tetrahydronaphthalene, I, in the presence of a palladium-on-charcoal catalyst also gave principally 2-benzylnaphthalene. An analogous internal dehydrogenation–hydrogenation has been reported with 2-acetyl-5,6,7,8-tetrahydronaphthalene.[4] Treatment of I with sulfur in the liquid phase gave 2-benzoylnaphthalene, in agreement with the work reported by Barbot.[5] In general, it appears that sulfur dehydrogenation of a hydroaromatic compound containing oxygen seldom results in elimination of oxygen. With palladium-on-charcoal, however, the hydrogen liberated from one part of a molecule during dehydrogenation is frequently used in the hydrogenation or hydrogenolysis of another susceptible portion of the molecule and may in suitable cases even be transferred intermolecularly.[6] It is of interest to note that, even in the vapor-phase reaction mentioned above, such an intramolecular dehydrogenation–hydrogenation occurred.

Experimental[7]

2-Benzoyl-5,6,7,8-tetrahydronaphthalene, I.—This compound was prepared from benzoyl chloride and tetrahydronaphthalene according to the directions of Scharwin,[8] except that nitrobenzene was used as the solvent instead of carbon disulfide. Purification by crystallization from methanol gave pure I, m. p. 40.4–41.2°, which has previously been reported[8] as an oil.

Sulfur Dehydrogenation of I.—A mixture of 10 g. of I and 2.7 g. of sulfur was heated at 200–270° for seventy minutes. The crude product was distilled, and the distillate (7.8 g.) was chromatographed on alumina–celite whereby 5.8 g. of phenyl 2-naphthyl ketone was isolated. Crystallization from ethanol gave colorless crystals, m. p. 81.4–81.8°. A stable picrate could not be prepared.[9]

Palladium Dehydrogenation of I.—A mixture of 10 g. of I and 0.09 g. of 30% palladium-on-charcoal[10] was heated gradually from 220 to 320° over a period of ninety-five minutes. Vacuum distillation of the product gave 8.2 g. of oil. Chromatography of the crude product on alumina gave as a first, less strongly adsorbed fraction, 6.1 g. (66%) of 2-benzylnaphthalene, which after crystallization from ethanol was obtained as thick, colorless prisms, m. p. 54.3–55.3°. The picrate had a melting point of 94.2–95.0°.[11] The more strongly adsorbed fractions from the chromatogram gave 1.6 g. (16%) of phenyl 2-naphthyl ketone.

Chromia-on-Alumina Dehydrogenation of I.—During three and one-half hours, 15 g. of I was passed over 92 g. of the chromia-on-alumina catalyst[10] at 450–470°, using the apparatus previously described.[10] The product, a mixture of green oil and water, weighed 12.03 g. It was dissolved in benzene, the water distilled off, and an aliquot containing 4.83 g. chromatographed on alumina–supercel. The percolate fractions gave 0.12 g. of naphthalene, identified by melting point and mixed melting point. The column was extruded and divided into three sections. The bottom portion (non-fluorescent, least strongly adsorbed) gave 3.28 g. of 2-benzylnaphthalene, identified by melting point and mixed melting point of the hydrocarbon and its picrate. The intermediate purple-fluorescent band gave 0.07 g. of material, identified as 3,4-benzfluorene by its ultraviolet absorption spectrum.[12] The uppermost, green-fluorescent band gave 0.02 g. of material, identified as 2,3-benzfluorene by its ultraviolet absorption spectrum.[12] It is of interest to note that the separation of 3,4- and 2,3-benzfluorene was easily achieved by chromatography, whereas the separation of 1,2- and 2,3-benzfluorene is extremely difficult.[13]

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[4] Newman and Zahm, This Journal, **65**, 1097 (1943).

[5] Barbot, *Bull. soc. chim.*, [4] **47**, 1314 (1930).

[6] Orchin, This Journal, **66**, 535 (1944).

[7] All melting points corrected.

[8] Scharwin, *Ber.*, **35**, 2511 (1902).

[9] Rousset, *Bull. soc. chim.*, [3] **15**, 71 (1896), reported the melting point of the ketone as 82° and stated that a picrate was formed which had a melting point of 112–113°.

[10] Orchin, Reggel, Friedel and Woolfolk, Bureau of Mines T. P. 708. This preparation is essentially the catalyst-*d* of Linstead and Thomas, *J. Chem. Soc.*, 1127 (1940).

[11] These properties are in agreement with those listed in Heilbron, "Dictionary of Organic Compounds," Vol. 3, p. 432 (1943).

[12] We wish to thank Dr. R. A. Friedel and Mrs. Lois Harnack for the spectra determinations. The comparison spectrum for 3,4-benzfluorene was obtained from the work of Mayneord and Roe, *Proc. Roy. Soc.* (*London*), **A158**, 634 (1937); that for 2,3-benzfluorene was obtained from a sample in our possession.[13]

[13] Orchin and Reggel, This Journal, **70**, 1245 (1948). A forthcoming paper will discuss the ultraviolet spectra and fine structure of the three benzfluorenes.

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1,2-Diphenylcyclohexane

By Stanley M. Parmerter[1]

Although several preparations of 1,2-diphenylcyclohexane have been reported[2,3,4,5] subsequent investigations[6,7] have shown that the product was actually the 1,4-isomer.

The synthesis of 1,2-diphenylcyclohexane has now been accomplished by an unequivocal method. The reaction between phenylmagnesium bromide and 2-phenylcyclohexanone produced a carbinol which was dehydrated to a diphenylcyclohexene. Hydrogenation of the diphenylcyclohexene with palladium–on–charcoal catalyst yielded 1,2-diphenylcyclohexane, which the author presumes to be the *cis*-form.

Experimental

Diphenylcyclohexene.—A solution of 62 g. (0.36 mole) of 2-phenylcyclohexanone[8] in 300 cc. of absolute ether was added in ninety minutes to a stirred, refluxing solution of phenylmagnesium bromide, prepared from 63 g. (0.40 mole) of bromobenzene and 9.7 g. (0.40 g. atom) of magnesium turnings in 250 cc. of absolute ether. After an additional two hours of stirring and refluxing, the mixture was left overnight at room temperature. The mixture was then decomposed with ammonium chloride solution and the product was extracted in two 300-cc. portions of ether. The dried ether solution upon evaporation left the crude carbinol which was dehydrated by stirring with an equal volume of 85% phosphoric acid for four hours on the steam-bath. The acid mixture was diluted with water and the product taken up in benzene. Distillation of the benzene solution gave a fraction of 64 g. boiling at 170–188° (10 mm.). Upon recrystallization from methanol there was obtained 44.5 g. (53%) of colorless needles, m. p. 50–52°. An analytical sample melted at 51–52°.

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[1] Present address: Eastman Kodak Co., Rochester, N. Y.

[2] Kursanoff, *Ann.*, **318**, 309 (1901).

[3] Gustavson, *Compt. rend.*, **146**, 640 (1908).

[4] Bodroux, *Ann. chim.*, [10] **11**, 511 (1929).

[5] Wertyporoch and Sagel, *Ber.*, **66**, 1306 (1933).

[6] Nenitzescu and Curcaneanu, *ibid.*, **70**, 346 (1937).

[7] Corson and Ipatieff, This Journal, **60**, 747 (1938).

[8] Price and Karabinos, *ibid.*, **62**, 1159 (1940).

Anal. Calcd. for $C_{18}H_{18}$: C, 92.28; H, 7.72. Found: C, 92.22, 92.10; H, 7.78, 7.71.

1,2-Diphenylcyclohexane.—A solution of 11.7 g. of the diphenylcyclohexene in 200 cc. of ethanol was shaken with hydrogen at two to three atmospheres pressure in the presence of 1 g. of 10% palladium-on-charcoal until absorption of hydrogen ceased. At this point approximately 1 mole equivalent of hydrogen had been absorbed. The catalyst was removed by filtration and the solution concentrated to 75 cc. on the steam-bath. Chilling produced 8.3 g. of colorless needles, m. p. 45–46°. Further concentration of the mother liquor gave an additional 2.1 g. of product, m. p. 42–46°. This represents a yield of 88%. An analytical sample, recrystallized three times from methanol, melted at 46–47°.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.50; H, 8.50. Found: C, 91.50, 91.48; H, 8.50, 8.56.

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Alkoxy-*s*-triazines. II

BY WILLIAM M. PEARLMAN AND C. K. BANKS

In the first paper of this series[1] a group of 2-alkoxy-4,6-diamino-*s*-triazines having antihistaminic activity was reported. Most of these compounds contained no alkyl substituents on nitrogen. Since the tautomeric possibilities of the triazine nucleus (I–III) are limited by the number and arrangement of alkyl substituents on nitrogen, it was considered of interest to prepare a series of ethers in which one to four of the hydrogens on the two amine groups were replaced by alkyl groups. These compounds were prepared by the reaction of the chosen sodium alkoxide with an appropriate 2-chloro-4,6-di-(amino or substituted amino)-*s*-triazine. The necessary chlorodiaminotriazines have been reported pre-

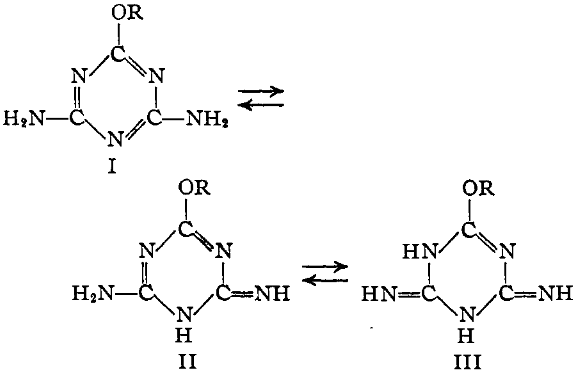
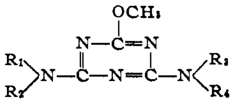


TABLE I

METHYL ETHERS



R_1	R_2	R_3	R_4	M. p., °C.	Yield, %	Recrystallization solvent	Analyses,[a] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	A. H.[b] Value
H	H	H	H	229–230	81	Ref. 1					50
Methyl	H	H	H	155–156	66	Benzene	38.70	38.97	5.85	5.81	50
Ethyl	H	H	H	168–170	24	Water	42.59	42.59	6.55	6.31	25
n-Propyl	H	H	H	148–150	81	Water	45.89	46.20	7.15	7.03	12
n-Butyl	H	H	H	125–127	89	Methanol–water	48.71	49.13	7.67	7.64	>50
n-Amyl	H	H	H	[c]	86	Benzene–isoöctane	51.38	51.19	8.13	8.23	12
n-Hexyl	H	H	H	104–106	92	Isoöctane	53.31	53.03	8.50	8.73	12
Allyl	H	H	H	148–150	89	Water	46.40	46.66	6.12	6.07	12
Methallyl	H	H	H	129–131	88	Methanol–water	49.22	49.30	6.71	6.66	>50
Cyclohexyl	H	H	H	170–172	99	Benzene	53.79	53.62	7.67	7.47	12
Methyl	Methyl	H	H	169–171	81	Water	42.59	42.62	6.55	6.31	25
Ethyl	Ethyl	H	H	113–115	73	Methanol–water	48.71	48.58	7.67	7.42	12
Allyl	Allyl	H	H	87–89	83	Methanol–water	54.31	54.12	6.83	6.59	>50
Methallyl	Methallyl	H	H	101–103	90	Methanol–water	57.80	57.84	7.68	7.65	50
$HOCH_2CH_2$	Ethyl	H	H	162–164	87	Methanol–water	45.06	45.02	7.09	7.04	>50
$HOCH_2CH_2$	Phenyl	H	H	224–226	91	Methylcellosolve–H_2O	55.12	55.47	5.78	5.74	50
$-C_5H_{10}-$[d]		H	H	137–139	95	Chloroform	51.66	51.59	7.23	7.42	6
$-C_2H_4OC_2H_4-$[e]		H	H	182–184	80	Methanol–water	45.49	45.65	6.20	6.07	50
Methyl	H	Methyl	H	184–186	76	Methanol–water	42.59	[h]	6.55	[h]	6
Ethyl	H	Ethyl	H	81–83	46	Ethanol–water	48.71	48.69	7.63	7.64	6
Allyl	H	Allyl	H	84–86	88	Methanol–water	54.28	54.28	6.83	6.92	25
Methallyl	H	Methallyl	H	112–114	93	Methanol–water	57.80	57.76	7.68	7.34	12
Methyl	Methyl	Methyl	H[f]	187–188	80	Methanol	45.89	45.64	7.15	7.00	25
Ethyl	Ethyl	Ethyl	H	107–109	99	Isoöctane	53.31	53.30	8.50	8.24	12
Methyl	Methyl	Methyl	Methyl	90–92	73	Methanol–water	48.71	48.75	7.66	7.48	25
Ethyl	Ethyl	Ethyl	Ethyl	146–149/1.5[g]	65		56.89	57.22	9.15	9.09	50
Allyl	Allyl	Allyl	Allyl	150–153/1[g]	93		63.76	64.07	7.69	7.88	>50
Methallyl	Methallyl	Methallyl	Methallyl	151–154/1.5[g]	71		67.19	66.83	8.74	8.44	>50
$-C_5H_{10}-$[d]		$-C_5H_{10}-$[d]		89–91	94	Isoöctane	60.62	60.60	8.36	7.93	>50
$-C_2H_4OC_2H_4-$[e]		$-C_2H_4OC_2H_4-$[e]		153–155	78	Methanol–water	51.23	51.38	6.81	6.86	12

[a] Analyses by Mr. A. W. Spang and Miss Patricia Keller. [b] Determined by Dr. Graham Chen and Mr. C. R. Ensor. Dose of compound in mg./kg. intraperitoneally allowing survival of 50% of histamine-shocked guinea pigs, see Ref. 1 for details. The comparable dose for Aminophylline is 50 and for Benadryl is 1.5. [c] Sinters 98–104°, plastic 104–108°, glass 108–122°. [d] Piperidino. [e] Morpholino. [f] Prepared by Mr. John Controulis. [g] Boiling point, not crystallized at −40°. [h] Concordant results not obtained on repeated assays. This may be due to solvation.

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(1) Controulis and Banks, THIS JOURNAL, 67, 1946 (1945).