TABLE I

MAXIMUM YIELD DATA (%) FOR OXIDATION OF DIVINYLCARBINOL WITH MANGANESE DIOXIDE

Manganese dioxide	Ratio divinyl carbinol/manganese dioxide 1/5	1/10	1/15
Type A	10–20	28–50	30–50
Type B	5–12	15–26	20–27
Type C	5–15	23–41	22–40
Type D	18–20	40–49	39–50

six hours. Extended reaction periods did not greatly improve the yield of the ketone.

The 3-pentadienone was isolated by vacuum distillation in the presence of a polymerization inhibitor, hydroquinone. It was identified by elemental analysis, refractive index, and infrared spectroscopy. Vapor phase chromatography showed the isolated product to be 98–99% pure, containing a small quantity of the carbinol as an impurity in some instances.

In one reaction the ketone was isolated as the 2,4-dinitrophenylhydrazone in a 96% yield indicating that a considerable part of the product may have been lost during its isolation. Attempts to prepare the oxime and dimethyl ketal were unsuccessful using conventional methods due to polymerization of the ketone.

Experimental[8]

Divinylcarbinol was prepared by the method of Ramsden.[9] The oxidation of the carbinol was carried out as follows: To a 200-ml. three-necked flask equipped with mechanical stirrer, condenser, and thermometer (all outlets covered with Drierite tubes) was introduced 10.0 g. (0.12 mole) of divinylcarbinol in 150 ml. of dry chloroform. One hundred grams of manganese dioxide (type A) was added over a period of 15 min. and the mixture stirred rapidly at ambient temperature for 24 hr. The infrared spectrum of the solution indicated a carbonyl-containing compound and only a trace of residual carbinol. The solid material was removed by filtration and the major part of the solvent removed at reduced pressure until the volume was reduced to 25–30 ml. The liquid residue to which 0.25 g. hydroquinone had been added was then distilled through an 18-in. semimicro spinning band column to give 4.97 g. (50%) 3-pentadienone, b.p. 37–38° (50 mm.), $n^{20}\text{D}$ 1.4497 [reported[2] b.p. 41–44° (75 mm.), $n^{20}\text{D}$ 1.4485]. The infrared spectrum showed absorption at 3050 cm.$^{-}$ (C—H valence stretching absorption), 1660 cm.$^{-1}$ (C=C stretching vibration absorption) and 1672 cm.$^{-1}$ (C=O). The latter absorption band is consistent with that reported by Bellamy[10] for the carbonyl absorption in vinyl ketones (1685–1665 cm.$^{-1}$). This general procedure was used employing all four types of manganese dioxide.

Anal. Calcd. for C_5H_6O: C, 73.17; H, 7.31. Found: C, 73.10; H, 7.39.

The ketone was examined by vapor phase chromatography[11] and found to be 98–99% pure in all instances.

The 2,4-dinitrophenylhydrazone of 3-pentadienone was obtained by treating a solution of the ketone [from 2.0 g. of divinylcarbinol and 20.0 g. of manganese dioxide (type C) in 50 ml. chloroform] with a solution of 4.0 g. of 2,4-dinitrophenylhydrazine and 8.0 ml. of concentrated sulfuric acid in 90 ml. of methanol. An immediate orange precipitate appeared which was collected by filtration and recrystallized from 95% ethanol, melting with polymerization at 95–102°. The yield was 6.0 g. (96%).

Anal. Calcd. for $C_{11}H_{10}N_4O_4$: C, 50.38; H, 3.81; N, 21.37. Found: C, 50.21; H, 3.71; N, 21.49.

---

[8] All melting and boiling points are uncorrected.

[9] H. E. Ramsden, *et al.*, *J. Org. Chem.*, **22**, 1602 (1957).

[10] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1959, p. 136.

[11] Vapor phase chromatography was carried out on an Aerograph Gas Chromatographic Instrument, Model A-100C, employing a 5-ft. dinonylphthalate column at 75°.

Hydroxy Alkylation of Primary Aromatic Amines

N. V. BRINGI[1] AND P. V. DESHMUKH

Research Laboratories, Hindustan Antibiotics Ltd., Pimpri (near Poona), India

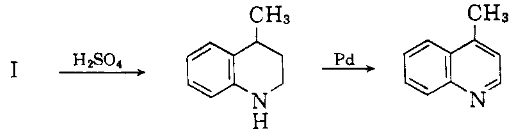
Received May 21, 1962

The one-step reaction of aniline with 1,3-butanediol in the presence of Raney nickel[2] furnished 4-anilino-2-butanol[3] I (R = C_6H_5) in 20% yield.

$$RNH_2 + HOCH_2\text{—}CH_2CHOHCH_3 \xrightarrow{Ni} \underset{\text{I}}{RNHCH_2CH_2CHOHCH_3}$$

o-Anisidine, *p*-anisidine, ethyl *p*-aminobenzoate, α-naphthylamine, and β-naphthylamine reacted similarly.[4] The physical properties and analyses of these products are shown in Table I.

Treatment of I (R = C_6H_5) with concentrated sulfuric acid at room temperature gave *dl*-1,2,3,4-tetrahydrolepidine in 90% yield. The latter was readily dehydrogenated in near quantitative yield to lepidine. 4-*p*-Anisidino-2-butanol I (R = *p*-$CH_3OC_6H_4$) gave *dl*-6-methoxy 1,2,3,4-tetrahydrolepidine in 60% yield.[5] Dehydrogenation furnished 6-methoxylepidine.



4-*p*-Carbethoxyanilino-2-butanol failed to undergo the intramolecular Friedal–Crafts reaction

---

[1] To whom inquiries should be addressed.

[2] Raney nickel induced alkylation of primary aromatic amines with primary and secondary alcohols is described by G. N. Kao, B. D. Tilak, and K. Venkataraman, *J. Sci. Ind. Res.* (India), **14B**, 624 (1955); R. G. Rice and E. J. Kohn, *J. Am. Chem. Soc.*, **77**, 4052 (1955); C. Ainsworth, *ibid.*, **78**, 1835 (1956); J. Horyna and O. Cerny, *Chem. listy*, **50**, 381 (1956); *Collection Czech. Chem. Commun.*, **21**, 906 (1956); R. G. Rice, E. J. Kohn, and L. W. Daasch, *J. Org. Chem.*, **23**, 1352 (1958).

[3] N. V. Bringi and P. V. Deshmukh, *Hindustan Antibiotics Bull.*, **3**, 66 (1960), report the preparation of 4-anilino-1-butanol from the primary glycol.

[4] J. Lichtenberger and L. Dürr, *Bull. soc. chim. France*, 664 (1956), report the preparation of I (R = C_6H_5, and R = *o*-$CH_3OC_6H_4$) by the reaction of 1,3-butanediol cyclic sulphate and the amine followed by hydrolysis.

[5] This has been prepared previously by catalytic hydrogenation of 6-methoxylepidine; M. Levitz and M. T. Bogert, *J. Org. Chem.*, **10**, 341 (1945).

TABLE I

$RNHCH_2CH_2CHOHCH_3$

I

I, R =	Yield, %	B.p. or m.p./mm.	Formula	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	Infrared spectra[a] μ
C_6H_5—	20	124/1.3 61[b]								2.9, 6.22, 6.65, 7.25, 7.6, 8.9
p-$CH_3OC_6H_4$—	40	162/2[c]	$C_{11}H_{17}NO_2$	67.69	8.71	7.18	67.79	8.50	7.21	2.88, 6.14, 6.55, 7.22, 7.65, 8.8
o-$CH_3OC_6H_4$—	10	152/3[d]								2.88, 6.18, 6.65, 7.25, 7.4, 7.65, 8.8
p-$C_2H_5O\overset{O}{\overset{\|}{C}}C_6H_4$	28	104[e]	$C_{13}H_{19}NO_3$	65.81	8.01	5.90	65.81	7.93	6.10	2.88, 5.85, 6.15, 6.5, 7.25, 7.41, 8.95
α-Naphthyl	10	168/1.7[f]	$C_{14}H_{17}NO$	78.13	7.90	6.51	77.73	8.12	6.50	2.9, 6.15, 6.3, 6.55, 7.25, 7.45, 8.95
β-Naphthyl	12	78[g]	$C_{14}H_{17}NO$	78.13	7.90	6.51	77.34[h]	7.81	6.50	2.9, 6.1, 6.22, 6.55, 7.25, 7.4, 8.87

[a] Solids in chloroform and liquids in film. [b] Colorless crystals from hexane; lit.,[4] m.p. 61°. Picrate crystallized from benzene, m.p. 118°. Calcd. for $C_{16}H_{18}N_4O_8$: C, 48.73; H, 4.57; N, 14.21. Found: C, 48.98; H, 4.31; N, 14.20. [c] $n^{25}\text{D}$ 1.5501. [d] Lit.,[4] b.p. 158–160°/8 mm., $n^{25}\text{D}$ 1.5508. [e] The compound was obtained by chilling the benzene filtrate of the reaction mixture after addition of one volume of ether or by chromatography of benzene solution on ethyl acetate-washed alumina and elution with 2:1 benzene–ether. Crystals from benzene. [f] $n^{25}\text{D}$ 1.6553. [g] Colorless crystals from benzene–petroleum ether (b.p. 60–80°). [h] Even though the carbon analysis was low, the infrared spectrum was satisfactory.

and was recovered unchanged on esterification after forty hours at room temperature. Similarly the amino alcohol from α-naphthylamine failed to close either at room temperature or at 80° for four hours.

The synthesis of tetrahydrolepidines in two steps from substituted primary amines is thus a variant from the established methods of synthesis.

Experimental[6]

The following procedure for the preparation of 4-p-anisidino-2-butanol served as a general procedure for the alkylation of other primary amines.

A mixture of p-anisidine (12.3 g.; 0.1 mole) and 1,3-butanediol (10 g.; 0.11 mole) in benzene (60 ml.) containing 2 drops of 4% aqueous sodium hydroxide was refluxed with Raney nickel[7] (20 g.) for 30 hr. The mixture was filtered, nickel washed with ether, and the filtrate was extracted with 10% hydrochloric acid. The acidic extract was made strongly basic and re-extracted into ether. The product obtained after removal of ether was fractionally distilled (see Table I.).

dl-1,2,3,4-Tetrahydrolepidine.—A solution of the alcohol I (R = C_6H_5) (200 mg.) in concentrated sulfuric acid (1 ml.) was kept at room temperature for 24 hr. The mixture was poured into crushed ice, made alkaline, and extracted with ether. Removal of ether and distillation yielded 160 mg. (90%) of dl-1,2,3,4-tetrahydrolepidine, b.p. 106°/7.5 mm. (lit.,[8] b.p. 110°/8 mm.). The infrared spectra of the compound was indistinguishable from the spectra of authentic compound prepared by sodium and alcohol reduction of lepidine.[9] The N-benzoyl derivative crystallized from alcohol and had m.p. and mixed m.p. with authentic specimen 138° (lit.,[8] m.p. 138°).

The picrate derivative, prepared in benzene solution, crystallized from benzene in yellow, feathery needles and had m.p. and mixed m.p. with authentic specimen 138° (reported[10] m.p. 157°).

Anal. Calcd. for $C_{16}H_{16}N_4O_7$: C, 51.06; H, 4.26; N, 14.89. Found: C, 51.20; H, 4.50; N, 14.74.

dl-6-Methoxy-1,2,3,4-tetrahydrolepidine.—The alcohol I (R = p-$CH_3OC_6H_4$) (750 mg.) was dissolved in concentrated sulfuric acid (3 ml.) and immediately poured into crushed ice. The solution was made alkaline and extracted with ether. Removal of ether and distillation of the residue yielded 410 mg. (60%) of dl-6-methoxy-1,2,3,4-tetrahydrolepidine, b.p. 118–120°/0.9 mm. (lit.,[5] b.p. 114–115°/0.5 mm.).

Dehydrogenation of the above tetrahydrolepidine (400 mg.) in the presence of palladium–charcoal (10%; 150 mg.) and p-cymene (5 ml.) under reflux in a nitrogen atmosphere for 10 hr. gave after usual work-up 350 mg. (90%) of 6-methoxylepidine; picrate, m.p. 224° (lit.,[11] m.p. 224–225°).

Acknowledgment.—We thank Dr. M. J. Thirumalachar and Dr. D. S. Bhate for their interest in the work.

---

[6] Melting points are uncorrected. We are thankful to A. V. Patankar for microanalysis.

[7] Raney nickel was prepared from nickel-aluminum alloy (B.D.H.) according to the method described in A. I. Vogel's "A Textbook of Practical Organic Chemistry," 3rd ed., Longmans, Green and Co., New York, N. Y., 1956, p. 871.

[8] J. C. Sauer and H. Adkins, *J. Am. Chem. Soc.*, **60**, 402 (1938).

[9] A. A. Zats and V. V. Levchenko, *Zh. Obshch. Khim.*, **22**, 2076 (1952); *Chem. Abstr.*, **47**, 9328 (1953).

[10] A. Chichibabin and C. Barkoysky, *Compt. rend.*, **212**, 914 (1941).

[11] A. T. Babayan and N. P. Gambaryan, *Sb. Statei Obshch. Khim., Akad. Nauk SSSR*, **1**, 666 (1953); *Chem. Abstr.*, **49**, 1048 (1955).

Thermal Elimination Reaction of Aliphatic Amine Salts

C. AINSWORTH AND NELSON R. EASTON

The Lilly Research Laboratories,
Eli Lilly and Company, Indianapolis, Indiana

Received January 29, 1962

We recently reported[1] the synthesis of highly hindered aliphatic tertiary amine salts of the type

---

[1] C. Ainsworth and N. R. Easton, *J. Org. Chem.*, **26**, 3776 (1961).