dation above was further concentrated to 15 ml. to yield the crude tetracarboxylic acid VIII, which was recrystallized from water with the aid of decolorizing carbon, m.p. 268–271° dec. (block preheated to 260°).

This acid also was prepared by ozonolysis of I.[13] To 3.95 g. (0.025 mole) of I was added 50 ml. of methanol and enough methylene chloride to effect solution at 0°. This solution was treated with a stream of ozonized oxygen[14] (8% O_3 in O_2) for 5.5 hours (twice theoretical). At the end of this time, the solvent was removed under reduced pressure leaving a glassy polymeric methoxy peroxide. To the peroxide was added 35 ml. of 98% formic acid and 17 ml. of 30% hydrogen peroxide. On gentle warming, a vigorous reaction took place (CAUTION!) which ceased after 15 minutes. The solution was heated under reflux for an additional 15 minutes, during which time white crystals formed and a test for peroxides with a potassium iodide solution was negative. The mixture was cooled to 0° and the crystalline precipitate was removed by filtration, yielding 4.1 g., 57%, of crude tetracarboxylic acid VIII, which was recrystallized from water to give 3.6 g. (50%) of pure VIII, m.p. 268–271° dec. (block preheated to 260°).

Anal. Calcd. for $C_{12}H_{14}O_8$: C, 50.35; H, 4.93. Found: C, 50.29; H, 5.01.

The titration of this acid with 0.1 *M* potassium hydroxide gave a smooth curve which did not distinguish the individual carboxyl groups but gave a sharp end-point; neut. equiv. 70.1, calcd. 71.5. The infrared spectra (KBr pellet) showed absorption maxima 2500–3200 (O–H bonded) and 1695–1720 cm.$^{-1}$ (C=O str.).

The Anhydride IX.—A solution of 0.8 g. (0.0028 mole) of VIII in 20 ml. of acetic anhydride was heated at the reflux temperature for 6 hr. The excess acetic anhydride and some acetic acid then was distilled from the reaction mixture and the residue was taken up in hot ethyl acetate. The solution was treated with charcoal, filtered, and the anhydride was crystallized by the addition of benzene, m.p. 239–240°. The infrared spectra showed bands at 1810 and 1765 cm.$^{-1}$ (C=O anhydride).

Anal. Calcd. for $C_{12}H_{10}O_6$: C, 57.60; H, 4.03. Found: C, 57.18; H, 3.76.

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(13) P. S. Bailey, *J. Org. Chem.*, **22**, 1548 (1957).

(14) L. I. Smith and F. L. Greenwood, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 673.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Nitrous Acid Deamination of *cis*-Cyclohexylamine-2-*d*

BY A. STREITWIESER, JR., AND C. E. COVERDALE

RECEIVED FEBRUARY 7, 1959

cis-Cyclohexylamine-2-*d* was obtained in low over-all yield by the reaction of cyclohexene oxide with lithium aluminum deuteride to yield *trans*-cyclohexanol-2-*d*, the tosylate of which was displaced by sodium azide to yield *cis*-cyclohexyl-2-*d* azide which was reduced with lithium aluminum hydride. The reaction of *trans*-cyclohexanol-2-*d* *p*-toluenesulfonate with potassium acetate gave a low yield of *cis*-cyclohexanol-2-*d* acetate which was hydrolyzed to the corresponding alcohol. The alcohol produced by the reaction of *cis*-cyclohexylamine-2-*d* with aqueous nitrous acid was *cis*-cyclohexanol-2-*d;* the solvolytic deamination proceeded with almost complete retention of configuration.

The deamination of aliphatic amines generally proceeds with solvolysis and elimination and often rearrangement. The unrearranged solvolysis products of monofunctional acyclic amines have been found generally to be racemized partially with net inversion of configuration.[1–3] The contrasting results afforded by cyclohexylamines must be considered by any comprehensive mechanism of the reaction. Generalizations derived from simple cyclohexylamines and from decalylamines are that axial amines give extensive elimination but form equatorial alcohol (with inversion) although equatorial amines give equatorial alcohol (with retention) and little or no olefin.[4–6] These results have an important bearing on the reaction mechanism. The difference in the amount of olefin formed from axial and equatorial amines is difficult to explain by the "hot carbonium ion" mechanism.[7–11] The same hot carbonium ion which should be formed from both amines would be expected to give identical products. Because of the significance of these results and the importance of conformational considerations in nitrous acid deamination of other systems,[3,8,12] we thought it desirable to study the stereochemistry of the deamination of a cyclohexylamine containing no additional substituents which could stabilize a particular conformation. For this purpose *cis*-cyclohexylamine-2-*d* and *cis*- and *trans*-cyclohexanol-2-*d* were prepared.

The syntheses of the starting amine and of the two possible alcohol products followed from analogous syntheses of deuterioalcohols in the cyclopentane series.[13] Unfortunately, the various displacement reactions involved were accompanied by extensive elimination and over-all yields were low. The reduction of cyclohexene oxide with excess lithium

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(1) K. B. Wiberg, Dissertation, Columbia University, July, 1950.

(2) P. Brewster, F. Hiron, E. D. Hughes, C. K. Ingold and P. A. D. S. Rao, *Nature*, **166**, 179 (1950).

(3) A. Streitwieser, Jr., and W. D. Schaeffer, THIS JOURNAL, **79**, 2888 (1957).

(4) (a) A. K. Bose, *Experientia*, **9**, 256 (1953); (b) J. A. Mills, *J. Chem. Soc.*, 260 (1953).

(5) (a) W. G. Dauben, R. C. Tweit and C. Mannerskantz, THIS JOURNAL, **76**, 4420 (1954); (b) W. G. Dauben and J. Jiu, *ibid.*, **76**, 4426 (1954); (c) W. G. Dauben, R. C. Tweit and R. L. MacLean, *ibid.*, **77**, 48 (1955).

(6) These generalizations apparently do not apply to axial-steroidal amines, in which elimination and retention of configuration seem to be the rule; *cf.* C. W. Shoppee, D. E. Evans and G. H. R. Summers, *J. Chem. Soc.*, 97 (1957), and C. W. Shoppee, R. J. W. Cremlyn, D. E. Evans and G. H. R. Summers, *ibid.*, 4364 (1957).

(7) (a) J. D. Roberts and M. Halmann, THIS JOURNAL, **75**, 5759 (1953); (b) J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954); (c) A. W. Fort and J. D. Roberts, *ibid.*, **78**, 584 (1956).

(8) D. J. Cram and J. E. McCarty, *ibid.*, **79**, 2866 (1957).

(9) (a) L. S. Ciereszko and J. G. Burr, *ibid.*, **74**, 145 (1952); (b) J. G. Burr and L. S. Ciereszko, *ibid.*, **74**, 5431 (1952); (c) P. S. Bailey and J. G. Burr, *ibid.*, **75**, 2591 (1953).

(10) D. Y. Curtin and M. C. Crew, *ibid.*, **76**, 3719 (1954).

(11) D. Semenov, C.-H. Shih and W. G. Young, *ibid.*, **80**, 5472 (1958).

(12) A. Streitwieser, *J. Org. Chem.*, **22**, 861 (1957).

(13) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, THIS JOURNAL, **80**, 2326 (1958).

aluminum hydride is reported to go in 91% yield.[14] Using equivalent amounts of reducing agent the yields were no better than about 50%; a number of reaction conditions were tried to no avail. The last hydrogen on the lithium aluminum hydride apparently does not react with normal epoxides. The product obtained from the reduction of cyclohexene oxide with lithium aluminum deuteride in 44–51% yield is assigned the structure *trans*-cyclohexanol-2-*d* by analogy with the inversion of configuration observed with other epoxides.[14,15] The conversion of alcohols to amines in good yield and with complete inversion of configuration has been demonstrated in the 2-octyl case by displacement of the tosylate with sodium azide followed by reduction with lithium aluminum hydride.[16] With cyclohexyl tosylate the azide displacement was generally rather poor. Several procedures were tried using lithium or sodium azide and cyclohexyl tosylate or *p*-nitrobenzenesulfonate in different solvents. Cyclohexene was isolated in several experiments. The best yield (40%) of cyclohexyl azide was obtained by refluxing cyclohexyl tosylate with sodium azide in aqueous acetone. The reduction of the azide with lithium aluminum hydride gave variable results—yields of 25–67%.

trans-Cyclohexanol-2-*d* was converted to the tosylate in the usual way with pyridine and tosyl chloride. The tosylate was treated with sodium azide in aqueous acetone and the product was reduced directly to the amine which is assigned the structure *cis*-cyclohexylamine-2-*d* by analogy with previous results[16]; the yield of pure amine was only 9%. The results of the nitrous acid deamination demonstrated that this amine was contaminated by no more than 6% of the *trans*-2-*d* compound (*vide infra*).

Samples of both *cis*- and *trans*-cyclohexanol-2-*d* were required for comparison with the deamination product. The *trans*-alcohol was converted to the *cis* by the same method used in the cyclopentyl series[13]; however, several attempts to displace cyclohexyl tosylate with tetramethylammonium acetate in acetone solution or with potassium acetate in alcohol solution gave yields of cyclohexyl acetate of no better than 7%. The latter procedure applied to *trans*-cyclohexyl-2-*d* tosylate gave ester in 8% yield to which the structure *cis*-cyclohexyl-2-*d* acetate is assigned. The reaction undoubtedly goes by elimination for the most part although the cyclohexene was not recovered.[17] Cleavage of the acetate with lithium aluminum hydride gave *cis*-cyclohexanol-2-*d*. The infrared spectra of samples of the *cis*- and *trans*-alcohols purified by vapor phase chromatography show several differences, some of which are suitable for analytical purposes (*cf*. Table I). For example, the *cis*-alcohol has bands at 8.51, 10.96 and 11.52 μ which are not present in the *trans*-alcohol. The *trans*-alcohol has a strong band at 11.38 μ which is very weak in the *cis*-alcohol. If this weak band is actually due to contamination of the *cis*-alcohol by the *trans*, the intensity corresponds to the presence of only 4% of the *trans*-alcohol.

TABLE I

INFRARED SPECTRA OF DEUTERATED CYCLOHEXANOLS ABSORPTION PEAKS IN μ[a]

Cyclohexanol	*trans*-Cyclohexanol-2-*d*	*cis*-Cyclohexanol-2-*d*
	4.60	4.66
	6.1w	6.1w
6.85s	6.86s	6.88s
7.33	7.36	7.35
	7.42w	7.44sh
7.52	7.50	7.54w
7.71	7.70	7.73
7.96	7.92w	8.00w
8.08	8.08w	8.06w
	8.30	8.28
8.53	8.58w	8.51
8.77	8.82	8.82w
	8.96w	8.98w
9.3–9.4s	9.3–9.4s	9.3–9.4s
9.66w	9.66w	9.70
9.73	9.81w	9.93
	10.09	
10.31s		10.30s
	10.51s	10.61s
10.82	10.81	10.84
	11.17	10.96
11.23	11.22sh	11.24w
	11.38	11.37w
11.61		11.52
11.84	11.75	11.75
11.98w	12.31w	12.21w
12.64	12.66	12.67w
	12.87	

[a] Spectra taken on liquid films 0.035-mm. thick; s, strong; w, weak; sh, shoulder.

The *cis*-cyclohexylamine-2-*d* in aqueous perchloric acid solution was treated with sodium nitrite in an ice-bath. The product alcohol was purified by vapor phase chromatography; the infrared spectrum was virtually identical with that of *cis*-cyclohexanol-2-*d*. The intensity of the band at 11.38 μ corresponds to 6% of the *trans*-alcohol. At least part of this 6% undoubtedly arose during the preparation of the amine; the deamination went with at least 94% retention of configuration.

This result makes these two useful contributions: First, it provides a quantitative lower limit to the amount of net retention of configuration given by an equatorial cyclohexylamine. The *A*-value[19] of an amino group may be taken as about 1[20]; hence, cyclohexylamine should exist as about 16% axial-amine and 84% equatorial-amine. The axial-amine population is expected to lead largely

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[14] L. W. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949).

[15] For further examples, see P. A. Plattner, H. Heuser and M. Feurer, *Helv. Chim. Acta*, **32**, 587 (1949), and W. G. Dauben, R. C. Tweit and R. L. MacLean, THIS JOURNAL, **77**, 48 (1955).

[16] A. Streitwieser, Jr., and W. D. Schaeffer, *ibid*., **78**, 5597 (1956).

[17] The large amounts of elimination observed in our displacement reactions which were run without strong bases (E2 reactions with azide ion and acetate ion are expected to be unimportant under our conditions) provide further support for Winstein's[18] postulate of merged displacement and elimination mechanisms.

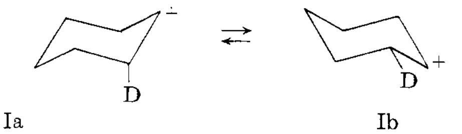
[18] S. Winstein, D. Darwish and N. V. Holness, THIS JOURNAL, **78**, 2915 (1956).

[19] S. Winstein and N. J. Holness, *ibid*., **77**, 5562 (1955).

[20] The *A*-value of an amino group would be expected to fall between the values for hydroxy, 0.8,[19] and methyl, 1.8.[19] The treatment given assumes that equatorial and axial amines react with nitrous acid at the same rate. A difference in reactivity will change the *effective* value of *A*. Such a difference should not materially affect the derived conclusions.

to elimination and the equatorial amine should give almost entirely alcohol by analogy with other cyclohexane systems (*vide supra*). Cyclohexylamine has been reported[21] to yield 80% of cyclohexanol and 16% of cyclohexene in agreement with this analysis. Consequently, the alcohol isolated in deamination should have arisen almost exclusively from the equatorial-amine population. Since part of the 6% *trans*-alcohol probably also arose from axial-amine, the solvolytic deamination of equatorial cyclohexylamine must have proceeded with *at least* 94% retention of configuration. Previous results did not allow a quantitative estimation of the relative amounts of retention and inversion because yields in deaminations are generally not quantitative and the differences in physical and chemical properties of the diastereomeric alcohol products allow for fractionation during isolation. This objection does not apply to the present work in which an isotopic difference is involved.

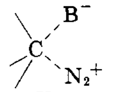
Second, the present results demonstrate that the net retention observed with cyclohexylamines is not due to the presence of other substituents which could stabilize individual conformations. In particular, if a cyclohexyl cation is involved as an intermediate, its reaction with solvent must be faster than the interconversion of conformational isomers of the carbonium ion, Ia $\rightleftarrows$ Ib, even in the absence of stabilizing substituent groups.[22] If such equilibration had occurred, a mixture of *cis*- and *trans*-alcohols would have resulted in our experiment.



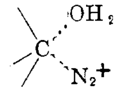
The slowness of this equilibration relative to solvolysis is reminiscent of the results of Benjamin, Schaeffer and Collins[23] who found that the carbonium ion resulting from deamination of 1,1-diphenyl-2-amino-1-propanol undergoes solvolysis faster than rotation about the C–C bond. These results demonstrate the importance of scrutinizing the reactions of individual conformations of carbonium ion intermediates.

With the present results, it is pertinent to review the several explanations suggested for the observed retention of equatorial cyclohexylamines. In the "hot carbonium ion mechanism" for solvolytic deamination, cyclohexylamine gives a high energy cation which could be expected to react predominantly with solvent in an equatorial direction.[8] In the "competing reactions mechanism"[8] equatorial-amino cyclohexylamine generates a "normal" cyclohexyl cation which is also expected to react predominantly along an equatorial path.[5a,12] However, these explanations do not satisfactorily account for the rather high stereospecificity actually observed. A pertinent argument is given. The *A*-value of a *p*-toluenesulfonate group is 1.7 kcal./mole.[19] Solvolysis of an axial-tosylate occurs about 3.5 times as fast as an equatorial tosylate,[19] corresponding to a difference in free energy of activation of 0.75 kcal./mole. If the carbonium ion intermediates which result from the two isomers are considered to have the same free energy content, application of the principle of microscopic reversibility to the reverse processes gives for the difference in free energy of activation for reaction of cyclohexyl cation with *p*-toluenesulfonate anion along an axial path and along an equatorial path simply the difference of the above quantities, or 0.95 kcal./mole; *i.e.*, the reaction of cyclohexyl cation with tosylate anion gives 83% equatorial tosylate, 17% axial tosylate. Comparable figures are expected for reaction of cyclohexyl cation with water.[24] A higher energy, "hot," carbonium ion would be expected to be even less discriminating.[26] This expectation seems valid for a planar "hot" carbonium ion; a tetrahedral "hot" carbonium ion is difficult to reconcile with the partial net inversion of configuration observed with other amines (*vide supra*). Hence, these explanations do not fully account for the substantially greater equatorial reaction actually observed, and a different mechanism must be involved, at least in part.

Starting from the assumption that the transition state for decomposition resembles closely the starting alkyldiazonium cation (*i.e.*, the three remaining bonds in the alkyl group are still approximately tetrahedral), Huisgen and Rüchardt[27] have suggested that the anionic component (B^-) of an assumed ion-pair intermediate could be involved in a front-side displacement (transition state structure II). A diazonium hydroxide ion-pair is not a plausible intermediate in an acidic *aqueous* solution, but their argument provides a justification for the front-side displacement by water proposed by Mills[4b] (transition state structure III).



II



III

This mechanism is consistent with the present results; unfortunately, there is neither other direct evidence nor established analogies for such a mechanism. Further study is clearly indicated. If such a mechanism does indeed operate at least in part as a competing pathway for reaction, it must be added to a growing list of other competing reactions, such as displacement,[1-3,28,29] and elimination (*vide*

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[21] W. Hückel and R. Kupka, *Ber.*, **89**, 1694 (1956).

[22] This result was anticipated by Dauben; *cf.* ref. 5a.

[23] B. M. Benjamin, H. J. Schaeffer and C. J. Collins, THIS JOURNAL, **79**, 6160 (1957).

[24] The *A*-value for a $-OH_2^+$ group should be roughly 1.3 kcal./mole (halfway between –OH and $-CH_3$).[19] The rate of dehydration of an axial alcohol relative to an equatorial is also about 3.5.[19,25] Hence, reaction of cyclohexyl cation with water should give about 70% equatorial, 30% axial product. The quantitative part of our argument depends on the values assumed for *A* and on some further assumptions, *e.g.*, that axial and equatorial alcohols are equally basic. However, reasonable variations in the assumed values will not affect the main point of our argument, namely, that the stereospecificity of the reaction is too high for the presumed mechanism of reaction of cyclohexyl cation with water, especially if the cation is a presumably less selective "hot" carbonium ion.

[25] G. Vavon and M. Barbier, *Bull. soc. chim.*, [4] **49**, 567 (1931).

[26] G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

[27] R. Huisgen and C. Rüchardt, *Ann.*, **601**, 1 (1956).

[28] J. A. Berson and D. S. Ben-Efraim, THIS JOURNAL, **81**, 4083 (1959).

[29] L. G. Cannell and R. W. Taft, Absts. of the 129th Meeting, American Chemical Society, Dallas, Tex., April 12, 1956, p. 46-N.

supra), which have been established to be independent of the formation of carbonium ions, "hot" or "cold." The operation of several competing modes of reaction would seem to render unnecessary the postulate of a special "hot" carbonium ion.

Experimental

***trans*-Cyclohexanol-2-*d*.**—In a typical experiment, 46.8 g. of cyclohexene oxide was reduced with 5.0 g. of lithium aluminum deuteride in ether. The product was distilled through a small column to yield 24.5 g. (51% yield), b.p. 156.5–159.5°, $n^{23.1}$D 1.4649–1.4656, $d^{25.4}{}_4$ 0.9539. Freshly distilled cyclohexanol had $n^{23.1}$D 1.4653, $d^{25.3}{}_4$ 0.9448. The density of the deuterioalcohol corresponds to 0.96 deuterium atom per molecule.[30]

***trans*-Cyclohexyl-2-*d* *p*-Toluenesulfonate.**—In a typical experiment 10.1 g. of *trans*-cyclohexanol-2-*d* was added to 20.9 g. of *p*-toluenesulfonyl chloride in 40 cc. of dried pyridine in an ice-bath and was stirred at 0° for 5 hours. After pouring into 1 l. of ice-cold water and extracting with petroleum ether, the organic phase was washed and dried. Cooling in a Dry Ice-bath gave 19.6 g. of product, m.p. 44.0–44.6°. A second crop of 2.0 g. also was obtained giving a combined yield of 85%.

***cis*-Cyclohexyl-2-*d* Acetate.**—A solution of 21.6 g. of *trans*-cyclohexyl-2-*d* *p*-toluenesulfonate and 19.6 g. of potassium acetate in 100 cc. of absolute alcohol was refluxed for 21 hours. The mixture was poured into ice-water containing sodium carbonate and was extracted with ether. The dried ether extract was distilled yielding 0.99 g. (8.2%) of acetate, b.p. 100–108° (76 mm.), $n^{20.5}$D 1.4390–1.4400.

***cis*-Cyclohexanol-2-*d*.**—The *cis*-cyclohexanol-2-*d* acetate above was treated with 0.6 g. of lithium aluminum hydride in 40 cc. of ether. The product was distilled, collecting 0.46 g. of alcohol, b.p. 147–8°, $n^{22.6}$D 1.4556.

***cis*-Cyclohexylamine-2-*d*.**—A mixture of 52.8 g. (0.207 mole) of *trans*-cyclohexyl-2-*d* tosylate and 20.8 g. of sodium azide in 400 ml. of acetone and 100 ml. of water was refluxed for 22 hours. More water was added and the acetone was distilled; the residual oil was steam distilled and the distillate was saturated with salt and extracted with ether. The dried ether solution was added to 6.8 g. (0.18 mole) of lithium aluminum hydride in ether. After the addition of water, the ether solution was dried and distilled. The yield, after a second distillation, was 1.8 g. (9%) of amine, $n^{21.0}$D 1.4571, b.p. 131–134°.

Deamination of *cis*-Cyclohexylamine-2-*d*.—To a solution of 1.57 g. (0.0157 mole) of *cis*-cyclohexylamine-2-*d* in 10 ml. of water cooled in an ice-bath, was added 3.14 ml. of 6 *N* perchloric acid, and then 1.30 g. of sodium nitrite in 6 ml. of water. After stirring in an ice-bath for 7 hours, 0.25 ml. of 6 *N* perchloric acid and 0.2 g. of sodium nitrite were added. After 22 hours in an ice-bath and 8 hours at room temperature, the mixture was saturated with salt and extracted with ether. The dried ether extract was distilled yielding 0.27 g. of product, b.p. 155–157° (17%). The infrared spectrum contained a band at 6.1 μ indicative of nitrate ester. This band as well as a few others including a sharp band at 6.4 μ indicative of impurities was not present in an alcohol sample purified by vapor phase chromatography with a silicone oil on Celite column. Samples of the *cis*- and *trans*-alcohols were purified in the same manner for comparison purposes. We are indebted to Miss Mary R. S. Weir for these purifications. The infrared spectra used for the quantitative analysis were taken on thin films of the pure liquids in a 0.035-mm. microcell using a Baird Atomic infrared spectrophotometer with sodium chloride optics run at "slow" speed.

BERKELEY, CALIF.

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[30] A. MacLean and R. Adams, THIS JOURNAL, **58**, 804 (1936).

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, CIBA PHARMACEUTICAL PRODUCTS, INC.]

The Reduction of Aromatic Acids and Amides by Sodium in Liquid Ammonia

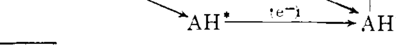
BY M. E. KUEHNE AND B. F. LAMBERT

RECEIVED NOVEMBER 24, 1958

A number of aromatic acids and amides were reduced with sodium in liquid ammonia. Variations in the type of product obtained in these reactions are explained in terms of differing mechanistic pathways. The formation of either dihydro or tetrahydro products is a function of the acidity and positional bond stability of an initial diene. Thus benzoic acid and N-acetyl-*p*-aminobenzoic acid led to 1,4-dihydrobenzoic acid; *p*-toluic acid to 1,2,3,4-tetrahydro-*p*-toluic acid and 1,4-dihydro-*p*-toluic acid; *m*-methoxybenzoic acid to 1,2,3,4-tetrahydro-5-methoxybenzoic acid; 3,4,5-trimethoxybenzoic acid to 1,4-dihydro-3,5-dimethoxybenzoic acid. With ethanol, the amide function is reduced in benzamide, but with *t*-butyl alcohol 1,4-dihydrobenzamide is obtained. Using ethanol, *m*-methoxybenzamide is reduced only with a very large excess of sodium to the 1,4-dihydro product. 3,4,5-Trimethoxybenzamide and a number of N-monosubstituted derivatives led to the corresponding 1,4-dihydro-3,5-dimethoxybenzamides.

The reduction of aromatic compounds by liquid ammonia solutions of alkali metals and a proton source such as alcohol,[1] has experienced a rapid development, led primarily by the school of Birch.[2,3] However reports of simple 2,5-cyclohexadiene carboxylic acids and their derivatives have been limited to 1,4-dihydro-*o*-toluic acid,[4] the unstable 1,4-dihydro-*o*-anisic acid[5] and a 1,4-dihydro-3-methoxybenzoic acid which constitutes ring E of a modified yohimban skeleton.[6] 1,4-Dihydrobenzoic acid[7] was described at the time of writing of this publication.

While it is most probable that the over-all mechanism of these reductions involves addition of two electrons to an aromatic system, followed by protonation of the organic anions,[2,3,8] a more detailed mechanism has remained the subject of much speculation. A number of variants were proposed.[2,3] Thus the reduction of an aromatic molecule A could proceed through protonation of a dianion, either simultaneously or successively or by protonation of an initial ion radical, followed by further reduction and protonation.



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[1] G. W. Watt, *Chem. Revs.*, **46**, 317 (1950).

[2] A. J. Birch, *Quart. Revs.*, **4**, 69 (1950).

[3] A. J. Birch and H. Smith, *ibid.*, **12**, 17 (1958).

[4] A. J. Birch, *J. Chem. Soc.*, 1551 (1950).

[5] M. E. McEntee and A. R. Pinder, *ibid.*, 4419 (1957).

[6] F. L. Weisenborn and H. E. Applegate, THIS JOURNAL, **78**, 2021 (1956).

[7] H. Plieninger and G. Ege, *Angew. Chem.*, **70**, 505 (1958).

[8] New evidence in favor of the nascent hydrogen theory was presented by W. Hückel, M. Maier, E. Jordan and W. Seeger, *Ann.*, **614**, 47 (1958).