prisms sintered above 176° and melted with strong effervescence at 181°.

Anal. Calcd. for $C_{18}H_{22}N_2O$: C, 72.44; H, 7.44. Found: C, 72.51; H, 7.65.

Summary

By application of the Mannich reaction to 3-acetyl-9-methylcarbazole, followed by reduction, 9-methylcarbazolyl amino alcohols have been prepared, in which the side chain $CHOHCH_2$-CH_2NR_2 ($-NR_2$ = dimethylamino, diethylamino, tetrahydroisoquinolino) is located at the 3-position. The Friedel–Crafts reaction with 9-acetylcarbazole and chloroacetyl chloride yields 2-chloroacetyl-9-acetylcarbazole, not the 3-derivative as claimed by other investigators. By amination of 2-chloroacetylcarbazole and reduction of the dialkylamino ketone, 2-(2-diethylamino-1-hydroxyethyl)-carbazole was obtained.

WASHINGTON, D. C. RECEIVED OCTOBER 16, 1940

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Catalytic Dehydrogenation of Tetralin and 1,2,3,4-Tetrahydro-naphthol-2 in the Liquid Phase

BY HOMER ADKINS AND WILLIS A. REID

In the course of attempts to develop practical and useful methods for the catalytic dehydrogenation in the liquid phase, a study has been made of the behavior of tetrahydronaphthalene and 1,2,3,4-tetrahydronaphthol-2 over Raney nickel and copper chromite catalysts. Earlier work had shown that ethylene was a useful acceptor for the hydrogen split from alcohols.[1] The irreversibility of the second reaction at 280° made it possible to

$$RCH_2OH \rightleftarrows RCHO + H_2$$

$$C_2H_4 + H_2 \longrightarrow C_2H_6$$

drive the first reaction to the right and thus enable aldehydes to be obtained in excellent yields.

Attempts thus to use ethylene as an oxidizing agent for hydronaphthalenes were not successful, for ethylene underwent polymerization to a light colored oil in the steel reaction vessel at 300 to 350° under a pressure of 100 to 200 atmospheres. When Raney nickel was present in the reaction vessel carbon was formed from the ethylene.

Tetralin under 60 atm. of nitrogen was stable over copper chromite but underwent dehydrogenation over Raney nickel at 300 to 350°. The reaction mixture might contain four different compounds, decalin, tetralin, dihydronaphthalene, and naphthalene.[2] It is not feasible to separate such a mixture into its components by fractional distillation. However, naphthalene forms a picrate and so may be estimated and separated from the other components of the mixture. The method was carefully worked out using mixtures of tetralin and naphthalene.

The results of typical experiments on the dehydrogenation of tetralin over Raney nickel are recorded in Table I. The figures given show that at 350° from 66 to 78% of the tetralin was converted to naphthalene within four hours. The highest yield was obtained when a rather large ratio of nickel was used. At 300° the yield of naphthalene is considerably lower, being from 31 to 45%.

TABLE I

DATA ON DEHYDROGENATIONS[a]

Moles	Catalyst, g.	Temp., °C.	Original pressure of gas in atm.	% yield of naphthalene[1] or β-naphthol[2]	
		Tetrahydronaphthalene			
0.15	2 Ni	300	33 N_2	45[1]	
.30	4 Ni	300	36 N_2	42[1]	
.15	2 Ni	350	36 N_2	71[1]	
.30	4 Ni	350	30 N_2	67[1]	
.15	8 Ni	350	35 N_2	78[1]	
		1,2,3,4-Tetrahydronaphthol-2			
0.135	8 Ni	350	33 C_2H_4	20[2]	60[1]
.135	8 Ni	250	35 C_2H_4	18[2]	64[1]
.135	10 $CuCr_2O_4$	300	65 N_2	76[2]	
.135	5 $CuCr_2O_4$	300	33 C_2H_4	67[2]	
.135	2.5 $CuCr_2O_4$	300	33 C_2H_4	63[2]	

[a] All of the reaction mixtures were held at the indicated temperature for 4 hours. All of those containing nickel also contained an amount of ethyl alcohol approximately equivalent to the weight of nickel. In addition the reaction mixtures of 1,2,3,4-tetrahydronaphthol-2 contained 20 ml. of dry dioxane.

The mixture of hydrocarbons left after the removal of the naphthalene as the picrate was examined. It was shown, if the picrate method

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[1] Reeve and Adkins, THIS JOURNAL, **62**, 2874 (1940).

[2] Zelinski, *Ber.*, **56**, 1924 (1923), stated that over platinum at 300° tetralin disproportionates to decalin and naphthalene. Linstead reported that no decalin was formed in his experiments under similar conditions. *J. Chem. Soc.*, 1146 (1937).

was applied to a synthetic mixture containing decalin and tetralin, that these compounds could be recovered after the separation of the naphthalene. No decalin could be found among the residual hydrocarbons and so it must be concluded that little or none was produced by disproportion of tetralin.

Dihydronaphthalene was also apparently produced by dehydrogenation of tetralin. The evidence on this point is as follows. If the mixture of products from dehydrogenation containing 35% naphthalene was submitted to hydrogenation over copper chromite, tetralin was the sole product. This fact demonstrates that during the dehydrogenation there had been no modification of the ring structure and that the unknown compound present is readily hydrogenated to tetralin. The amount of hydrogen absorbed in the hydrogenation of the mixture was in excess of that for the hydrogenation of the amount of naphthalene known to be present. In several experiments it was ascertained that the excess of hydrogen absorbed was sufficient for the conversion of about 0.067 mole of dihydronaphthalene to tetralin. This agrees almost exactly with the amount of material not otherwise accounted for as naphthalene or tetralin in the mixture of products after dehydrogenation.

It seems reasonable to conclude that at 300 to 350° over Raney nickel an equilibrium is set up between tetralin, dihydronaphthalene and naphthalene. These compounds are apparently present in the mixture in approximately the ratio 35:25:40 at 300°. At 350° the amount of naphthalene has been almost doubled at the expense of the other two components of the mixture.

When 1,2,3,4-tetrahydronaphthol-2 was heated with Raney nickel at 250 or 350° for four hours naphthalene was found to the extent of 60 to 64% and β-naphthol to the extent of about 20%. However, the latter substance was produced in much higher yields over copper chromite. Under the most favorable conditions the yield of β-naphthol over copper chromite was 76% with no more than 1% of naphthalene. The presence of the hydroxyl group in the tetralin nucleus considerably facilitates the dehydrogenation of the ring, for while copper chromite was not active against tetralin even at 350° this catalyst induced the dehydrogenation of the alcohol to take place rapidly at 300°.

Both tetralin and 1,2,3,4-tetrahydronaphthol-2 were obtained by catalytic hydrogenation of naphthalene and β-naphthol, respectively, over copper chromite. With this catalyst at 200° there is no tendency to hydrogenate the second ring of the naphthalene nucleus. The yields in both cases were about 80%. It is interesting to note that while naphthalene, subjected to the most rigorous purification, requires a temperature of about 190° for hydrogenation to tetralin over copper chromite, a sample of naphthalene obtained by the dehydrogenation of tetralin was hydrogenated completely to tetralin at 150°.

Tetralin.—Resublimed naphthalene (m. p. 80–81°) was purified by shaking 400 g. in 300 ml. of dry alcohol with 40 g. of Raney nickel at 100° under 75 atm. pressure of hydrogen for one hour. The naphthalene was dissolved away from the nickel with acetone, the solution filtered and the solvent evaporated. In an alternative method 350 g. of naphthalene was refluxed with 25 g. of sodium for four hours. The naphthalene was distilled from the sodium through a Vigreux column, 10 cm. in length. The naphthalene (320 g.) in 500 ml. of dry alcohol with 50 g. copper chromite was hydrogenated at 150 to 200 atm. pressure at 200° for seven hours. The catalyst was removed by centrifuging and washed with 95% alcohol. After fractionation through a modified Widmer column[3] at 46–47° (2 mm.) or 78–78.5° (10 mm.), or 86.5–87.5° (17 mm.), 260 g. of product $n^{25}\text{D}$ 1.5395 was obtained.

1,2,3,4-Tetrahydronaphthol-2.—β-Naphthol (300 g. U. S. P. grade) was distilled from a Claisen flask containing 30 g. of Raney nickel to give 255 g. of β-naphthol suitable for hydrogenation. β-Naphthol (360 g. in 500 ml. of dry alcohol) was hydrogenated over 50 g. of copper chromite for seven hours at 200° under 200 atm. pressure of hydrogen. After centrifuging and removing the solvent, the product was fractionated as for tetralin to give 282 g. of product, $n^{25}\text{D}$ 1.5630, b. p. 130–131° (6.5 mm.). The phenylurethan had a m. p. 96.5–97.5°.

Dehydrogenations were carried out by shaking the sample and catalyst in a steel vessel of 180-ml. capacity under various pressures of ethylene or nitrogen. The procedure was the same as in a hydrogenation. The product was removed from the bomb with ether, the catalyst centrifuged and washed with three 30-ml. portions of ether. The solvent was removed through a modified Widmer, and the last traces at 70° (25 mm.) for ten minutes. The recovery of materials was 87 to 92%.

Estimation of Naphthalene Content of Reaction Mixtures.—For analysis, 1 g. of solvent-free material was dissolved in a mixture of 10 ml. of 95% alcohol, 33 ml. of a saturated solution of picric acid in 95% alcohol and heated to boiling. The picrate separated in yellow needles on cooling. Naphthalene (0.2 g.) with tetralin (0.8 g.) gave 0.15 g. of picrate. One gram of naphthalene gave 1.9 g. of picrate. Between these two extremes of samples containing 20 and 100%, respectively, of naphthalene, the weight of picrate was found to be a linear function of the weight of naphthalene in the sample.

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(3) Smith and Adkins, THIS JOURNAL, **60**, 662 (1938).

The naphthalene content of mixtures of naphthalene and tetralin was also estimated by means of the refractive indices of the mixtures of 1-g. samples dissolved in 5 ml. of toluene, $n^{25}\mathrm{D}$ 1.4936. The refractive indices of these solutions were found to be a linear function of the naphthalene content between 20 and 80% for which the refractive indices were 1.464 and 1.528, respectively, measured at 25°. In 5 ml. of benzene, $n^{25}\mathrm{D}$ 1.4960, the variation in refractive indices was less, being from 1.507 to 1.517 in two samples containing 25 and 90% naphthalene, respectively.

The picrate and refractive index methods of analysis gave approximately the same values even if the reaction mixture contained as much as 25% of dihydronaphthalene. The refractive index method is unreliable where other hydrocarbons may be present, as for example when the dehydrogenation has been carried out under ethylene.

The separation of naphthalene from tetralin and decalin was accomplished by the following procedure. The mixture of hydrocarbons (20 g.) and 28 g. of picric acid was added to 500 ml. of 95% alcohol and the solution heated to boiling and allowed to cool slowly. The solid was removed by filtration and the volume of the solution concentrated to 300 ml. After the second crop of crystals had separated out the mother liquor was concentrated to 200 ml. and a third crop of crystals obtained. Each of the crops of crystals was washed with two 20-ml. portions of ether. The combined mother liquor and washings was evaporated at 90° (20 mm.). Sodium hydroxide (10 g.) in 250 ml. of distilled water was added to the residue on the steam-bath. The cold water solution was then extracted with five 40-ml. portions of ether and the hydrocarbons fractionated after the evaporation of the ether. From a sample containing 10 g. of tetralin, 6.5 g., b. p. 80–81° (11 mm.), $n^{25}\mathrm{D}$ 1.5392, was recovered and from a sample containing 12 g. of decalin, 7.4 g., b. p. 59–59.5° (9.5 mm.), $n^{26}\mathrm{D}$ 1.4670, was recovered.

Hydrogenations of Mixtures from Dehydrogenation of Tetralin.—A mixture (38 g.) containing 35.1% naphthalene in 60 ml. of dry alcohol was hydrogenated over 5 g. of copper chromite at 190–200° under 200 atm. of hydrogen in a little over two hours. The amount of hydrogen taken up was 0.067 mole in excess of that required by the naphthalene present. In another run a mixture (32 g.) containing 38.3% naphthalene showed an absorption of hydrogen 0.064 mole in excess of that required by the naphthalene. This amount of hydrogen would be sufficient for the hydrogenation of 8.3 g. of dihydronaphthalene. The product of the two experiments cited above was a single compound and had a b. p. 72.5–73.0° (6.5 mm.), and $n^{25}\mathrm{D}$ 1.5389, figures which correspond with those for pure tetralin. A sample of tetralin which had been previously partially dehydrogenated and rehydrogenated was again dehydrogenated over Raney nickel at 300° and the mixture of products (39 g.), analyzing 37.2% naphthalene, was subjected to hydrogenation over copper chromite. Thirty-eight grams of this mixture was hydrogenated over copper chromite at 150° in eight hours giving pure tetralin. The amount of hydrogen taken up in excess of that required by the naphthalene present was 0.068 mole.

Dehydrogenation of 1,2,3,4-Tetrahydronaphthol-2.—The dehydrogenation was carried out as with tetralin. The yellowish-brown dehydrogenation product was washed from the bomb with ether and the catalyst removed by centrifuging; the ether extract was then shaken with six 75-ml. portions of a 5% water solution of potassium hydroxide. The β-naphthol was liberated from this solution with carbon dioxide. The naphthol was sublimed and recrystallized twice from petroleum ether (b. p. 60–68°). The β-naphthol had a m. p. of 119–121° and gave a picrate m. p. 155–156.5°. The ether was evaporated and the residual naphthalene steam distilled and sublimed. Its m. p. was 79.5–80.5° and the picrate had a m. p. of 150–151°.

Polymerization and Decomposition of Ethylene.—A steel reaction vessel having a void of 180 ml. was filled with ethylene to a pressure of 60 atm. The pressure rose to 221 atm. when the vessel was heated to 350° and the pressure then slowly fell to 161 atm. during a four-hour period of heating. When the vessel was cooled to room temperature the pressure was 80 atm. From the reaction vessel was obtained 7.1 g. of light brown oil, b. p. above 112° (2 mm.). Four 1-g. fractions were obtained, boiling over the range 112–295° (2 mm.) whose refractive indices at 25° varied from 1.452 to 1.463.

When the same experiment was carried out except that 4 g. of Raney nickel was placed in the bomb, there was obtained about 9 g. of a finely divided black solid in addition to the Raney nickel originally added. With an original pressure of 33 atm. of ethylene the weight of carbonaceous material produced was only 5.5 g. At 300° only 3.1 g. of solid was produced. No oil or solid was produced from ethylene at 300° in the absence of nickel.

Summary

Pure tetralin and 1,2,3,4-tetrahydronaphthol-2 are best prepared by the hydrogenation of naphthalene and β-naphthol, respectively, at 150 to 200° over copper chromite.

Tetrahydronaphthalene has been dehydrogenated in the liquid phase over Raney nickel at 350° to give yields up to 78% of naphthalene. At 300° the yields of naphthalene are of the order of 40%, and apparently an equilibrium is set up between tetralin, dihydronaphthalene and naphthalene in which these compounds are present in approximately the ratio 35:25:40. Tetralin is stable over copper chromite at 350°.

1,2,3,4-Tetrahydronaphthol-2 has been dehydrogenated in the liquid phase over copper chromite at 300° to give β-naphthol in yields up to 76% without the formation of naphthalene in amounts greater than 1%. Over Raney nickel dehydrogenation takes place as low as 250° but naphthalene is the major product.

Ethylene at 350° undergoes polymerization in a steel bomb to give hydrocarbons boiling above 112° (2 mm.). Ethylene is decomposed to carbon over Raney nickel to a varying extent at 300

to 350°, depending upon the pressure of ethylene. Because of these facts ethylene is not suitable for use as an hydrogen acceptor during the dehydrogenation of hydroaromatic compounds over Raney nickel.

MADISON, WISCONSIN RECEIVED AUGUST 19, 1940

[CONTRIBUTION FROM THE SUN OIL COMPANY, EXPERIMENTAL DIVISION, NORWOOD, PA.

The Synthesis of Multicyclopentyls[1]

BY GILBERT E. GOHEEN

It has been well established that natural petroleum oils consist mainly of a mixture of aliphatic, naphthenic and aromatic hydrocarbons or chemical combinations of these types in various proportions. Relative to the naphthenic or saturated ring portion, the average number of rings per molecule can be determined by known methods of ring analysis.[2] For lubricating oils the values generally range from one to five or more rings per molecule.

With respect to the size of the rings present, some evidence has caused several investigators to assume that six-carbon membered (cyclohexane) rings predominate in the naphthenic portion.[2] However, more recent indications are that five-carbon membered (cyclopentane) rings may be present and may even, in many cases, be in the majority.[3] This latter theory is also supported by the fact that cyclopentane rings have generally been found in the naphthenic acids occurring in petroleum.[4]

Attempts to solve this problem have been hindered by the absence of physical data on pure multicyclic compounds containing cyclopentane rings. Only bicyclopentyl itself has been investigated to any great extent.[5] Important additions to the field of dicyclopentyl and bicyclopentyl derivatives have been made recently by several investigators[6a,b,c] but practically nothing is known concerning hydrocarbons containing more than two cyclopentyl rings in the molecule. In the present communication there are described the synthesis and physical properties of three saturated multicyclopentyls[7] of the type

where $x = 0$, 1, and 2.

The series of reactions selected for the synthesis of the multicyclopentyls is outlined in Fig. 1. A search of the literature indicated that these intermediates would be free from possible rearrangements to six-carbon membered rings under the conditions necessary for their preparation. The reactions as a whole were carried out at relatively low temperatures and under mild conditions. Two starting compounds were used, cyclopentanone (II) which was prepared from adipic acid (I), and cyclopentadiene (VI), from dicyclopentadiene (V). The first series of reactions consisted in the catalytic hydrogenation of cyclopentanone (II) to cyclopentanol (III) and conversion of this to cyclopentyl bromide (IV) by means of phosphorus tribromide at 0°. The unsaturated bicyclic compound, 1-cyclopentylcyclopentene-2 (VIII) was then produced by the reaction of the Grignard reagent of cyclopentyl bromide with 1-chlorocyclopentene-2 (VII) also at 0°. Catalytic hydrogenation of VIII then produced bicyclopentyl whose physical constants corresponded with those given in the literature for bicyclopentyl prepared by other methods. Thus, the procedures up to this point were proven to be satisfactory.

By the addition of hydrobromic acid to the cyclopentylcyclopentene (VIII) at room temperature, there was obtained 3-bromobicyclopentyl (IX) whose chemical structure has been investigated by von Braun, Kamp and Kopp.[6a]

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(1) Presented before the Division of Petroleum Chemistry of the American Chemical Society, Detroit, Mich., Sept. 11, 1940.

(2) Vlugter, Waterman and van Westen, *J. Inst. Petroleum Tech.*, **21**, 661–676 (1935); **18**, 735–750 (1932); Grosse, *Refiner Natural Gasoline Mfr.*, **18**, 149–157 (1939); Grosse and Mavity, Div. of Petroleum Chem., Am. Chem. Soc. Meeting, Boston, 1939.

(3) Kurtz and Lipkin, Div. of Petroleum Chem., Am. Chem. Soc. Meeting, Boston, 1939; Lipkin and Kurtz, *ibid.*, Detroit, 1940; Rossini, *Proc. Am. Petroleum Inst.*, **18**, III, 51 (1937); Glasgow, *J. Research Natl. Bur. Standards*, **24**, 509–529 (1940).

(4) Harkness and Bruun, *Ind. Eng. Chem.*, **32**, 499–502; Goheen, *ibid.*, **32**, 503–508 (1940); Hancock and Lochte, THIS JOURNAL, **61**, 2448–2452 (1939); Shive and Bailey, Div. of Petroleum Chem., Am. Chem. Soc. Meeting, Cincinnati, 1940.

(5) Evans, *J. Inst. Petroleum Tech.*, **24**, 548, 551 (1938).

(6) (a) Von Braun, Kamp and Kopp, *Ber.*, **70B**, 1750–1760 (1937); (b) Suida and Gemassmer, *ibid.*, **72B**, 1168–1173 (1939); (c) Zelinskiĭ, Mikhlina and Eventova, *ibid.*, **66B**, 1422–1426 (1933).

(7) Class name suggested by Dr. Austin M. Patterson.