Relative pK_a data[9] and gas–liquid chromatographic (g.l.c.) retention data[10] (see Table I) agree with the above assignments (I and II)[12] when compared with the data obtained for the conformationally related epimers of 2-hydroxyquinolizidine,[11] 7-hydroxyindolizidine,[13] and 3-granatanol.[13]

Experimental

Samples of tropine (m.p. 63.0–64.5°, cor.) and pseudotropine (m.p. 106.0–107.5°, cor.) were obtained from Regis Chemical Co. and shown to be epimerically pure and free of any detectable contaminants by gas–liquid chromatography[14] (see Table I). The carbon disulfide and carbon tetrachloride solvents were Baker and Adamson reagent grade chemicals which were used without further purification. Eastman White label tetrachloroethylene was fractionally distilled through a Vigreux column to remove the ethanol stabilizer. All spectra were obtained immediately after the solutions were prepared. In carbon tetrachloride solutions, a fine white precipitate slowly formed upon standing.[15]

The data for the fundamental O–H stretching bands were obtained on a Perkin-Elmer Model 421 grating spectrophotometer, using 1-cm. matched quartz high infrared transmission cells (The Ultracell Co.). The maxima of the free O–H stretching bands were read directly from the frequency dial as summarized in Table I. The 12- to 14-cm.$^{-1}$ shift in the absorption maxima upon going from carbon disulfide to carbon tetrachloride or tetrachloroethylene is in agreement with recent studies.[16]

The first overtone of the hydroxyl stretching band was scanned on a Cary Model 14 spectrophotometer, using 0.020 M carbon tetrachloride solutions in 10-cm. matched quartz cells. The observed maxima (mμ) were as follows: tropine, 1413 (symmetrical band); pseudotropine, 1415 (unsymmetrical band). pK_a values (see Table I) were measured electrometrically[12] and found to agree with those previously reported.[17]

The per cent of boat conformers present in the pseudotropine system was determined to be less than 2% by measuring the concentration of intramolecularly bonded lupinine (Mann Research Laboratories) which was detectable in a pseudotropine solution.[18] Thus, a 1.0×10^{-4} M concentration of lupinine could be detected as a slight bonded absorption ($\tilde{\nu}_{max}$ 3290 cm.$^{-1}$) in a 4.7×10^{-3} M solution of pseudotropine in carbon tetrachloride in a 2-cm. quartz cell. A 4.6×10^{-3} M solution of pseudotropine showed no detectable bonded hydroxyl absorption in the 2-cm. cell.

(9) For substituted N-alkyl 4-piperidinols in the chair conformation, that epimer which has an *anti* diaxial hydroxyl/N-electron pair relationship has been found to be a slightly stronger base (0.4 ± 0.1 pK_a unit at 0.005 μ) than its corresponding *syn* (OH equatorial) epimer. Although not measured under the same conditions, three such pairs of epimeric azabicycloalkanols which were recently reported[6b] apparently also show this pK_a correlation. It is our intention to discuss the pK_a data for an extended series of epimeric amino alcohols more fully at a later date.

(10) Strongly intramolecularly bonded amino alcohols show g.l.c. retention times on a Carbowax column which are significantly shorter than that of their corresponding ketones.[11] Nonintramolecularly bonded amino alcohols have longer retention times than their corresponding ketones. Generally speaking, the equatorial hydroxyl isomer has a longer retention time than its axial epimer.

(11) H. S. Aaron, G. E. Wicks, Jr., and C. P. Rader, *J. Org. Chem.*, **29**, 2248 (1964).

(12) These assignments have also been made on the basis of a recent high resolution n.m.r. study by J. Parello, P. Longevialle, W. Vetter, and J. A. McCloskey, *Bull. soc. chim. France*, 2787 (1963).

(13) H. S. Aaron and C. P. Rader, to be published.

(14) G.l.c. data for this system on an Apiezon L column has recently been reported: C. Van der Vlies and B. C. Caron, *J. Chromatog.*, **12**, 533 (1963).

(15) Presumably the hydrochloride; *cf.* J. Sicher, M. Horak, and M. Svoboda, *Collection Czech. Chem. Commun.*, **24**, 950 (1959); R. F. Collins, *Chem. Ind.* (London), 704 (1957). This phenomenon resulted in an experimental problem only in obtaining spectra of the overtone region on the Cary Model 14 spectrophotometer. Here, the high-intensity light source accelerates the reaction; hence, the available scanning time was limited to a few minutes.

(16) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 371 (1963).

(17) T. A. Geissman, B. D. Wilson, and R. B. Medz, *ibid.*, **76**, 4182 (1954).

(18) These measurements were kindly performed for us by Mr. C. Parker Ferguson of these laboratories.

A Study of the Rhodium Catalyzed Hydrogenation of 1-Naphthol. An Improved Preparation of 1- and 2-Decalols[1]

A. I. MEYERS, W. BEVERUNG, AND G. GARCIA-MUNOZ[2]

Department of Chemistry,
Louisiana State University in New Orleans,
New Orleans, Louisiana 70122

Received April 11, 1963

Due to the interest in recent years in total steroid synthesis wherein the 1-decalones have been employed as a starting material, it seemed advisable to investigate improved methods of obtaining these substances, particularly *via* the 1-decalols. Previous methods involved the hydrogenation of 1-naphthol using platinum catalysts[3] which required several days and relatively large amounts of this costly element. High pressure reduction of 1-naphthol using Raney nickel[4] or Raney copper[5] resulted in low yields and a high degree of hydrogenolysis. Similar results have been obtained with 2-naphthol although in several instances[6] selective ring reduction has been accomplished in high yields. Upon reexamination of several of the methods for the reduction of the naphthols in an attempt to achieve more efficient and complete reaction, the yields could not be improved upon. On many occasions little or no reduction was observed unless considerable care was taken to clean the apparatus to remove catalyst poisons.

The recent interest in rhodium catalysts[7] for aromatic ring hydrogenations at ambient temperatures and moderate pressures (3 atm.) suggested that this element might afford a convenient route for obtaining improved yields of the decalols. The fact that the degree of hydrogenolysis was reportedly[7c,d] small was also attractive.

The hydrogenation of 1-naphthol in ethanol and methanol gave good yields (Table I, entries 1 and 2) of the isomeric decalols in the ratio of 13.3:3.2:1 (integrated areas under gas chromatographic peaks) and a small amount of the isomeric decalones. The major decalol product was isolated and shown to be the *cis,cis* isomer by comparison with an authentic sample.[3b] The two minor components in the decalol mixture were not isolated in sufficiently pure form to afford positive identifications. The degree of hydrogenolysis in these experiments was extremely low as evidenced by a 3% yield of the decalins. The hydrogenation was complete within 12 hr. at room temperature using a starting pressure of 60 p.s.i. When dioxane and ethyl acetate (en-

(1) This study was supported, in part, by funds granted by the National Institutes of Health, DGMS-RG-6248(C5) and AI05611.

(2) Research Associate on leave from the Institute of Chemistry, "Alonso Barba," Madrid, Spain.

(3) (a) W. G. Dauben, R. C. Tweit, and C. Mannerskantz, *J. Am. Chem. Soc.*, **76**, 4424 (1954); (b) C. D. Gutsche and H. H. Peter, *ibid.*, **77**, 5974 (1955); (c) H. E. Zimmerman and A. Mais, *ibid.*, **81**, 3648 (1959).

(4) D. M. Musser and H. Adkins, *ibid.*, **60**, 665 (1938).

(5) J. Jardot and R. Braine, *Bull. Soc. Roy. Sci. Liege*, **25**, 62 (1956).

(6) (a) H. Adkins and G. Krsek, *J. Am. Chem. Soc.*, **70**, 412 (1948); (b) H. J. Dauben, B. C. McKusick, and G. P. Mueller, *ibid.*, **70**, 4179 (1948); G. Stork, *ibid.*, **69**, 576 (1947).

(7) (a) H. Gilman and G. Cohn, "Advances in Catalysis," Vol. 9, Academic Press, New York, N. Y., 1957, pp. 707–715; (b) H. A. Smith and B. L. Stump, *J. Am. Chem. Soc.*, **83**, 2740 (1961); (c) J. H. Stocker, *J. Org. Chem.*, **27**, 2288 (1962); (d) M. Friefelder and R. M. Robinson, *ibid.*, **27**, 284 (1962).

TABLE I

HYDROGENATION DATA[a]

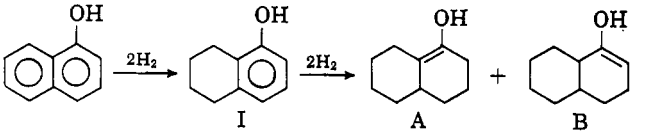
Entry	Solvent	g. of catalyst / g. of acceptor	Reaction time, hr.	% yield[b]	% 1-decalones[c]	% 1-decalols[c]
			1-Naphthol[d]			
1	Ethanol[f]	0.50	12[e]	85	6.7	93.3
2	Methanol[f]	0.50	12	90	10.2	89.8
3	Ethyl acetate	0.50	30	2	...	...
4	Dioxane	0.50	30	2	...	...
5	Acetic acid	0.50	48	75	69.8	30.2
6	Acetic acid	0.50	96	70	68.0	32.0
7	Acetic acid	0.50	120	70	62.5	37.5
8	Acetic acid	1.00	24	90	35.8	64.2
9	Acetic acid	0.75	25	90	37.5	62.5
10	Acetic acid	0.25	72	2	...	...
11	Acetic acid[g]	0.50	36	40	69.5	30.5
12	Acetic acid[h]	0.50	7	64	50.5	49.5
			2-Naphthol[d]			
13	Ethanol[f]	0.50	15	90	6[i]	94.0[i]
14	Acetic acid	0.50	72	75	63.5	36.5

[a] Using 5% rhodium on alumina, 25° (4 atm.). [b] Refers to combined yields of the decalones and decalols after removing the phenolic components. [c] Obtained by triangulation of gas chromatographic peaks and are accurate to ±2.5%. [d] All runs were performed on 10.0 g. of naphthol in 100 ml. of solvent. [e] Refers to length of time required for no further hydrogen absorption by the reaction bottle (not necessarily theoretical hydrogen absorption). [f] Contains 1 ml. of acetic acid per 100 ml. of solvent. [g] Catalyst employed was recovered from entry 5, washed with acetic acid, and dried for 36 hr. at 400°. [h] Reduction interrupted at 50% of theoretical hydrogen absorption. [i] Yields of 2-decalones and 2-decalols, respectively.

tries 3 and 4) were employed as the solvent, the extent of the reduction after 30 hr. was less than 2%. Changing quantities of catalyst and length of reaction time showed no significant changes in behavior. Neither of these solvents therefore proved to be useful for reductions under these conditions.

Hydrogenations using acetic acid as the solvent resulted in considerably more reduction (entry 5) but required 48 hr. before no further pressure drop was observed. Analysis of the products exhibited that the 1-decalones were the major products in the ratio greater than 2:1. The extent of reduction was slightly less than in the case where ethanol was employed although the amount of decalins formed was 8%. When this reduction was repeated allowing for longer reaction times (entries 5–7) the product composition did not change significantly. The high percentage of decalones obtained was found to be due to the inability of the rhodium catalyst to promote reduction of the carbonyl group after extended periods of use. When a fresh sample of the catalyst was employed in the reduction of 1-decalone, the hydrogen absorption was rapid and complete within 15 min. However, when previously used catalyst (recovered from entry 12) was employed, no reduction of 1-decalone occurred after 30 hr. To determine more specifically the rate of loss of catalyst activity, a series of experiments was performed by using progressively aged catalyst (in acetic acid) in the reduction of the decalones. It was found that the catalyst loses most of its activity after 2 hr. of previous use and all of its activity after 4 hr. of previous use. When the catalyst is recovered and then heated (entry 11) it regains a portion of its activity.

The reduction of 1-naphthol was interrupted after 50% of the theoretical hydrogen had been absorbed (entry 12). This required only 7 hr. (it required, as mentioned previously 48 hr. to absorb the theoretical quantity). The products were examined and although no naphthol was present, there was obtained in pure form 5,6,7,8-tetrahydro-1-naphthol (I), along with an almost equal mixture of decalones and decalols. Reduction of I under the usual conditions showed that it reduced at the same rate as 1-naphthol. It is therefore reasonably certain that I is an intermediate in the reduction of 1-naphthol. The fact that no naphthol was found at 50% hydrogenation suggests that the unsubstituted ring reduces quite readily during the initial period of reaction.



It should be noted that since the decalones arise most probably through the intermediate enols A and/or B and since the acetic acid solvent resulted in high percentages of decalones, the reduction probably proceeds primarily to these intermediates. In the early stages of the reduction the catalysts are still capable of promoting the reduction of the carbonyl group, thus resulting in decalols. After approximately 2 hr., the concentration of A and B begins to build up faster than their tautomeric keto form can be reduced and eventually predominates in the product composition.

The reduction of 2-naphthol was also examined in ethanol and in acetic acid and the results are included in Table I (entries 13 and 14).

The effect of varying the amount of catalyst employed in the hydrogenation is also shown in Table I (entries 5 and 8–10). When the catalyst–acceptor ratio was increased to 1.00, the reduction proceeded at a much faster rate and the percentage of decalones was decreased to 35.8% while the decalols were increased to 64.2%. Similar results were obtained when a catalyst–acceptor ratio of 0.75 was used. However, when this ratio was decreased to 0.25, no appreciable reduction occurred after 72 hr. Thus, the reaction rate was significantly dependent upon the weight of the catalyst used. This effect has been observed previously[7b] when this catalyst

was employed in the reduction of hydroxybenzene derivatives.

Experimental

1-Naphthol was obtained from commercial sources and was first distilled *in vacuo* and then recrystallized from aqueous ethanol, m.p. 96–97°. The rhodium on alumina (5%) was purchased from Engelhard Industries, Newark, N. J., and used directly. All solvents (acetic acid, methanol, ethyl acetate, and dioxane) were reagent grade and used without further purification. The ethanol employed was the usual 95% azeotropic mixture which was freshly distilled.

Reduction Procedures.—The hydrogenations were performed in a Parr low-pressure apparatus. All metal parts in contact with the reaction bottle were cleaned with acetone and the rubber stopper was soaked overnight in 35% sodium hydroxide. The reductions were carried out at room temperature at an initial hydrogen pressure of 50–60 p.s.i. After the hydrogen absorption had ceased to change significantly for several hours the reaction was assumed complete and the catalyst was removed by filtration. The products were isolated in a fashion depending upon whether the hydrogenation solvent was (1) ethanol, dioxane, ethyl acetate, methanol, or (2) acetic acid. If the solvent was 1 it was removed under vacuum using a rotary evaporator and the residue was dissolved in benzene. The resulting solution was washed with 10% sodium hydroxide and then with water. After drying the benzene solution over sodium sulfate the benzene was partially evaporated and the concentrated solution was analyzed by gas chromatography. The instrument settings for this analysis were always the same; column temperature 150°, helium flow 50 ml./min., column composition 10% Carbowax 20M on chromsorb P (nonacid-washed), column length 8 ft. If the solvent was acetic acid (2), the reaction mixture was neutralized with 20% sodium hydroxide and then extracted with benzene, dried, and concentrated as above.

Analytical Methods.—The identification of decalones (*cis* and *trans*) and the decalols (three isomers) were made by comparing retention times with authentic samples of mixtures of *cis* and *trans* decalones, and of the three decalols. The relative amounts of decalones and decalols were calculated by triangulation of the peaks. The method was checked by using standard mixtures of the two compounds and found to be accurate to ±2.5%. All reduction experiments were repeated at least three times and the calculated amounts did not differ for each run by more than 1%.

***cis,cis*-1-Decalol.**—The ethanolic solution from the hydrogenation of 10.0 g. of 1-naphthol and 5.0 g. of 5% rhodium on alumina was concentrated and worked up as described above. The residue, which contained 93.3% decalols and 6.7% decalones, was recrystallized from hexane and then from petroleum ether (b.p. 100°) to yield 6.6 g. of pure *cis,cis*-1-decalol, m.p. 93–94° (lit.[3b] 94°).

Reaction of a Schiff Base with Nitrogen Tetroxide. A Novel Synthesis of an Anhydrous Diazonium Salt

RICHARD M. SCRIBNER

Contribution No. 983 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

Received June 18, 1964

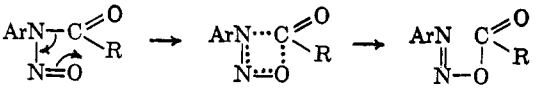
In connection with our recently published[1] study of the chemistry of nitrogen dioxide, we have noted an interesting reaction in which a Schiff base of an aryl amine is converted in high yield to an anhydrous[2] diazonium salt. Although the scope of this reaction has not been investigated, we are reporting it because it appears to bear a mechanistic resemblance to the well-known thermal decomposition of N-nitrosamides, which in recent years has received considerable attention.[3]

Benzylidene aniline reacts with a solution of nitrogen tetroxide in ether to afford a precipitate of benzenediazonium nitrate in about 90% yield. (Caution[4]!)

$$C_6H_5N{=}CHC_6H_5 + N_2O_4 \longrightarrow C_6H_5N_2{}^+NO_3{}^- + C_6H_5CHO$$

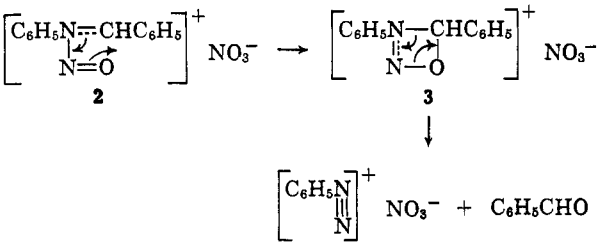
Benzaldehyde can be isolated from the ethereal solution as the 2,4-dinitrophenylhydrazone.

Huisgen[5] and Hey[6] and their collaborators have studied the first-order decomposition of acylarylnitrosamines and have concluded that these reactions involve rearrangements to diazoesters. They found evidence for the participation of a four-membered cyclic transition state (1), formed by an intramolecular nucleophilic attack of the oxygen of the nitroso function at the electrophilic carbon atom of the carbonyl group.



1

In view of the known ability of nitrogen tetroxide to nitrosate secondary amines and N-alkylamides,[7] it seems likely to us that reaction of nitrogen tetroxide with benzylidene aniline would first produce an N-nitrosonium nitrate 2.[8] By a reaction analogous to the formation of 1, intramolecular attack of the nitroso oxygen at the strongly electrophilic carbon atom of the



2 3

nitrite to the appropriate amine salt suspended in cold glacial acetic acid [*cf.* also W. Smith and C. E. Waring, *J. Am. Chem. Soc.*, **64**, 469 (1942)]. Recently L. Friedman and F. M. Logullo [*ibid.*, **85**, 1549 (1963)] reported the synthesis of benzynes by diazotization of anthranilic acids with alkyl nitrites in aprotic media, *e.g.* refluxing dichloromethane.

(3) E. H. White (Abstract of Papers, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964, p. 2N) discussed the nitrosamide decomposition as one of the three general methods available for the conversion of aliphatic amines into alcohols or their derivatives. An interesting example of the use of this stereospecific reaction for the synthesis of epitestosterone has been reported recently by F. Alvarez [*Steroids*, **2**, 3 (1963)].

(4) This salt is no exception to the well-known generalization that aryldiazonium nitrates are explosive and extremely sensitive to shock in the dry state. Only very small batches of such compounds should be prepared at a time if they are to be isolated.

(5) R. Huisgen and L. Krause, *Ann.*, **574**, 157 (1951).

(6) D. H. Hey, J. Stuart-Webb, and G. H. Williams, *J. Chem. Soc.*, 4657 (1952).

(7) E. H. White, *J. Am. Chem. Soc.*, **77**, 6008 (1955), and J. L. Riebsomer, *Chem. Rev.*, **36**, 157 (1945).

(8) It is interesting to note, however, that R. Ciusa and U. Pestalozza [*Gazz. chim. ital.*, [I]**39**, 304 (1909); *Chem. Abstr.*, **3**, 1168, 1531 (1909)] reported that nitrogen tetroxide in ether reacts with the phenylhydrazones of aromatic aldehydes primarily, and in some cases almost quantitatively, by nitration of the benzal carbon atom.

$$ArCH{=}NNHAr + N_2O_4 \longrightarrow ArC(NO_2){=}NNHAr$$

In some instances small amounts of aryldiazonium nitrate were found among the products of reaction.