from acetic acid and one from dilute acetone gave brownish-yellow prisms, m.p. 222–223°.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.19; H, 5.63.

The compound was moderately soluble in acetic acid, acetone and benzene, less so in ethanol, and insoluble in ligroin. Its solutions exhibited bright bluish-violet fluorescence.

Decarboxylation of By-products of Ring Closure.—Various samples of the tarry residues from the isolation of the dibenzanthracene and dibenzphenanthrene derivatives were decarboxylated with copper in boiling quinaldine and the mixtures worked up as above. In no case was an ether-insoluble product formed, so that no dibenzanthracene derivative had remained in the mixture. None of the samples yielded anything but tarry products; the decarboxylated material, however, had a strong phenolic odor and gave a brown coloration with alcoholic ferric chloride. Steam distillation of the tarry product gave a trace of oily white material, but the amount isolated was insufficient for identification.

3′,7′-Dihydroxy-1,2,5,6-dibenzanthracene (XI).—The dimethyl ether X proved entirely resistant to cleavage by 48% hydrobromic acid in acetic acid, alcoholic potassium hydroxide and alcoholic sodium ethoxide; in each case the starting material was recovered quantitatively. Treatment with anhydrous aluminum chloride in refluxing benzene gave only unchanged ether accompanied by a small amount of oily product. Demethylation of X was, however, accomplished very smoothly by pyridine hydrochloride. The dimethoxy compound (73 mg., 0.22 millimole) was heated with 3 g. of freshly fused pyridine hydrochloride until a homogeneous melt was obtained; dilution of the cooled melt with 20 ml. of water precipitated a very fine white powder which was readily coagulated by heating but darkened somewhat in the process. After filtration this product was dissolved in dilute sodium hydroxide solution (leaving no insoluble residue), reprecipitated with acid, and recrystallized from dilute acetone. Sixty-eight milligrams (100%) of **3′,7′-dihydroxydibenzanthracene** (XI) was obtained as flat grayish needles of analytical purity, m.p. 357–360°.

Anal. Calcd. for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55. Found: C, 85.02; H, 4.58.

The compound is sparingly soluble in acetone, ethanol and acetic acid and the solutions exhibit intense violet fluorescence. The alkaline solution is yellow with bright green fluorescence. On exposure to daylight the material darkens appreciably in a few hours.

The ultraviolet spectrum of XI (Fig. 1) was determined in absolute ethanol from 220 to 420 mμ using a Beckman model DU spectrophotometer.

3′,7′-Diacetoxy-1,2,5,6-dibenzanthracene (XII).—Acetylation of 50 mg. (0.16 millimole) of XI with 5 ml. of acetic anhydride and a few drops of pyridine was complete in about 15 minutes at the boiling point. After decomposition of excess anhydride with water the acetyl derivative XII crystallized from the hot solution in fine, lustrous white plates of m.p. 291–292° (55 mg., 87%). Recrystallization from acetic acid did not change the melting point.

Anal. Calcd. for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60. Found: C, 79.07; H, 4.57.

3′,7′-Diacetoxy-1,2,5,6-dibenzanthra-9,10-quinone (XIII).—The diacetyl derivative XII (55 mg., 0.14 millimole), suspended in 10 ml. of boiling acetic acid, was oxidized by addition of 50 mg. of chromic anhydride; the starting material dissolved rapidly and the quinone XIII (50 mg., 85%) crystallized from the boiling solution in small, well-shaped orange prisms of m.p. 295–298°. One recrystallization from acetic acid gave analytically pure material, m.p. 296.5–298°, in lustrous, slender orange needles.

Anal. Calcd. for $C_{26}H_{16}O_6$: C, 73.58; H, 3.81. Found: C, 73.35; H, 3.84.

The quinone gives a bright crimson vat on warming with alkaline hydrosulfite solution; shaking with air, however, does not decolorize the solution but produces instead a deep maroon solution of the hydrolysis product, the dihydroxyquinone (XIV). Addition of fresh hydrosulfite to the maroon solution gives a cherry-red vat of 3′,7′,9,10-tetrahydroxydibenzanthracene.

3′,7′-Dihydroxy-1,2,5,6-dibenzanthra-9,10-quinone (XIV).—The diacetoxyquinone (XIII) (25 mg., 0.059 millimole) was dissolved in a little alcohol, a few drops of sodium hydroxide solution added, and the mixture refluxed until solution was complete. The resulting deep maroon solution was acidified to yield a gelatinous red precipitate which appeared nearly black when filtered and dried. On brief heating in acetic acid it turned brick red; it dissolved very slowly in a large volume of this solvent and crystallized, on concentration of the solution to 5 ml., in small deep crimson needles, m.p. 375–385° dec. Eight milligrams (40%) of analytically pure material was obtained.

Anal. Calcd. for $C_{22}H_{12}O_4$: C, 77.64; H, 3.56. Found: C, 77.59; H, 3.55.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Stereochemistry of the Leuckart Reaction

BY DONALD S. NOYCE AND FRANK W. BACHELOR

RECEIVED MARCH 15, 1952

The Leuckart reaction has been carried out on 2-methylcyclohexanone to give a mixture of the *cis*- and *trans*-2-methylcyclohexylamines. By analysis of the binary melting point diagram of *cis*- and *trans*-N-(2-methylcyclohexyl)-benzamide the product has been shown to consist of 60% of the *cis*-amine. These results have been interpreted in terms of a transition complex of the immonium salt and formate ion, specifically oriented.

The Leuckart reaction, the formation of amines from carbonyl compounds and ammonia or amines in the presence of formic acid, has been the subject of several recent investigations.[1–5] It has been shown to be suitable for the preparation of tertiary amines[6] and for the preparation of benzylamines.[7]

Recent interest in the mechanism of the reaction has led to a study of the kinetics of the reaction,[3] the reactivity of possible intermediates,[1,2] and a variety of proposals concerning the more intimate pathway of the reduction.[2,3] Less information is available however concerning the hydrogen transfer stage of the reaction. Alexander and Wildman[1] have shown that imines and certain benzyl alcohols may be reduced by formic acid; Pollard and Young[3] suggest a 1,3-migration of hydrogen in a formate ester; while Staple and Wagner[2] suggest reduction of the "carbenium ammonium salt" by hydride transfer.

It seemed of value to us to investigate the stereochemical course of the Leuckart reaction since such

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[1] E. R. Alexander and R. B. Wildman, THIS JOURNAL, **70**, 1187 (1948).

[2] E. Staple and E. C. Wagner, *J. Org. Chem.*, **14**, 559 (1949).

[3] C. B. Pollard and D. C. Young, *ibid.*, **16**, 661 (1951).

[4] V. J. Webers and W. F. Bruce, THIS JOURNAL, **70**, 1422 (1948).

[5] F. S. Crossley and M. L. Moore, *J. Org. Chem.*, **9**, 529 (1944).

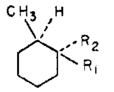
[6] J. F. Bunnett and J. L. Marks, THIS JOURNAL, **71**, 1587 (1949).

[7] K. G. Lewis, *J. Chem. Soc.*, 2249 (1950).

studies have been of value in helping to elucidate the details of other types of reduction reactions. The recent example of Mosher and LaCombe[8] in clarifying the pathway of abnormal reduction in the Grignard reaction, and the partial asymmetric reduction with the Meerwein–Pondorff reaction reported by Doering and Young[9] are illustrative of this point.

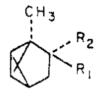
For this purpose the preparation of the isomeric 2-methylcyclohexylamines from 2-methylcyclohexanone was investigated. The mixture of isomeric amines was obtained in 55% yield using the modification of the Leuckart procedure suggested by Webers and Bruce.[4] Since this work was completed, Metayer, Mastagli and Larramona[10] have reported the preparation of 2-methylcyclohexylamine (mixture of isomers) in similar yields. The relative proportion of the isomers was determined from the binary melting point diagram for the system: N-(*cis*-2-methylcyclohexyl)-benzamide (Ia), N-(*trans*-2-methylcyclohexyl)-benzamide (Ib). The mixture of amides from the amine formed in the Leuckart reaction consisted of 60% *cis*-amide and 40% *trans*-amide. The proportions of isomers resulting from the sodium and alcohol reduction of 2-methylcyclohexanone oxime was (*cis* 20:*trans* 80), while the platinum oxide reduction of aceto-*o*-toluidide afforded a mixture containing 80% of the *cis*-amine.

It is of interest to examine other cases in which similar information concerning the stereochemical course of the Leuckart reaction is available. The reduction of camphor[11] by the Leuckart reaction leads to 70% isobornylamine (neobornyl) (IIa) and 30% of bornylamine (IIb). Menthone is reported to give a somewhat more complex mixture containing about 65% of neomenthylamine (IIIa), about 25% of menthylamine (IIIb), and smaller percentages of iso- and neoisomenthylamines.[12] Isomenthone gives a very similar mixture.[12] Ingersoll has reported the very careful characterization of the mixture of amines resulting from the reduction of thujone[13] and from fenchone.[14] Less complete information is available on the amines prepared by the Leuckart reaction from carvomenthone[15] and 2-ethylcyclohexanone.[16]



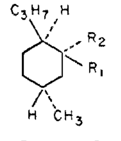
Ia $R_1 = NH_2, R_2 = H$

Ib $R_1 = H, R_2 = NH_2$



IIa $R_1 = NH_2, R_2 = H$

IIb $R_1 = H, R_2 = NH_2$



IIIa $R_1 = NH_2, R_2 = H$

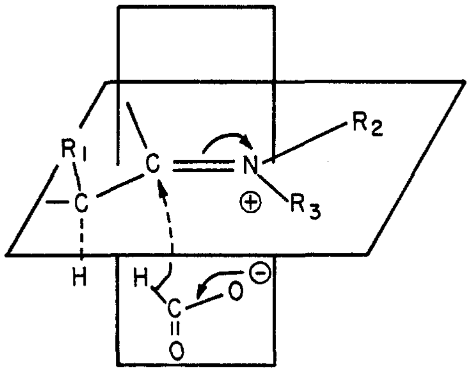
IIIb $R_1 = H, R_2 = NH_2$

These results are all consistent with the postulate that predominant addition of hydrogen occurs from the relatively unhindered side of the molecule leading to the formation of the "more *cis*" amine. Comparison with other methods of reduction and with the preparation of alcohols from ketones[17] is immediately suggested. Such a comparison is outlined in Table I.

TABLE I

Cmpd. reduced Method of reduction →	Product, % 2-Methylcyclohexanone *cis*	 Camphor Isobornyl	 Menthone Neomenthyl
Leuckart	60	70[11]	65[12]
Pt on oxime	85[18]	"Chiefly"[19]	"Chiefly"[20]
Electrolytic		30[21]	
Na–ROH on oxime	20	27[22]	7[23]

The stereochemical specificity of the Leuckart reaction very nearly approximates that of the Meerwein–Pondorff–Verley reduction which has been shown by Doering[9] to involve an activated complex of the quasi-ring type. It is attractive therefore to suggest that in the present case the critical step in the pathway of the reaction is the formation of an activated complex which may be represented (IV) with the orientation of the formate ion conditioned by the dipolar attraction of the immonium ion.



IV

This formulation is consistent with the data available, in particular the successful preparation of tertiary amines,[6,24] the ready reduction of other anils, but only in the presence of high concentration of formate ion,[1] and the rather intricate dependence on water concentration. Smith and MacDonald[24] have suggested reduction of the immonium ion as the pathway for the formation of tertiary amines. It is not inconsistent with the kinetics reported.[3]

Experimental[25]

N-(*cis*-2-Methylcyclohexyl)-benzamide (Ia).—A sample

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[8] H. S. Mosher and E. LaCombe, THIS JOURNAL, **72**, 3994 (1950).

[9] W. von E. Doering and R. W. Young, *ibid.*, **72**, 631 (1950).

[10] M. Metayer, P. Mastagli and H. Larramona, *Bull. soc. chim. France*, 1052 (1950).

[11] R. Leuckart and E. Bach, *Ber.*, **20**, 104 (1897); O. Wallach and J. Griepenkerl, *Ann.*, **269**, 347 (1892).

[12] J. Read and G. J. Robertson, *J. Chem. Soc.*, 2209 (1926).

[13] H. L. Dickison and A. W. Ingersoll, THIS JOURNAL, **61**, 2477 (1939).

[14] A. W. Ingersoll and H. D. Dewitt, *ibid.*, **73**, 3360 (1951).

[15] J. Read and R. G. Johnston, *J. Chem. Soc.*, 226 (1934).

[16] F. E. King, J. A. Baltrop and R. J. Walley, *ibid.*, 277 (1945).

[17] D. S. Noyce and D. B. Denney, THIS JOURNAL, **72**, 5743 (1950).

[18] P. Anziani and R. Cornubert, *Compt. rend.*, **221**, 103 (1945).

[19] K. Alder, G. Stein and H. F. Rickert, *Ann.*, **525**, 221 (1936).

[20] G. Vavon and I. Chilouet, *Compt. rend.*, **203**, 1526 (1936).

[21] J. Tafel and E. Pfeffermann, *Ber.*, **35**, 1515 (1902).

[22] V. N. Krestinskii and I. I. Bardyshev, *J. Gen. Chem. U.S.S.R.*, **10**, 1894 (1940); *C. A.*, **35**, 4366 (1941).

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[24] P. A. S. Smith and A. J. MacDonald, THIS JOURNAL, **72**, 1037 (1950).

[25] Melting points are corrected, boiling points uncorrected. Analyses are by the Microanalytical Laboratory of the University of California.

for the binary melting point diagram was very kindly supplied by Professor W. G. Dauben,[26] m.p. 109.9°.

N-(*trans*-2-Methylcyclohexyl)-benzamide (Ib).—2-Methylcyclohexylamine was prepared by the sodium–alcohol reduction of 2-methylcyclohexanone oxime.[27] After conversion to the benzamide in the usual manner with benzoyl chloride, Ib was obtained by three crystallizations from ethanol, m.p. 151.0°.

Mixed Melting Point Behavior of Ia and Ib.—The binary melting point diagram of N-(*trans*-2-methylcyclohexyl)-benzamide was determined using various mixtures in a modified Hershberg melting point apparatus according to the method described in detail by Cason and Winans.[28] The temperature at which the last crystalline material was no longer visible was easily reproducible to 0.1°. The results are shown in Fig. 1.

2-Methylcyclohexylamine by the Leuckart Reaction.—In a 100-ml. round-bottomed flask fitted with a take-off condenser, were placed 10 g. of 2-methylcyclohexanone, 40.4 g. of formamide and 1 g. of magnesium chloride. The mixture was heated at 175–180° for three hours, the water being formed removed periodically, and the ketone codistilling returned to the reaction mixture. The reaction mixture was poured into 100 ml. of water, and extracted continuously with ether. The ethereal solution was concentrated, and to the crude N-2-methylcyclohexylformamide was added 25 ml. of concentrated hydrochloric acid. This mixture was heated under reflux for three hours, cooled, and neutral compounds removed by extraction with ether. The aqueous solution was basified, saturated with sodium chloride, and continuously extracted with ether. After drying over sodium hydroxide, distillation afforded 5.52 g. (55%) of mixed *cis*- and *trans*-2-methylcyclohexylamine, b.p. 74–75° (52 mm.). Skita[29] reports 153° (760 mm.).

N-(2-Methylcyclohexyl)-benzamide.—To a mixture of 6.04 g. of 2-methylcyclohexylamine and 50 ml. of 20% sodium hydroxide was added with shaking 14.0 g. of benzoyl chloride. The precipitate of crude benzamide was ground and thoroughly washed with sodium carbonate and water. The yield of colorless benzamide was 10.2 g. (88.5%), final melting temperature, 113.1°.

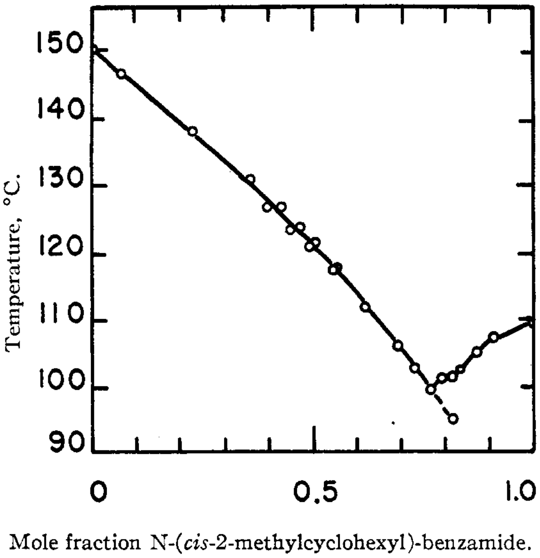

Fig. 1.

Anal. Calcd. for $C_{14}H_{19}ON$: C, 77.42; H, 8.76; N, 6.45. Found: C, 77.54; H, 8.77; N, 6.59.

A small sample was sublimed (97% recovery), and the melting point redetermined in the manner used in constructing the binary melting point diagram, m.p. 114.1° (corresponding to 60% *cis* isomer in this mixture).

From Sodium–Alcohol Reduction of the Oxime.—A sample of the amine prepared by sodium–alcohol reduction of 2-methylcyclohexanone oxime[27] was converted to the benzamide as above. It melted at 141.0° (corresponding to 80% *trans* isomer in this mixture).

From Hydrogenation of Aceto-*o*-toluidide.—Aceto-*o*-toluidide was hydrogenated with platinum oxide in acetic acid solution. The 2-methylcyclohexylamine resulting from hydrolysis of the N-(2-methylcyclohexyl)-acetamide was converted to the benzamide as above. It melted at 98.5° (corresponding to 79% *cis* in this mixture).

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[26] See W. G. Dauben and E. Hoerger, THIS JOURNAL, **73**, 1504 (1951).

[27] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 318.

[28] J. Cason and W. Robert Winans, *J. Org. Chem.*, **15**, 148 (1950).

[29] A. Skita, *Ber.*, **56**, 1014 (1923).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Small-Ring Compounds. X. Molecular Orbital Calculations of Properties of Some Small-Ring Hydrocarbons and Free Radicals[1]

BY JOHN D. ROBERTS, ANDREW STREITWIESER, JR.,[2] AND CLARE M. REGAN

RECEIVED MARCH 17, 1952

The molecular orbital (LCAO) method has been used to calculate the electron delocalization energies, bond orders and free-valence indexes of some cyclic small-ring hydrocarbons and free radicals including a number of cyclobutadiene derivatives. It is concluded that the $(4n + 2)$ π-electron rule of aromatic stability can only be justified by the simple molecular orbital treatment for monocyclic conjugated polyolefins.

One of the substantial successes of the simple molecular orbital theory as developed by Hückel[3] is the prediction that, of the completely-conjugated planar monocyclic polyolefins as cyclobutadiene, benzene, etc., those which possess $(4n + 2)$ π-electrons ($n = 0, 1, 2, 3 \ldots$) will be peculiarly stable by virtue of having fully-filled molecular orbitals with substantial electron delocalization (resonance) energies as compared to the classical valence bond structures. The same rule may be applied[3,4] without known exceptions, to the cyclopropenyl, cyclopentadienyl, cycloheptatrienyl, etc., cations, anions and free radicals although but few quantitative cal-

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[1] Supported in part by the program of research of the United States Atomic Energy Commission under Contract AT(30-1)-905.

[2] U. S. Atomic Energy Commission Post-Doctoral Fellow, 1951–1952.

[3] E. Hückel, *Z. Physik*, **70**, 204 (1931); "Grundzüge der Theorie ungesättiger and aromatischer Verbindungen," Verlag Chemie, Berlin, 1938, pp. 77-85.

[4] (a) H. J. Dauben, Jr., and H. J. Ringold, THIS JOURNAL, **73**, 876 (1951); (b) W. v. E. Doering and F. L. Detert, *ibid.*, **73**, 876 (1951).