acetic acid as possible since the crude acetates are very soluble in this material.

Dialkoxyphosphinylmercuric Chlorides and Bromides. (a) From the Acetates.—A solution of 0.74 g. (0.01 mole) of potassium chloride in 25 ml. of water was added to a solution of 3.96 g. (0.01 mole) diethoxyphosphinylmercuric acetate in 25 ml. of water and the clear mixture evaporated to about half its volume under an infrared lamp. After filtration from a small amount of free mercury, further concentration gave 1.9 g. (50.8% yield) of diethoxyphosphinylmercuric chloride, m.p. 85–95°. Two recrystallizations from water gave material having m.p. 104.0–104.5°.

Anal. Calcd. for $C_4H_{10}O_3ClPHg$: Hg, 53.75; P, 8.29. Found: Hg, 53.30; P, 8.40.

The bromide, iodide and thiocyanate were prepared similarly in 74.2, 88.4 and 94.0% yields, respectively; the latter two compounds were insoluble in water and the crudes were thus collected by filtration. This method is suited to water-soluble acetates only; the other acetates may be converted to the halides in acetone solution.

(b) From the Dialkyl Phosphonates.—Di-*n*-propoxyphosphinylmercuric bromide may be taken as a typical example of this procedure. A mixture of 8.3 g. (0.05 mole) di-*n*-propyl phosphonate, 5.4 g. (0.025 mole) mercuric oxide and 9.0 g. (0.025 mole) mercuric bromide in 50 ml. of dry benzene was refluxed three hours, water being continuously removed with a trap. Soon after the reflux period began, the orange mercuric oxide color changed to white. After cooling, 2.6 g. of inorganic material was removed by filtration; evaporation of the filtrate gave a sirup which crystallized readily upon the addition of petroleum ether. The yield was 14.8 g. (66.4%), m.p. 67–68.5°; two recrystallizations from hot hexane gave pure di-*n*-propoxyphosphinylmercuric bromide, m.p. 70.0–70.4°.

Anal. Calcd. for $C_6H_{14}O_3BrPHg$: Hg, 45.01; P, 6.94. Found: Hg, 45.06; P, 7.00.

The halides listed in Table I were prepared by this procedure. With the exception of the ethyl derivatives, they are soluble in hot hexane; all are soluble in ordinary organic solvents.

Di-*n*-propoxyphosphinylmercuric Iodide.—A mixture of 8.3 g. (0.05 mole) of di-*n*-propyl phosphonate, 5.4 g. (0.025 mole) of mercuric oxide and 11.35 g. (0.025 mole) of mercuric iodide in 50 ml. of dry benzene was refluxed 5 hours; due to excessive foaming, no attempt was made to collect the water formed in the reaction. The red iodide color was soon discharged, but the final precipitate had the appearance of mercuric oxide. After filtration of the inorganic salts, the filtrate was dried with Drierite and evaporated, during which a considerable quantity of an unidentified amorphous yellow material formed. The yellow mixture of solids was taken up in boiling hexane, filtered to remove the yellow material, and concentrated to give 12.1 g. (49.1%) of crude product, m.p. 74.6–75.6°; recrystallization from warm hexane yields pure di-*n*-propoxyphosphinylmercuric iodide, m.p. 75.2–76.0°.

Anal. Calcd. for $C_6H_{14}O_3IPHg$: Hg, 40.71; P, 6.28. Found: Hg, 39.98; P, 6.22.

The other iodides were prepared similarly.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Syntheses and Relative Dehydration Rates of Some Methyl-substituted 1-Phenylcyclohexanols[1]

BY ROBERT B. CARLIN AND HAROLD P. LANDERL

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Eleven methyl-substituted 1-phenylcyclohexanols and the unsubstituted parent compound have been synthesized and arranged in the order of their dehydration rates in the presence of *p*-toluenesulfonic acid under identical conditions. Evidence is presented which demonstrates that carbon skeleton rearrangements do not occur during dehydration. Examination of the relative dehydration rates indicates that the presence of ortho or para methyl groups in the benzene ring tends to accelerate the dehydration rate, but methyl groups in the 2-, 4- or 6-positions of the cyclohexanol ring tend to slow the rate. A study of the ultraviolet absorption spectra of the phenylcyclohexenes reveals that methyl groups in either ring diminish the absorption band in the ultraviolet which is associated with conjugation of side-chain unsaturation with that of the aromatic ring; however, the aromatic methyl groups exert a more profound effect than alicyclic methyls. The observations of the effects of methyl substitution on the spectra of the phenylcyclohexenes can be explained in terms of steric interference by the methyls with the coplanarity of the ethylenic system with the aromatic ring. The effects of the methyl groups on the dehydration rates of the carbinols, on the other hand, are more complex, and a satisfactory interpretation cannot be given until more is known about the reaction mechanism, the stereochemistry of the carbinols and the position of the alicyclic double bond.

The apparent sluggishness of 1-(2,4-dimethylphenyl)-2,6-dimethylcyclohexanol in acid-promoted dehydration reactions[2,3] prompted a study of the relative dehydration rates of a series of methyl-substituted 1-phenylcyclohexanols. A detailed kinetic analysis of the reactions was not attempted during this study; the objective was to obtain enough reliable data to permit the carbinols to be arranged in the order of their decreasing ease of dehydration under the imposed conditions. The results of this study are presented here, and an account is also given of efforts to discover whether the substituent methyl groups affect the dehydration rates of the carbinols and the ultraviolet absorption spectra of their dehydration products, the methyl-substituted phenylcyclohexenes, in any related way.

Previous experience[2] indicated that in general methyl-substituted 1-phenylcyclohexanols should be prepared in better yield by treating the appropriate cyclohexanones with aryl lithium compounds than can be realized when the corresponding Grignard reagents are used. Accordingly, the aryl lithium compounds were employed exclusively in this work. The methyl-substituted cyclohexanones required for the syntheses were prepared by oxidizing the related methylcyclohexanols, which in turn were the hydrogenation products of methylphenols. The synthesis of 1-(2,4-dimethylphenyl)-2,4-dimethylcyclohexanol (VII) provides typical examples of the reactions used throughout the series.

The methyl-substituted 1-phenylcyclohexenes were prepared for spectral study by heating the corresponding cyclohexanols with anhydrous oxalic acid; in the rate determinations the dehydration catalyst was *p*-toluenesulfonic acid, and the reactions were carried out in glacial acetic acid

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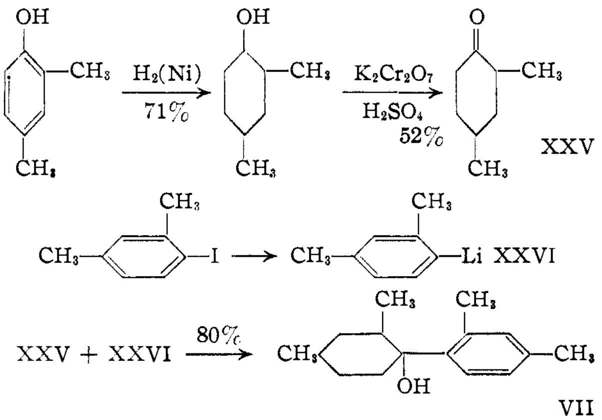
[1] From the D.Sc. Thesis by Harold P. Landerl.

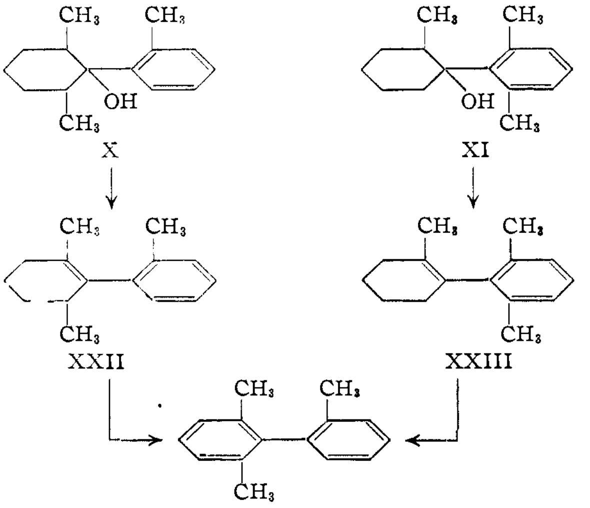
[2] R. B. Carlin, THIS JOURNAL, **67**, 928 (1945).

[3] R. B. Carlin and D. A. Constantine, *ibid.*, **69**, 50 (1947).



solution. Samples of one carbinol (VII) were subjected to dehydration under each of the two sets of conditions; the olefin samples from the two procedures had essentially identical properties. It therefore seems most probable that the olefins studied spectroscopically were identical with those obtained from the carbinols in the rate determinations.

The possible occurrence of carbon-skeleton rearrangements accompanying the acid-promoted dehydration of the carbinols was investigated by comparing the behavior of two isomeric carbinols in dehydration and subsequent dehydrogenation reactions. The following formulations show that the two carbinols X and XI should yield isomeric methyl-substituted 1-phenylcyclohexenes, (XXII) and (XXIII), respectively, if dehydration occurs without carbon-skeleton rearrangement. Dehydrogenation of either phenylcyclohexene would be expected to yield 2,2',6-trimethylbiphenyl. However, should the carbon structure of either or of both carbinols be altered during dehydration, the olefins formed could not possibly yield identical trimethylbiphenyls under the mild conditions of dehydrogenation (treatment with chloranil in boiling xylene) selected to effect the final transformation. Therefore, isolation of identical trimethylbiphenyls from both X and XI would constitute proof that neither had suffered rearrangement of the carbon structure during dehydration. Furthermore, the carbinols X and XI should be as susceptible as any of the twelve studied to rearrangement during acid-catalyzed dehydration, so that a demonstration that X and XI do not rearrange would constitute strong presumptive evidence that rearrangement does not occur during dehydration of any of the carbinols. In actual fact, the oxalic acid dehydration products of X and XI did give identical specimens of trimethylbiphenyl after chloranil dehydrogenations. The trimethylbiphenyl samples were identified by means of their physical properties and by their separate conversions to identical crystalline tetranitro derivatives. Thus the skeletal structures of the olefins were established as identical with those of the carbinols from which they were formed; only the positions of the alicyclic ring double bonds remained in doubt.



Experimental

Materials. Methyl-substituted cyclohexanols were prepared from the corresponding phenols by means of a hydrogenation procedure previously described.[2]

2-Methylcyclohexanol (78% yield).—B.p. 165–167°, n^{20}_{D} 1.4632. Skita and Faust[4] reported for the *cis* isomer: b.p. 165°, $n^{18.2}_{\mathrm{D}}$ 1.4648; *trans*, b.p. 166.5°, $n^{19.7}_{\mathrm{D}}$ 1.4613. Our product therefore appears to have been a mixture of the stereoisomers.

2,4-Dimethylcyclohexanol (71% yield).—B.p. 178.5–180.5°, n^{20}_{D} 1.4588. Skita[5] reported a "*cis*" isomer, b.p. 176–177°; n^{20}_{D} 1.4582, and a "*trans*" isomer, b.p. 175–176.5, n^{20}_{D} 1.4560.

2,6-Dimethylcyclohexanol (54% yield).—B.p. 172–176°, n^{20}_{D} 1.4623, phenylurethan m.p. 158°. Previous investigators have reported b.p.'s from 171 to 175.5°,[2,6,7] n^{20}_{D} from 1.4612 to 1.4628,[2,6,7] and stereoisomeric phenylurethans, m.p.'s 132 and 158°.[2,8] A previous publication described a synthesis for 2,6-xylenol and contained some comments about the diastereoisomeric phenylurethans of the 2,6-dimethylcyclohexanols formed by the hydrogenation of the xylenol.[9]

Cyclohexanone (Eastman Kodak Co.) was distilled before use, b.p. 155–156°.

2-Methylcyclohexanone.—A stirred solution of 23.5 g. of potassium dichromate and 20 g. of concentrated sulfuric acid in 120 ml. of water was cooled to 15°, stirred and treated dropwise with 13.2 g. of 2-methylcyclohexanol. After addition of all of the alcohol the mixture was permitted to warm to 28°. Stirring was continued for 4.5 hours, then the mixture was allowed to stand overnight. The oil layer was separated and the water layer was extracted with three 50-ml. portions of ether. The oily product was dissolved in the combined ether extracts, and this solution was washed with three 40-ml. portions of 5% aqueous sodium hydroxide and with water once; then it was dried over anhydrous magnesium sulfate. The residual liquid after removal of the ether yielded on distillation 9.9 g. (76%) of crude 2-methylcyclohexanone, b.p. 164–166°.

A mixture of 9.7 g. of the crude ketone, 12 g. of semicarbazide hydrochloride, 14 g. of sodium acetate, 3.5 ml. of 10% sodium hydroxide and 35 ml. of water was shaken until a heavy white precipitate formed. The mixture was cooled, and the solid was collected by filtration and recrystallized from 70% ethanol, from which the semicarbazone formed small white needles (13.1 g., 67% from the alcohol), m.p. 191°. Skita reported the same melting point.[10] The ketone was regenerated from the semicarbazone by means of a procedure identical with that reported previously[2] for 2,6-dimethylcyclohexanone; 7.2 g. (55% from the alcohol) of colorless liquid was obtained, b.p. 165–166°, n^{20}_{D} 1.4492. Skita[10] observed the b.p. 166°, n^{20}_{D} 1.4488.

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(4) A. Skita and W. Faust, *Ber.*, **64**, 2878 (1931).

(5) A. Skita, *Z. angew. Chem.*, **34**, 230 (1921); *Ann.*, **427**, 255 (1922).

(6) A. Haller, *Compt. rend.*, **157**, 179 (1913).

(7) A. Skita, *Ber.*, **56**, 2234 (1923).

(8) P. Anziani and R. Cornubert, *Compt. rend.*, **217**, 233 (1943).

(9) R. B. Carlin and H. P. Landerl, THIS JOURNAL, **72**, 2762 (1950).

(10) A. Skita, *Ber.*, **56**, 1014 (1923).

TABLE I

PREPARATION AND PROPERTIES OF 1-PHENYLCYCLOHEXANOLS

Phenylcyclohexanols Methyl(s) on phenyl	Methyl(s) on cyclohexanol	No.	B.p. °C.	B.p. Mm.	nD	Yield, %	Analyses Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
None	None	I[a]	123	4.5		96				
None	2-	II	105–106	1	1.5359[b]	83	82.11	81.99	9.54	9.45
2-	None	III	131–132[e]	2	1.5480[b,c]	63	82.11	82.10	9.54	9.42
2-	2-	IV	117	1	1.5377[b]	82	82.30	82.21	9.87	9.92
2-	2,4-	V	126–127	2.5	1.5325[b]	73	82.51	82.61	10.16	10.04
2,4-	2-	VI	138	1	1.5380[b]	58	82.51	82.37	10.16	10.06
2,4-	2,4-	VII	140–141	1.5	1.5301[b]	80	82.69	82.72	10.42	10.26
None	2,6-	VIII	118–119	1.5	1.5320[d]	87	82.30	82.14	9.87	9.78
2,6-	None	IX	140	1.5	1.5520[d]	61	82.30	82.63	9.87	9.66
2-	2,6-	X	125	1	1.5319[b]	89	82.51	82.37	10.16	9.85
2,6-	2-	XI	117	0.5	1.5439[b]	38	82.51	82.54	10.16	10.00
2,6-	2,6-	XII	140	2	1.5429[d]	20	82.69	82.62	10.42	10.41

[a] M.p. 62°. Reported m.p. 61.°[12] [b] At 25°. [c] Super-cooled liquid. [d] At 20°. [e] Reported b.p. 149–151° (14 mm) (I. R. Sherwood, W. F. Short and R. Stansfield, *J. Chem. Soc.*, 1832 (1932).

TABLE II

PREPARATION AND PROPERTIES OF 1-PHENYLCYCLOHEXENES

Phenylcyclohexenes Methyl(s) on phenyl	Methyl(s) on cyclohexene	No.	B.p. °C.	B.p. Mm.	nD	Yield, %	Analyses Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
None	None	XIII	82[a]	1	1.5660[b,c]	78				
None	2- or 6-	XIV	78	1	1.5460[b]	67	90.76	90.47	9.24	9.12
2-	None	XV	102.5	2.5	1.5411[b]	84	90.76	90.46	9.24	9.31
2-	2- or 6-	XVI	91	1	1.5350[b]	75	90.26	90.29	9.74	9.29
2-	2,4- or 4,6-	XVII	102.5	1.5	1.5258[b]	83	89.73	89.81	10.27	10.25
2,4-	2- or 6-	XVIII	112	1	1.5320[b]	63	89.73	89.79	10.27	10.52
2,4-	2,4- or 4,6-	XIX	114	1.5	1.5243[b]	70	89.65	89.50	10.35	10.26
None	2,6-	XX	91–92	1.5	1.5379[d]	83	90.26	90.12	9.74	9.59
2,6-	None	XXI	114	2	1.5374[d]	89	90.26	89.91	9.74	9.61
2-	2,6-	XXII	103–104	1.5	1.5322[b]	65	89.73	89.89	10.27	10.30
2,6-	2- or 6-	XXIII	112	2	1.5330[d]	90	89.73	89.89	10.27	10.49
2,6-	2,6-	XXIV	117	2	1.5336[d]	48	89.65	89.93	10.35	10.15

[a] Reported b.p. 133° (17 mm.).[12] [b] At 25°. [c] Reported n^{20}D 1.5690.[12] [d] At 20°.

2,4-Dimethylcyclohexanone was prepared and purified through its semicarbazone in 52% over-all yield by means of the procedure just described for 2-methylcyclohexanone. The colorless liquid had the b.p. 177–179°; n^{20}D 1.4448, semicarbazone, m.p. 185–189°. Reported[11] for the *cis* isomer: b.p. 177°, $n^{15.5}$D 1.4493, semicarbazone, m.p. 190°. For the *trans* isomer[11]: b.p. 171°, n^{16}D 1.4429, semicarbazone, m.p. 136°. Our sample apparently consisted chiefly in the reported *cis* isomer.

2,6-Dimethylcyclohexanone was prepared and purified in 53% yield by means of a procedure previously described[2]; b.p. 170–172°, n^{20}D 1.4500, semicarbazone, m.p. 179–184°. Reported[2] values of these constants were identical.

Halogenated benzene derivatives were obtained from Eastman Kodak Co. Bromobenzene and *o*-bromotoluene were distilled before use, b.ps. 154–155° and 180–181°, respectively. 4-Iodo-1,3-xylene and 2-iodo-1,3-xylene were steam distilled from 10% aqueous sodium hydroxide and then vacuum distilled through a Widmer column; b.ps. 70–75° (1–2 mm.) and 81–83° (2.5 mm.), respectively; n^{20}D 1.5995 and n^{24}D 1.6008, respectively.

1-Phenylcyclohexanol and homologs were prepared by means of the same procedure previously given[2] for the synthesis of 1-(2,4-dimethylphenyl)-2,6-dimethylcyclohexanol. In Table I pertinent data on the preparation and properties of these compounds are summarized.

1-Phenylcyclohexene and Homologs. A. By Dehydration with Oxalic Acid.—The oxalic acid promoted dehydration of the 1-phenylcyclohexanols was carried out in accordance with the procedure previously applied to the preparation of 1-(2,4-dimethylphenyl)-2,6-dimethylcyclohexene.[3] The data in Table II refer to olefins prepared by this method.

B. By Dehydration with *p*-Toluenesulfonic Acid.—A mixture of 5 g. of 1-(2,4-dimethylphenyl)-2,4-dimethylcyclohexanol (VII) and 0.0503 g. (1 mole per cent.) of *p*-toluenesulfonic acid was heated to 100° for one hour. The olefin was separated from the reaction mixture by the same method employed in procedure A. The distillate (2.7 g., 59%) was a colorless, viscous liquid, b.p. 117–119° (2 mm.), n^{25}D 1.5245 (compare with No. XIX, Table II for physical properties of product by procedure A). The yield of olefin was raised only to 63% when the heating time was increased to 3.5 hours.

2,2′,6-Trimethylbiphenyl. A. From **1-(2-Methylphenyl)-2,6-dimethylcyclohexene (XXII).**—A mixture of 10.3 g. of XXII, 25 g. of chloranil and 50 g. of xylene was boiled for 15 hours. The mixture was cooled in ice and diluted with an equal volume of petroleum ether. The precipitated tetrachlorohydroquinone (16.75 g., 67% of the chloranil used) was removed by filtration and the filtrate was washed with three portions of 4% aqueous potassium hydroxide and one of water. The solvents were removed and the residue was distilled under reduced pressure. The major fraction (5.6 g., 56%) had the b.p. 103–106° (1.5 mm.). Redistillation of this fraction gave 4.6 g. of a colorless liquid, b.p. 107–109° (2 mm.), n^{20}D 1.5600.

A solution of this product and 5 g. of chloranil in 30 ml. of xylene was treated in the same manner described above. An additional 1.31 g. of tetrachlorohydroquinone was isolated, and the liquid product was a colorless oil, b.p. 110–113° (2.5 mm.), n^{20}D 1.5639. The analytical sample obtained by redistilling this liquid had the b.p. 117° (3 mm.), n^{20}D 1.5642.

Anal. Calcd. for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.51; H, 8.27.

Tetranitro Derivative.—A mixture of 0.7 g. of the trimethylbiphenyl and 3 ml. of concentrated sulfuric acid was

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(11) M. Godchot and P. Bedos, *Compt. rend.*, **180**, 751 (1925).

(12) K. v. Auwers and W. Treppmann, *Ber.*, **48**, 1207 (1915).

TABLE III

PER CENT. WATER EVOLVED ON HEATING 1-PHENYLCYCLOHEXANOLS WITH *p*-TOLUENESULFONIC ACID IN ACETIC ACID

Phenylcyclohexanol			Per cent. water evolved						
			At 75°			At 60°			At 45°
Methyl(s) on phenyl	Methyl(s) on cyclohexanol	No.	15 min.	30 min.	60 min.	15 min.	30 min.	60 min.	30 min.
None	None	I	83.0	90.7	88.8	63.9	74.3	83.5	41.0
None	2-	II	40.1	58.2	75.4				
2-	None	III	86.9	90.7	91.5	76.8	86.1	87.4	66.5
2-	2-	IV	55.3	76.2	88.7				
2-	2,4-	V	27.5	37.4	47.5				
2,4-	2-	VI	83.0	90.4	89.7	74.4	81.7	83.7	50.8
2,4-	2,4-	VII	47.3	65.5	80.0				
None	2,6-	VIII	15.4	20.7	27.4				
2,6-	None	IX				68.4	84.0	87.4	
2-	2,6-	X	8.4	13.7	15.0				
2,6-	2-	XI	75.5	87.4	92.0				
2,6-	2,6-	XII		76.5					

shaken while 3 ml. of fuming nitric acid was added dropwise. The mixture was warmed on the steam-bath for ten minutes and then poured into 25 g. of ice. Recrystallization of the precipitated solid yielded 0.55 g. of tiny yellow needles, m.p. 188–200°. This crude product was purified by pouring its solution in 30 ml. of benzene and 30 ml. of petroleum ether (b.p. 66–71°) onto a 15 × 1.8 cm. alumina column which had been washed with 50 ml. of petroleum ether. The chromatogram was developed with 100 ml. of 1:1 benzene–petroleum ether. The column was extruded and streaked with a solution of potassium hydroxide in ethanol to which a few drops of acetone had been added just before use. The location of the nitro compound was determined by the position of a deep blue-green streak, and this section of the column was eluted with acetone. The solid obtained by removing the acetone from the eluate gave pale yellow needles, m.p. 222–223°, after recrystallization from benzene–petroleum ether.

Anal. Calcd. for $C_{15}H_{12}N_4O_8$: C, 47.88; H, 3.22; N, 14.89. Found: C, 48.31; H, 3.25; N, 15.36.

B. From 1-(2,6-Dimethylphenyl)-2-methylcyclohexene (XXIII).—When XXIII was accorded the same treatment with chloranil to which XXII was subjected, a colorless liquid was formed in 43% yield, b.p. 110° (2 mm.), $n^{20}D$ 1.5639. Nitration of this liquid and purification of the product in accordance with the directions contained in the preceding paragraph gave pale yellow needles, m.p. 222–223°, alone or when mixed with a specimen obtained by Procedure A.

Rate Measurements.—The rates of dehydration of 1-phenylcyclohexanol and its homologs were followed by titrating with Karl Fischer reagent the water evolved after solutions of the carbinol in acetic acid which contained fixed and constant amounts of *p*-toluenesulfonic acid were kept at constant temperature for known periods of time.

Reagents.—The equivalence ratio between the Karl Fischer reagent (Eimer and Amend) and a stock solution made by diluting 2.1377 g. of water to 2000 ml. with absolute methanol was determined by direct titration of the former with the latter, using the conductometric deadstop end-point apparatus and procedure described by Wernimont and Hopkinson.[13] Then both of the solutions were standardized by adding a measured excess of Karl Fischer reagent to a known weight of water and back-titrating excess Karl Fischer reagent with the stock water–methanol solution. Because the Karl Fischer reagent deteriorates on standing, the equivalence ratio was determined daily. The stability on standing of the stoppered water–methanol solution made it possible to compute each new water equivalence of the Karl Fischer reagent from the newly determined equivalence ratio and the originally determined concentration of water in the water–methanol stock solution.

Procedure.—About 0.5 g. of a 1-phenylcyclohexanol was weighed accurately into a 10-ml. volumetric flask. One ml. of a solution of 0.1017 g. of *p*-toluenesulfonic acid in 100 ml. of glacial acetic acid was added, and the flask was stoppered and immediately placed in a thermostatic bath in which the temperature was regulated within a ±0.2° range. After a measured time interval the flask was removed from the thermostat and permitted to cool for five minutes. The contents of the flask were diluted to the mark with absolute methanol and the solution was transferred to the vessel in which the titration was to be carried out. The empty flask was rinsed by filling to the mark with absolute methanol, and the washings were also transferred to the titration vessel. The solution was stirred and a measured excess of Karl Fischer reagent was added from a buret. The excess reagent was back-titrated with water–methanol by the method of Wernimont and Hopkinson.[13] A correction was applied for the water determined to be present in the absolute methanol. No blank corrections were found to be necessary for the carbinols or for the catalyst solutions. Stock solutions in storage and in burets and the solutions being titrated were protected from atmospheric moisture by means of drying tubes packed with "Drierite."

The per cent. of the theoretical yield of water from each carbinol was determined by means of the procedure just described after time intervals of 15, 30 and 60 minutes. Measurements were made on all but one carbinol at 75°, and runs on four of the carbinols were carried out at 60°. The per cent. of the theoretical yield of water from three carbinols after 30 minutes at 45° was determined. Duplicate runs agreed within 1.5%.

Results and Discussion

The data obtained by the rate measurements (Table III) reveal certain generalizations which may be derived concerning the influence of structural features on the dehydration rates of the carbinols measured under the conditions imposed in this work. The twelve carbinols may be divided arbitrarily into three groups on the basis of their relative dehydration rates. The first group, comprising the five carbinols which undergo dehydration most rapidly, includes those which lose at least 75% of the theoretical amount of water in 15 minutes at 75° under the conditions chosen. The intermediate group consists of four carbinols which lose less than 80% of the theoretical amount of water in 30 minutes but at least 75% in an hour under identical conditions and the third, or "slow," group is composed of three carbinols which lose less than 50% of the theoretical amount of water in an hour at 75°. Because the dehydration rates of some members of the "fast" group could not be distinguished on the basis of the 75° data, measurements at 60° were carried out on four of the five members of this group and three of the four were run for 30 minutes at 45°. Assignments of the four "fast" carbinols to their relative positions in the series were made as

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[13] G. Wernimont and F. J. Hopkinson, *Ind. Eng. Chem., Anal. Ed.*, **15**, 272 (1943).

a result of the slight differences in their dehydration velocities at the lower temperatures. The order of decreasing ease of dehydration of the carbinols under the imposed conditions is

Fast group: III ≥ IX > VI > I > XI
Intermediate group: XII ≈ IV > VII > II
Slow group: V > VIII > X

Of the twelve carbinols examined, 1-(2,6-dimethylphenyl)-2,6-dimethylcyclohexanol (XII) was obtained in amounts only sufficient to permit rate determinations to be carried out at one temperature for one time interval. The single figure resulting from these runs was essentially identical with that given by the carbinol IV under the same conditions; therefore the dehydration rates of XII and of IV are indistinguishable on the basis of available information.

The following effects of the introduction of methyl groups into 1-phenylcyclohexanol on the rates of dehydration under the chosen conditions are apparent from the order of velocities shown above.

1. If the number of methyl groups on the cyclohexanol ring is kept constant, the rate of dehydration is increased by the introduction of methyl groups into the ortho or para positions of the benzene ring (Examples: VI > XI > IV > II; VII > V; XII > VIII). The only exception to this rule appears to be X, which, according to this generalization, should undergo dehydration more rapidly than VIII. This discrepancy may owe its existence to stereochemical factors which will be mentioned presently. In addition to the examples already cited in support of this generalization, the carbinols I, III and IX might be expected to serve. However, all three of these compounds underwent dehydration so rapidly and at such nearly equal rates that the slight differences among them can have little meaning.

2. If the number of methyl groups on the benzene ring is kept constant, the rate of dehydration is decreased by the introduction of methyl groups into the 2-, 4- or 6-positions of the cyclohexane ring (Examples: III > IV > V > X; I > II > VIII; VI > VII; IX > XI > XII).

A comparison of but one pair of compounds (V and X) suggests that a methyl group in the 4-position of the alicyclic ring retards the rate to a lesser degree than does a methyl group in the 2- or 6-position. This observation would be anticipated if the retardation effect has steric causes. The rates of dehydration of another pair of carbinols (VI and XI) are not markedly different, but there is a suggestion that a para methyl group on the aromatic ring exerts a greater accelerating effect on the rate than an ortho methyl group.

The rate data from this investigation were of course inadequate to disclose the nature of the rate equations governing the dehydration reactions. It was possible, however, to derive from the data a suggestion that the rates were of the first order in carbinol concentration under the imposed conditions. When the per cent. of carbinol dehydrated was plotted against time, three experimental points (15, 30 and 60 minutes) were in general available for each carbinol at each temperature at which it was examined. Smooth curves were drawn through these points, and the times of 75% and of 50% conversion were read from each curve. For twelve runs on eleven different carbinols the ratio $t_{75\%}/t_{50\%}$ was 1.9 ± 0.1; of course the ratio should be two for a reaction of the first order in carbinol concentration.

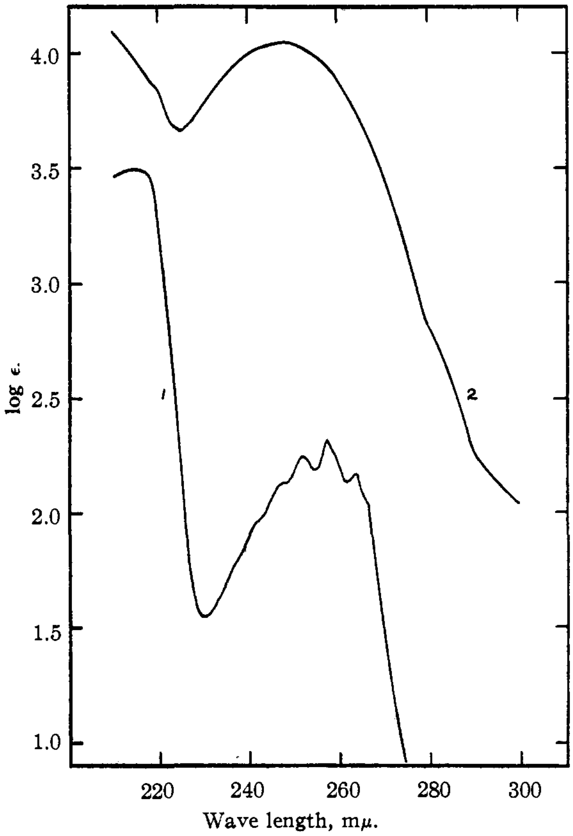

Fig. 1.—The ultraviolet absorption spectra of: 1, 1-phenyl-1-cyclohexanol (I); 2, 1-phenylcyclohexene (XIII).

The ultraviolet absorption spectra of the twelve phenylcyclohexanols and of the twelve related phenylcyclohexenes were determined. The extinction curves for the unsubstituted 1-phenylcyclohexanol and for 1-phenylcyclohexene are shown in Fig. 1, and those of 1-(2,6-dimethylphenyl)-2,6-dimethylcyclohexanol (XII) and of the corresponding olefin XXIV are given in Fig. 2. Because these two pairs of compounds represent the minimum and maximum, respectively, in space consumption by methyl groups in the region of the functional groups, their extinction curves should show the minimum and maximum effects of these methyl groups on the spectra of the compounds. A comparison of the two carbinol curves indicates that substitution of methyl groups into one or both rings at positions adjoining the inter-ring bond brings about no profound change in the nature of the curve. In fact, the curves for the remaining ten carbinols show no fundamental differences in outline.

In contrast to the ultraviolet spectral behavior of the carbinols, that of the phenylcyclohexenes is characterized by pronounced variations. The ex-

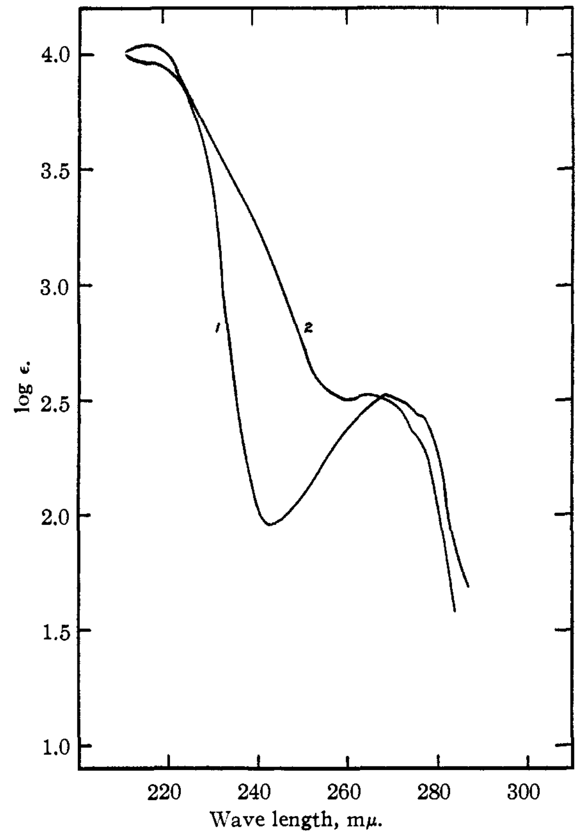

Fig. 2.—The ultraviolet absorption spectra of: 1, 1-(2,6-dimethylphenyl)-2,6-dimethyl-1-cyclohexanol (XII); 2, 1-(2,6-dimethylphenyl)-2,6-dimethylcyclohexene (XXIV).

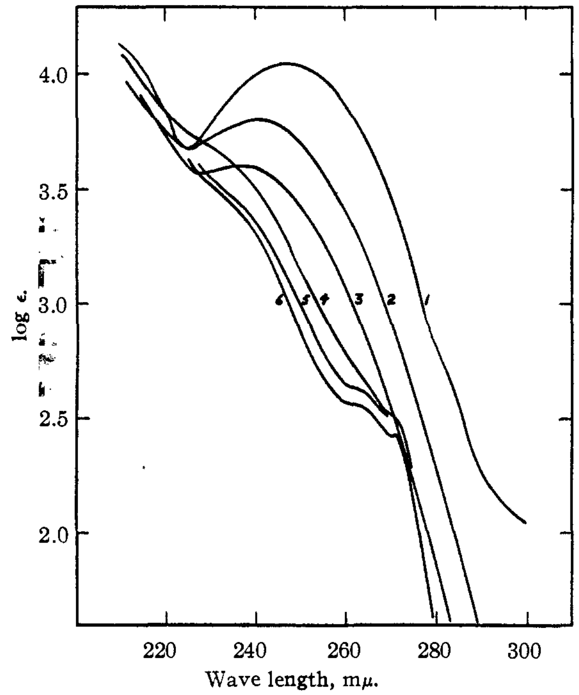

Fig. 3.—The ultraviolet absorption spectra of six 1-phenylcyclohexenes: 1, 1-phenylcyclohexene (XIII); 2, 1-phenyl-2- or 6-methylcyclohexene (XIV); 3, 1-phenyl-2,6-dimethylcyclohexene (XX); 4, 1-(2-methylphenyl)-cyclohexene (XV); 5, 1-(2-methylphenyl)-2,4- or 4,6-dimethylcylohexene (XVII); 6, 1-(2-methylphenyl)-2 or 6-methylcyclohexene (XVI).

tinction curve for the unsubstituted compound XIII is very different (Fig. 1), particularly in the 230–290 mμ region, from that (Fig. 2) of its tetramethyl homolog XXIV. The presence in the spectra of phenylethylenes of a strong absorption band with a maximum at about 250 mμ has long been attributed to the conjugation of the aliphatic unsaturation with that of the aromatic ring; however, this band appears only if the side-chain ethylenic system and the aromatic ring can assume a co-planar configuration.[14] A discussion of the effect of methyl groups in the ortho positions of one or both rings of 1-phenylcyclohexene on the coplanarity of the ethylene and benzene systems of this compound has appeared in a previous communication.[3] In Fig. 3 the extinction curves of 1-phenylcyclohexene and of five methyl-substituted 1-phenylcyclohexenes are shown. It is apparent from these curves that a single *o*-methyl group on the benzene ring destroys the main absorption band almost completely (curve 4), whereas one and even two methyl groups in the 2- and 2,6-positions of the cyclohexene ring are substantially less effective (curves 2 and 3) in diminishing the absorption in this region. Examination of Fisher–Taylor–Hirschfelder models of these structures reveals a correlation between the diminution of the main absorption band caused by the presence of *o*-methyl groups and the amount of mechanical interference which these groups offer to the configurations in which the ethylene and benzene systems are co-planar. The models show that steric interference with co-planarity increases in the order 1-phenyl-2-methylcyclohexene < 1-phenyl-2,6-dimethylcyclohexene < 1-(2-methylphenyl)-cyclohexene, which is also the order of decreasing absorption in the 230–290 mμ region. Curves 5 and 6 of Fig. 3 are typical of all of the remaining methyl-substituted 1-phenylcyclohexenes. The structures of all of these compounds have at least one *o*-methyl group on the benzene ring, and in addition all but one (XXI) has at least one methyl group in the 2- and 6-positions of the cyclohexene ring. None of their spectra shows more than a trace of the main absorption band present in the curve for the unsubstituted parent. It is therefore clear that the principal effect of the methyl groups on the ultraviolet absorption spectra of the 1-phenylcyclohexenes is the partial or complete elimination of the band between 230 and 290 mμ and that this effect may be related to the mechanical interference offered by the methyl groups with co-planar configurations of the ethylene and benzene systems.

The effects of neighboring methyl groups on the rates of dehydration under the imposed conditions of methyl-substituted 1-phenylcyclohexanols do not parallel their effects on the ultraviolet absorption in the 230–290 mμ region of the related 1-phenylcyclohexenes. Whereas *o*-methyl groups on the benzene ring accelerate dehydration of the carbinol, even one such group nearly eliminates the main ultraviolet absorption band of the olefin. Although *o*-methyl groups on the aliphatic ring

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[14] *Cf.* W. H. Rodebush and I. Feldman, THIS JOURNAL, **68**, 896 (1946).

serve to diminish both the rate of dehydration of the carbinol and the intensity of the main absorption band of the olefin, the latter effect is not nearly as large as the effect of *o*-methyl groups located on the aromatic ring. A review of the evidence, therefore, indicates that the effect of neighboring methyl groups on the ultraviolet absorption spectra of 1-phenylcyclohexenes is primarily a steric one, but that other forces are superimposed upon steric ones in determining the influence of the methyl groups on the dehydration rates of the 1-phenylcyclohexanols.

Any effort to identify and appraise the forces other than steric ones which are exerted by neighboring methyl groups on the dehydration rates of the 1-phenylcyclohexanols must be relegated to the realm of speculation until far more elaborate studies on these compounds and their rates of dehydration can be carried out. A rational interpretation of dehydration rate studies requires detailed knowledge of (a) the reaction mechanism, (b) the steric configurations of the 1-phenylcyclohexanols and (c) the position of the double bond in the phenylcyclohexenes. Even if the El mechanism can be assumed for the acid-catalyzed dehydration of these tertiary carbinols, the structures of the olefins cannot be predicted when the carbinol structure includes an *o*-methyl group on the aliphatic ring. In such cases complications must be taken into account by such factors as probable *trans* elimination, influences which operate to determine whether the Hofmann or the Saytzeff rule governs the direction of elimination, and stabilization of the transition state of elimination through the interaction of the aromatic ring unsaturation with the developing double bond, which requires co-planarity. These factors are not independent of each other. For example, both the configuration of 1-phenyl-2-methylcyclohexanol (II) and the stereochemical course of the dehydration reaction (*cis* or *trans*) must be known in order that it be possible to postulate whether the product will be 1-phenyl-2-methylcyclohexene (Saytzeff rule) or 1-phenyl-6-methylcyclohexene (Hofmann rule) or a mixture of both. Furthermore, if both *cis* and *trans* elimination can occur, the conclusions from recent investigations indicate that if the direction of elimination is governed by electromeric forces the Saytzeff rule will be followed[15] while direction of the reaction by steric effects leads to elimination in accordance with the Hofmann rule.[16] Experiments which are now being planned should yield evidence relating to the sensitive interplay among the factors of reaction mechanism, stereochemistry of the carbinols and the structures of the olefins.

[15] M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. I. Woolf, *J. Chem. Soc.*, 2093 (1948).

[16] C. H. Schramm, *Science*, **112**, 367 (1950); H. C. Brown and H. L. Berneis, THIS JOURNAL, **75**, 10 (1953).

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Coupling of Lithium Alkyls and Alkyl Halides. Metal–Halogen Exchange Reactions

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1-Butyllithium and (+)2-bromobutane react with inversion of configuration to give (−)3-methylheptane. Extensive racemization accompanies the inversion. The results are compared with those reported for sodium alkyls and are explained on the basis of the ionic character of the reagents. Metal–halogen exchange reactions occur prior to coupling of lithium alkyls and secondary chlorides but do not take place at slightly lower temperatures in the absence of coupling.

From a comparison of *n*-hexyl and neopentyl chlorides in the reaction with ethylsodium, it was suggested that coupling occurs by a metathetical reaction of the Walden type.[2]

$$C_2H_5Na + RX \longrightarrow RC_2H_5 + NaX$$

Studies with optically active secondary halides have furnished excellent evidence for this mechanism in certain displacement reactions.[3] However, almost complete racemization occurs in the reaction of sodium alkyls with secondary bromides. Displacement reactions involving the more covalent lithium alkyls have been studied kinetically and have been interpreted in terms of either a direct or an ionic mechanism.[4]

A study of this displacement on optically active secondary halides was undertaken several years ago in this Laboratory in the hope that less racemization would occur with lithium alkyls than with the more ionic sodium compounds. This result was not realized. For example, 1-butyllithium reacts with (+)2-bromobutane, $[\alpha]^{25}D$ 15.82, in dodecane at 65° to give a 37% yield of (−)3-methylheptane, $[\alpha]^{25}D$ −0.12, along with butane and butene. An inversion of configuration is indicated in the coupling process, because the configurations of (+)2-bromobutane and (+)3-methylheptane can be related.[5] From the maximum values of the rotations of the halide and hydrocarbon, racemization to the extent of 98% is calculated.

These results are of interest in connection with the recent theory of Lane and Ulrich, whereby optical activity is retained more readily when the organometallic compound is essentially ionic and

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[1] A part of this work was taken from the M.S. thesis of R. N. Goldey, The Pennsylvania State College, 1948.

[2] F. C. Whitmore and H. D. Zook, THIS JOURNAL, **64**, 1783 (1942).

[3] N. G. Brink, J. F. Lane and E. S. Wallis, *ibid.*, **65**, 943 (1943); R. L. Letsinger, *ibid.*, **70**, 406 (1948); R. L. Letsinger and J. G. Traynham, *ibid.*, **72**, 849 (1950); S. E. Ulrich, F. H. Gentes, J. F. Lane and E. S. Wallis, *ibid.*, **72**, 5127 (1950).

[4] S. J. Cristol, J. W. Ragsdale and J. S. Meek, *ibid.*, **73**, 810 (1951); S. J. Cristol, W. C. Overhults and J. S. Meek, *ibid.*, **73**, 813 (1951).

[5] P. A. Levene and A. Rothen, *J. Org. Chem.*, **1**, 76 (1936); R. L. Letsinger and J. G. Traynham, THIS JOURNAL, **72**, 850 (1950), footnotes 8 and 9.