-Decalylamine[5], m.p. 15°	nil	100%	trans-β-Decalol[5], m.p. 75°	5

[1] Conformational analysis indicates that "trans"-1,3-methylcylohexylamine should actually be termed cis.
[2] M. M. CLAUDON, Bull. Soc. chim. France, *1950*, 627.
[3] D. V. NIGHTINGALE, J. D. KERR, J. A. GALLAGHER, and M. MAIENTHAL, J. Org. Chem. *17*, 1017 (1952).
[4] A. K. BOSE, Exper. *8*, 458 (1952).
[5] W. HÜCKEL, Ann. Chem. *533*, 1 (1938).
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[7] D. H. R. BARTON, Exper. *6*, 316 (1950).
[8] J. READ, A. M. COOK, and M. I. SHANNON, J. Chem. Soc. *1926*, 2223.
[9] R. G. JOHNSTON and J. READ, J. Chem. Soc. *1935*, 1138.

Table II

Cyclohexylamine (NH_2 polar)	Composition of product		Cyclohexanol produced	Ref.
	Cyclohexene	Cyclohexanol		
"cis"-3-Methylcyclohexylamine[1]			45% WALDEN inversion	2
cis-4-Methylcyclohexylamine[5]			25% WALDEN inversion	2
neo-Menthylamine	81%	19%	Mixture of epimers	6
neo-iso-Menthylamine	80%	20%	Mixture of epimers	6
neo-Carvomethylamine[3]	80%	20%	60% WALDEN inversion	3
trans-α-Decalylamine[4], m.p. – 18°	70%	30%	90% WALDEN inversion	4
trans-β-Decalylamine[4], m.p. – 47°	70%	30%	90% WALDEN inversion	4

[1] Conformational analysis indicates that "Cis"-1,3-methylcylohexylamine should actually be termed trans.
[2] M. M. CLAUDON, Bull. Soc. chim. France, *1950*, 627.
[3] A. K. BOSE, Exper. *8*, 458 (1952).
[4] W. HÜCKEL, Ann. Chem. *533*, 1 (1938).
[5] D. V. NIGHTINGALE, J. D. KERR, J. A. GALLAGHER, and M. MAIENTHAL, J. Org. Chem. *17*, 1017 (1952).
[6] J. READ and G. J. ROBERTSON, J. Chem. Soc. *1927*, 2168.
[7] R. G. JOHNSTON and J. READ, J. Chem. Soc. *1935*, 1138.

The reaction of nitrous acid with cyclohexylamines possesses diagnostic value and promises to be useful for conformation determination[1].

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Applied Chemistry Department, Indian Institute of Technology, Kharagpur, India, December 30, 1952.

Zusammenfassung

Wenn die Aminogruppe in Zyklohexylaminen durch eine äquatoriale Bindung verknüpft ist, ist das Hauptprodukt bei der Reaktion mit salpetriger Säure das entsprechende Zyklohexanol mit einer äquatorialen Hydroxylgruppe (das heisst, die Waldensche Umkehrung findet nicht statt). Wenn die Aminogruppe durch eine polare Bindung verknüpft ist, werden beträchtliche Mengen von Zyklohexenen, begleitet von einer Mischung beider epimeren Formen des entsprechenden Zyklohexanols, gebildet (das heisst, die Waldensche Umkehrung findet statt).

[1] A. K. BOSE, Exper. *8*, 458 (1952).

The Enzymatic Hydrolysis of Glutathione by *Vibrio Cholerae*

The pathway of metabolism of glutathione, which is normally considered to be comparatively stable towards enzymes because of the γ-linkage in it, is fairly well known in animals. Thus GRASSMANN, DYCKERHOFF, and EIBELER[1] showed that oxidized glutathione was hydrolyzed into glycine and di-glutamyl cystine by pancreas. Later SCHROEDER, MUNRO, and WEIL[2] and SCHROEDER and WOODWARD[3] reported the complete breakdown of reduced glutathione into its constituent amino acids by the enzymes present in the rat kidney. The work of DYER and DU VIGNEAUD[4] on the replacement of cystine

[1] W. GRASSMANN, H. DYCKERHOFF, and H. EIBELER, Z. physiol. Chem. *189*, 112 (1930).
[2] E. F. SCHROEDER, M. P. MUNRO, and L. WEIL, J. Biol. Chem. *110*, 181 (1935).
[3] E. F. SCHROEDER and G. E. WOODWARD, J. Biol. Chem. *120*, 209 (1937).
[4] H. M. DYER and V. DU VIGNEAUD, J. Biol. Chem. *115*, 543 (1936).