acid chloride thus obtained was poured drop by drop into 10 cc. of aniline. The reaction mixture solidified on cooling and was purified as described in B. By recrystallization of the product from 95% alcohol 2.2 g. of the β-dianilide was obtained. The yield was 75% of the theoretical.

Phenylimide of 1,2-Cyclobutanedicarboxylic Acid.—Two grams of the β-dianilide of 1,2-cyclobutanedicarboxylic acid was heated in a test-tube. The temperature was raised slowly until aniline began to come off. This took place at a temperature of about 240°. The mixture was then maintained at 240–250° for sixteen hours. The contents of the test-tube was dissolved in alcohol, boiled with animal charcoal and filtered. The filtrate, on being allowed to cool, deposited long needles, melting at 126.5–127°. The yield of the imide was 1 g. or 73% of the theoretical.

Summary

The acid chloride of *trans*-1,2-cyclobutanedicarboxylic acid has been shown to react normally with benzene in the presence of aluminum chloride to give a mixture of the *cis* and *trans* forms of 1,2-dibenzoylcyclobutane.

The structure of one of these diketones has been proved by its transformation successively into the dioxime and the corresponding dianilide, which in turn has been shown to be that of 1,2-cyclobutanedicarboxylic acid.

In their reactions these compounds differ widely from the isomeric dihydro-1,4-pyran derivatives. The cyclobutane structures previously considered for the latter compounds are, accordingly, eliminated as possibilities. By the exclusion principle, therefore, the present work strongly supports the dihydro-1,4-pyran structures for the derivatives obtained from 1,4-dibromo-1,4-diaroylbutanes by the cyanide ring-closure.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE PINACOL–PINACOLIN REARRANGEMENT. THE RELATIVE MIGRATION APTITUDES OF ARYL GROUPS[1]

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The rearrangement of symmetrical mixed pinacols of the type RR′(OH)C—C(OH)RR′ has been recognized as one of the best means of comparing migration aptitudes[2] of groups since the groups are in structurally identical positions. Moreover, the nature of the pinacolin which is formed indicates which of the two groups has migrated. The two possibilities may be represented as follows:

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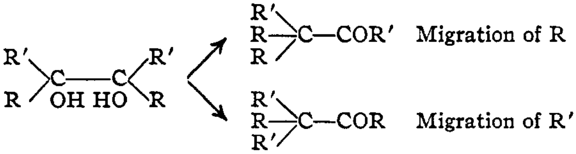
[1] The material here presented is from a dissertation submitted by Frank H. Moser to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1931.

[2] See Tiffeneau and Orekhoff, *Bull. soc. chim.*, **35**, 1639 (1924), and *Ann. Reports*, **27**, 114 (1930), for reviews of the subject.



The study of this rearrangement has been retarded by the lack of good methods for preparing pinacols. The new reaction of Gomberg and Bachmann[3] involving the reduction of ketones by a mixture of magnesium and magnesium iodide has stimulated interest in the pinacol rearrangement, for the reaction has proved to be an excellent method for making symmetrical aromatic pinacols. We have employed this method for synthesizing pinacols containing aryl groups whose migration aptitudes we wished to determine.

We desired particularly to determine whether the migration aptitudes of two groups in a symmetrical pinacol are properties of the groups themselves or are dependent on the particular molecule in which they happen to be found. If the migration aptitudes depend only on the groups, then it should be possible, knowing the relative migration aptitude of group R_1 to R_2 and of R_1 to R_3, to predict the course of rearrangement of a pinacol containing the groups R_2 and R_3. Accordingly, we synthesized and rearranged those pinacols which allowed us to make predictions of this kind, and we then proceeded to check these predictions by experiment. We found that the predicted values agreed with the experimental results, indicating that *in symmetrical aromatic pinacols* the nature of the rearrangement depends upon the characteristic groups present.

Experimental

Reduction of Ketones by Magnesium + Magnesium Iodide.—Eleven ketones were reduced to pinacols by the reaction of Gomberg and Bachmann. The quantity of metallic magnesium that reacted with a given amount of ketone and magnesium iodide corresponded to that required by the formulation: $2RR'CO + Mg + MgI_2 \longrightarrow 2RR'COMgI \rightleftarrows (RR'COMgI)_2$. In every case the reaction proceeded through the intermediate formation of free ketyl radicals, as was indicated by the color and by the reactions[3] of the solution. The colors of the ketyl varied from red to purple. On exposure to air these colors disappeared, but they appeared again when air was excluded. The behavior of these radicals with iodine and with oxygen was studied and, as a rule, a large yield of ketone was produced. For all of the pinacols, the identical equilibrium mixture, ketyl $\rightleftarrows$ pinacolate, was obtained by the action of the Grignard reagent on the pinacol as resulted from the ketone and the binary system. In Table I are given the yields and the melting points of the pinacols which were obtained by hydrolysis of the iodomagnesium pinacolates.

In the preparation of the pinacols several new ketones were synthesized, all by means of the Friedel and Crafts reaction from biphenyl and the required acid chloride.

3-Methyl-4′-phenylbenzophenone.—Yield, 77%; b. p. 234° at 10 mm.; m. p. 80–81°. The ketone was recrystallized by dissolving it in a small amount of chloro-

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[3] Gomberg and Bachmann, This Journal, **49**, 236 (1927).

TABLE I

PINACOLS OBTAINED BY REDUCTION OF KETONES BY Mg + MgI_2

Benzopinacol	Yield, %	M. p., °C.
Sym.-4,4′-dimethyl-	96	173
Sym.-4,4′-dimethyl-4″,4‴-diphenyl-[a]	93	180–182
Sym.-3,3′-dimethyl-	82	151–152
**Sym.*-3,3′-dimethyl-4″,4‴-diphenyl-[b]	96	174–175
Sym.-2,2′-dimethyl-	22	167
**Sym.*-2,2′-dimethyl-4″,4‴-diphenyl-[c]	35	182–183
Sym.-4,4′-dimethoxy-[d]	45	173–174
**Sym.*-4,4′-dimethoxy-4″,4‴-dimethyl-[e]	4	175–176
**Sym.*-4,4′-dimethoxy-4″,4‴-diphenyl-[f]	22	172–174
Sym.-4,4′-dichloro-4″,4‴-dimethyl-	89	175–176
**Sym.*-4,4′-dichloro-4″,4‴-diphenyl-[g]	98	190–191

* New pinacols.

[a] The solution containing the ketyl is red by transmitted light and blue by reflected light. Bailar, THIS JOURNAL, **52**, 3596 (1930), reported 175–176° as the melting point of this pinacol.

[b] The ketyl solution has a wine color by transmitted light and is dark blue by reflected light. The pinacol was recrystallized from a mixture of benzene and petroleum ether. *Anal.* Calcd. for $C_{40}H_{34}O_2$: C, 87.87; H, 6.27. Found: C, 88.30; H, 6.22.

[c] The color of the ketyl is dark purple. The pinacol crystallized well from a mixture of benzene and petroleum ether. *Anal.* Calcd. for $C_{40}H_{34}O_2$: C, 87.87; H, 6.27. Found: C, 87.66; H, 6.35.

[d] The ketyl is blood red in color. The pinacol crystallized from a mixture of benzene and alcohol in the form of glistening diamond-like crystals. Reduction of 5 g. of 4-methoxybenzophenone with zinc dust and acetic acid in the cold gave 4.4 g. (88%) of the same pinacol. Using the same reducing mixture, Tiffeneau and Orékhoff, *Bull. soc. chim.*, **37**, 430 (1925), obtained only pinacolin (m. p. 125–126°); this was undoubtedly due to the fact that they heated the reduction mixture, thereby causing a rearrangement to take place.

[e] The ketyl is blood red in color. The pinacol was recrystallized from a mixture of benzene and alcohol. *Anal.* Calcd. for $C_{30}H_{30}O_4$: C, 79.25; H, 6.66. Found: C, 79.20; H, 6.54. By allowing a mixture of 5 g. of 4-methoxy-4′-methylbenzophenone, 55 cc. of acetic acid and 10 g. of zinc dust to stand at room temperature for three days, 4.65 g. (93%) of the same pinacol was obtained. Employing the same reaction but heating the mixture, Orékhoff and Brouty, *Bull. soc. chim.*, **47**, 621 (1930), obtained a product melting at 130–131° which they considered was pinacol. They obtained the same product by the action of *p*-tolylmagnesium bromide on anisil; we tried this reaction and obtained only the pinacol of melting point 175–176°. It should be noted that the pinacolin which is obtained on rearrangement of our pinacol melts at 130–131°.

[f] The ketyl solution was bright red in color. Large losses of pinacol occurred in recrystallization. The pinacol was also prepared by the action of anisylmagnesium bromide on 4,4′-diphenylbenzil. *Anal.* Calcd. for $C_{40}H_{34}O_4$: C, 83.01; H, 5.93. Found: C, 83.59; H, 5.92.

[g] The ketyl was dark red in color. The pinacol crystallized from a mixture of carbon tetrachloride and alcohol in small colorless granules. *Anal.* Calcd. for $C_{38}H_{28}Cl_2O_2$: Cl, 12.08. Found: Cl, 12.06, 12.02.

form and adding alcohol. It is extremely soluble in benzene, ether, carbon tetrachloride, chloroform and acetone in the cold. It is very soluble in hot alcohol but not very soluble in the cold.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 87.93; H, 5.82.

2-Methyl-4′-phenylbenzophenone.—Yield, 88%; b. p. 283–285° (20 mm.). It crystallized from alcohol in glistening white plates; m. p. 107–109°.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.28; H, 5.92. Found: C, 88.28; H, 5.89.

4-Methoxy-4′-phenylbenzophenone.—Yield, 35%. The product crystallizes from benzene in colorless flakes; m. p. 165–167°.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.30; H, 5.59. Found: C, 83.41; H, 5.54.

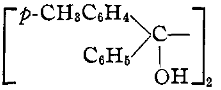
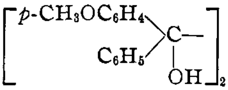
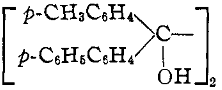
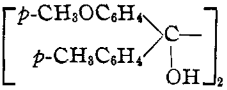
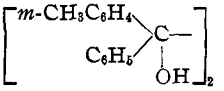
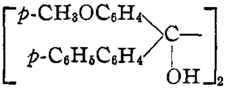
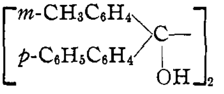
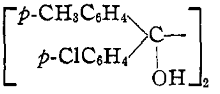
4-Chloro-4′-phenylbenzophenone.—Yield, 79%; b. p. 300° (10 mm.). The ketone crystallized from chlorobenzene in light fluffy plates.

Anal. Calcd. for $C_{19}H_{13}ClO$: Cl, 12.12. Found: Cl, 12.15, 11.92.

Rearrangement of Pinacols. Comparison of Migration Aptitudes.—Since there is some question whether the nature of the rearranging medium has an effect on the course of the rearrangement, all of the pinacols were rearranged with the same rearranging mixture. This consisted of a mixture of acetyl chloride, acetic acid and benzene; it has a good solvent action as well as a higher boiling point than acetyl chloride alone. Several runs were made on each pinacol and the results checked each other closely. The nature and amounts of the pinacolins which were formed were found in each case by scission of the pinacolins into triarylmethanes and acids by the reaction: $R_3CCOR + KOH \longrightarrow R_3CH + KOOCR$. In some cases the mixture of acids so formed was resolved into its components by taking advantage of the differences in their solubilities. The yields of acids varied between 90–99%. Usually the methane formed in the larger amount was isolated in a pure state. The results of the rearrangements are summarized in Table II.

Table II

Migration of Groups

Pinacol	Groups	Migration, %	Pinacol	Groups	Migration, %
	*p*-Tolyl	94		Anisyl	98.6
	Phenyl	6		Phenyl	1.4
	*p*-Tolyl	57		Anisyl	96.7
	p-Biphenyl	43		*p*-Tolyl	3.3
	*m*-Tolyl	66		Anisyl	96.8
	Phenyl	34		*p*-Biphenyl	3.2
	*m*-Tolyl	13		*p*-Tolyl	82
	p-Biphenyl	87		*p*-Chlorophenyl	?

Several of the pinacols which were rearranged are not listed in the table because the reactions were not complete. It is noteworthy that in every rearrangement that could be studied quantitatively both of the groups migrated. In several cases, previous investigators had reported that only one group of a particular pinacol had migrated.

General Procedure for Rearrangement and Scission.—One hundredth of a gram mole of pinacol was placed in a 200-cc. round-bottomed flask connected by a ground-glass joint to a condenser, and a mixture of 40 cc. of acetyl chloride, 20 cc. of glacial acetic acid and 80 cc. of benzene was added. The solution was refluxed on a steam-bath for a varying period of time (depending on the pinacol). The solvents were distilled off under reduced pressure and a solution of 6 g. of potassium hydroxide in 100 cc. of absolute alcohol was added. Refluxing was carried on until the splitting of the pinacolins was complete. The alcohol was then distilled off and 100 cc. of water was added; this dissolved the potassium salts of the organic acids while the methanes were present as precipitates. The methanes were extracted from the aqueous solution with benzene three times and the benzene was allowed to evaporate in order to obtain the methanes. The aqueous solution was acidified with hydrochloric acid and was extracted with benzene in order to get out all organic acids.

4,4'-Dimethylbenzopinacol.—The rearrangement was allowed to proceed for thirty-six hours; the splitting reaction proceeded for six days. Thörner and Zincke[4] reported that the acid obtained was for the most part benzoic acid since it melted only a few degrees lower than pure benzoic acid; as a result they reported that the *p*-tolyl group migrated exclusively. It was found impossible to separate a mixture of 95% of benzoic acid and 5% of toluic acid into its components by means of the difference in solubility of the two acids. A determination of the amount of *p*-toluic acid was obtained by oxidizing it to terephthalic acid, which is practically insoluble in water and which can therefore be easily separated from the more soluble benzoic acid. The mixture of acids was heated for one-half hour with 1 g. of potassium dichromate, 3 cc. of sulfuric acid and 6 cc. of water. A correction for the losses occurring during oxidation was determined by oxidizing several synthetic mixtures of benzoic acid and *p*-toluic acid of approximately the same composition in the same manner. The methane obtained on recrystallization of the crude product was identified as 4,4'-dimethyltriphenylmethane.

4,4'-Dimethyl-4'',4'''-diphenylbenzopinacol.—Time for rearrangement, thirty-six hours; time for scission, six days. The acids were separated by virtue of the slight solubility of *p*-phenylbenzoic acid in hot water. A correction for its solubility was made by treating similar mixtures of *p*-phenylbenzoic acid and *p*-toluic acid in the same manner. Bailar[5] found equal quantities of the two pinacolins; he used acetic acid and iodine as the rearranging agent and determined the proportions of the two acids in the mixture by a determination of the equivalent weight.

The mixture of methanes weighed 2.58 g. and was resolved into its two components by dissolving the mixture in 20 cc. of warm ether. Upon cooling, 1.13 g. of 4,4'-diphenyl-4''-methyltriphenylmethane (synthesis given below) crystallized out; m. p. 160–162°. From the filtrate 0.74 g. of 4-phenyl-4',4''-dimethyltriphenylmethane was obtained; m. p. 123–125°. The same melting point was observed when this substance was mixed with synthetic 4-phenyl-4',4''-dimethyltriphenylmethane.

1,1-Dibiphenyl-1,2-di-*p*-tolylethanone-2.—It was possible to isolate this pinacolin from the mixture because of its slight solubility in organic solvents. Two grams of *sym.*-4,4'-dimethyl-4'',4'''-diphenylbenzopinacol was heated for twelve minutes with 15 cc. of glacial acetic acid containing a crystal of iodine. A yield of 0.58 g. (30%) of colorless crystals melting at 227–229° was obtained. The structure of these crystals was proved by quantitative scission into 4-methyl-4',4''-diphenyltriphenylmethane and *p*-toluic acid.

Anal. Calcd. for $C_{40}H_{32}O$: C, 90.87; H, 6.11. Found: C, 91.18; H, 6.02.

4,4'-Diphenyl-4''-methyltriphenylcarbinol.—This carbinol was synthesized from *p*-tolylmagnesium bromide and dibiphenyl ketone; yield, 58%. The compound

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[4] Thörner and Zincke, *Ber.*, **10,** 1473 (1877); **11,** 65 (1778).

[5] Bailar, THIS JOURNAL, **52,** 3596 (1930).

crystallized from a mixture of ether and benzene in fine colorless crystals; m. p. 143–144°; it gives a red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{32}H_{26}O$: C, 90.10; H, 6.15. Found: C, 90.24; H, 6.10.

4,4′-Diphenyl-4″-methyltriphenylmethane.—The carbinol was reduced to the methane by heating it with zinc and acetic acid. The methane crystallized in fine colorless needles from benzene; m. p. 162–163°.

Anal. Calcd. for $C_{32}H_{26}$: C, 93.61; H, 6.39. Found: C, 93.97; H, 6.37.

4,4′-Dimethyl-4″-phenyltriphenylmethane.—The corresponding carbinol was prepared from *p*-tolylmagnesium bromide and *p*-tolyl biphenyl ketone; the product was an oil which did not crystallize. It was reduced by zinc and acetic acid to the methane. On recrystallization from ether the methane was obtained in the form of colorless needles which melted at 123–125°.

Anal. Calcd. for $C_{27}H_{24}$: C, 93.05; H, 6.95. Found: C, 93.02; H, 6.99.

3,3′-Dimethylbenzopinacol.—Time for rearrangement, three hours; time allowed for scission, one day. The mixture of acids was dissolved in a solution of 1 g. of potassium hydroxide in 50 cc. of water, 1.4 g. of powdered potassium permanganate was added and the solution was heated for one hour on a steam-bath. This treatment oxidized the *m*-toluic acid to isophthalic acid and left the benzoic acid unchanged; the benzoic acid was then extracted from the mixture by means of water. As usual, a correction for the solubility of the isophthalic acid was determined by oxidation of a synthetic mixture of benzoic and *m*-toluic acids. From the mixtures of methanes, crystals of 3-methyltriphenylmethane were isolated and identified by a mixed melting point determination with an authentic specimen.

Recently Bailar determined the migration aptitudes of the phenyl and *m*-tolyl groups and reported that the *m*-tolyl group migrated 37 to 63% for the phenyl group, values that are practically the reverse of ours. He did not separate the two acids but determined the equivalent weight of the mixture. We repeated the rearrangement, used that method of analysis and confirmed our results. Bailar employed a mixture of acetic acid and iodine for rearranging the pinacol.

3,3′-Dimethyl-4″,4‴-diphenylbenzopinacol.—Twenty-four hours were allowed for rearrangement while seven days were given for splitting. The mixture of acids was resolved by making use of the solubility of *m*-toluic acid in hot water. By recrystallization of the methanes (2.72 g.), pure 3-methyl-4′,4″-diphenyltriphenylmethane was obtained; its structure was confirmed by synthesis.

3-Methyl-4′,4″-diphenyltriphenylcarbinol.—This new carbinol was prepared by refluxing a mixture of 6.7 g. of dibiphenyl ketone suspended in 100 cc. of benzene with the Grignard reagent from 7.25 g. of *m*-bromotoluene. The carbinol crystallized from a mixture of benzene and petroleum ether in small colorless rods; m. p. 124–125°; yield, 5.32 g. The compound gives a red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{32}H_{26}O$: C, 90.10; H, 6.15. Found: C, 89.88; H, 6.23.

3-Methyl-4′,4″-diphenyltriphenylmethane.—Two grams of carbinol was heated with zinc and a mixture of acetic and hydrochloric acids (6:1) for two hours; yield of methane, 1 g. It was recrystallized by adding petroleum ether to a hot saturated benzene solution; m. p. 144–145°. No change in melting point was observed when this substance was mixed with the methane obtained by scission of the pinacolins.

Anal. Calcd. for $C_{32}H_{26}$: C, 93.61; H, 6.39. Found: C, 93.35; H, 6.49.

4,4′-Dimethoxybenzopinacol.—Time allowed: for rearrangement, twenty-four hours; for scission, two days. In order to determine the amount of anisic acid present in the mixture of acids, a methoxyl estimation was made. Trial runs using synthetic mixtures gave good results. Recrystallization of the crude methanes gave pure 4,4′-

dimethoxytriphenylmethane of m. p. 100–101°, confirming the results obtained by analysis of the acid mixture. Tiffeneau and Orékhoff[6] have reported that the anisyl group migrates exclusively in preference to the phenyl group. Our more careful method of analysis shows that the phenyl group migrates to the extent of 1.4%.

4,4′-Dimethoxy-4′′,4′′′-dimethylbenzopinacol.—Time required: for rearrangement, two hours; for splitting, three days. The mixture of acids was analyzed for anisic acid by making a methoxyl determination. Recrystallization of the methane from a mixture of ether and petroleum ether gave white fibers of dianisyl-*p*-tolylmethane, melting at 45–46°. Orékhoff and Brouty[7] report 40–42° for this value. These investigators reported that the anisyl group migrates exclusively with respect to the *p*-tolyl group, while our results show that the *p*-tolyl group migrates to the extent of 3.3%. It appears that they recrystallized the crude pinacolin mixture before splitting it.

1,1-Dianisyl-1,2-di-*p*-tolyl-ethanone-2.—Inasmuch as the rearrangement of the pinacol gave this pinacolin to the extent of 96%, we were able to isolate it easily in a pure state by recrystallizing the crude mixture of pinacolins; yield, 80%; m. p. 129–130°. Orékhoff and Brouty reported a melting point of 81° for this pinacolin.

Anal. Calcd. for $C_{30}H_{28}O_3$: C, 82.53; H, 6.47. Found: C, 82.40; H, 6.54.

4,4′-Dimethoxy-4′′,4′′′-diphenylbenzopinacol.—Time allowed: for rearrangement, two hours; for splitting, eleven days. A methoxyl determination was run on the mixture of acids; the material remaining after the determination was found to be principally *p*-phenylbenzoic acid. Recrystallization of the methanes from a mixture of benzene and petroleum ether gave a product of m. p. 118–119° which was proved by synthesis to be 4,4′-dimethoxy-4″-phenyltriphenylmethane.

4,4′Dimethoxy-4″-phenyltriphenylmethane.—The carbinol was prepared by the action of anisylmagnesium bromide on 4-methoxy-4′-phenylbenzophenone; the product could not be made to crystallize. Two grams of the oily carbinol was reduced to the corresponding methane by heating it with 35 cc. of formic acid[8] for two days. The product was recrystallized from benzene and petroleum ether and was obtained in clusters of diamond-shaped crystals; m. p. 118–119°; yield, 0.59 g.

Anal. Calcd. for $C_{27}H_{24}O_2$: C, 85.22; H, 6.36. Found: C, 85.43; H, 6.28.

4,4′-Dichloro-4′′,4′′′-dimethylbenzopinacol.—The pinacol was heated with the rearranging mixture for sixty-six hours; the scission reaction mixture was refluxed for five days; 200 cc. of alcohol was used in order to get the pinacolin completely in solution. A 52% yield of practically pure *p*-chlorobenzoic acid (m. p. 230–232°) was isolated; in addition, a 30% yield of unchanged pinacolin, which proved to be 1,1-di-*p*-tolyl-1,2-di-*p*-chlorophenylethanone-2, was obtained. These results show that, although the scission was not complete, at least 82% migration of the *p*-tolyl group had occurred. A small amount of pure 4-chloro-4′,4″-dimethyltriphenylmethane was isolated; it was identified by comparison with a synthetic product.

1,1-Di-*p*-tolyl-1,2-di-*p*-chlorophenylethanone-2.—This pinacolin was the principal product of the rearrangement of *sym.*-dichlorodimethylbenzopinacol; after recrystallization from alcohol it melted at 204–205°. Its structure was proved by scission into 4-chloro-4′,4″-dimethyltriphenylmethane and *p*-chlorobenzoic acid; this splitting, however, was not quantitative.

Anal. Calcd. for $C_{28}H_{22}OCl_2$: Cl, 15.93. Found: Cl, 15.74, 16.13.

4-Chloro-4′,4″-dimethyltriphenylcarbinol.—This carbinol was prepared by the action of *p*-tolylmagnesium bromide on 4-chloro-4′-methylbenzophenone; the product

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[6] Tiffeneau and Orékhoff, *Bull. soc. chim.*, **37**, 430 (1925).

[7] Orékhoff and Brouty, *ibid.*, **47**, 621 (1930).

[8] Kaufmann and Panwitz, *Ber.*, **45**, 769 (1912).

was recrystallized from petroleum ether; m. p. 94–95°; yield, 62%. The carbinol gives an orange color with concentrated sulfuric acid.

Anal. Calcd. for $C_{21}H_{19}ClO$: Cl, 10.99. Found, Cl, 11.01, 10.90.

4-Chloro-4′,4″-dimethyltriphenylmethane.—A mixture of 1.22 g. of carbinol and 30 cc. of formic acid was heated on a steam-bath for fourteen hours. The methane which was obtained on diluting the reaction mixture with water was recrystallized from petroleum ether and was obtained as colorless, granular crystals melting at 66–68°; yield, 0.52 g.

Anal. Calcd. for $C_{21}H_{19}Cl$: Cl, 11.57. Found: Cl, 11.51, 11.94.

4,4′-Dichloro-4″,4‴-diphenylbenzopinacol.—Time allowed: for rearrangement, twenty-four hours; for scission, nine days. Only 0.10 g. of acid (*p*-chlorobenzoic acid) was obtained. Splitting of the pinacolin was not accomplished by heating it with potassium hydroxide in a sealed tube at 150°. The pinacolin, undoubtedly 1,1-dibiphenyl-1,2-di-*p*-chlorophenylethanone-2, was recrystallized twice from benzene and melted at 250–255°. Koopal[9] experienced similar difficulties in attempting to split halogen substituted pinacolins.

2,2′-Dimethylbenzopinacol.—Hatt[10] reported that this pinacol was rearranged by warming it with acetic acid and iodine. Bailar, however, was unable to rearrange this pinacol and explained the lack of rearrangement on the basis of affinity capacities. We obtained an uncrystallizable resin-like product when we used acetyl chloride for rearrangement. The resinous product was not cleaved by potassium hydroxide. However, heating the resin with acetic acid and iodine converted it to a pinacolin which gave *o*-toluic acid (63% yield), indicating migration of the phenyl group.

2,2′-Dimethyl-4″,4‴-diphenylbenzopinacol.—Treatment of the pinacol with the customary rearranging mixture gave a transparent resin which was not split by potassium hydroxide. Hot acetic acid and iodine converted this resin to pinacolin which gave *o*-toluic acid on scission with alkali; this shows that the biphenyl group migrated in preference to the *o*-toyl group.

2-Methylbenzopinacol.—After our unsuccessful attempts to rearrange pinacols containing two *o*-methyl groups, by means of acetyl chloride, we attempted the rearrangement of a pinacol with only one *o*-methyl group. However, there resulted a resinous product which was not cleaved by potassium hydroxide. Acetic acid and iodine converted the resin to pinacolin which on scission gave a 93% yield of a mixture of acids consisting chiefly of benzoic acid.

This new pinacol was synthesized as follows. The Grignard reagent prepared from 19 g. of *o*-bromotoluene and 2.4 g. of magnesium in 40 cc. of ether was added to a solution of 21.0 g. of benzil and the resulting mixture was allowed to stand for twenty-four hours. The product obtained by hydrolysis of the reaction mixture was dissolved in 100 cc. of benzene and this solution was added to the Grignard reagent which had been prepared from 50 g. of bromobenzene in 100 cc. of ether. The solution was refluxed for three hours and was then allowed to stand for twelve hours. Upon hydrolysis the pinacol was obtained as a colorless solid. It was recrystallized from chloroform; yield, 14 g.; m. p. 175–176°.

Anal. Calcd. for $C_{27}H_{24}O_2$: C, 85.22; H, 6.36; Found: C, 84.73; H, 6.41.

Discussion

Predicting Migration Aptitudes.—The method of predicting the relative migration aptitudes of two groups from the values of the relative

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[9] Koopal, *Rec. trav. chim.*, **34**, 115 (1915).

[10] Hatt, *J. Chem. Soc.*, 1633 (1929).

migrations of each of these groups with respect to a third mutual group may be illustrated by an example. The rearrangement of a phenyl-*p*-tolyl pinacol gave the following results: *p*-$CH_3C_6H_4$ (94%) : C_6H_5 (6%). Rearrangement of the pinacol containing the *p*-biphenyl[3] and phenyl groups gave the relation: *p*-$C_6H_5C_6H_4$ (92%), C_6H_5 (8%). Then the relative migration aptitudes of the *p*-tolyl group with respect to the biphenyl group is found as follows

$$\frac{p\text{-}CH_3C_6H_4}{p\text{-}C_6H_5C_6H_4} = \frac{p\text{-}CH_3C_6H_4/C_6H_5}{p\text{-}C_6H_5C_6H_4/C_6H_5} = \frac{94/6}{92/8} = \frac{58}{42}$$

This means that the pinacol containing the *p*-tolyl and the *p*-biphenyl groups should rearrange with 58% migration of the *p*-tolyl group and 42% migration of the *p*-biphenyl group. The values found experimentally are: *p*-$CH_3C_6H_4$ (57%) and *p*-$C_6H_5C_6H_4$ (43%).

In Table III the predicted values for the rearrangement of a number of pinacols are compared with the experimental results. The group in parentheses is the mutual group employed in the calculation of the predicted values.

TABLE III

MIGRATION OF GROUPS

Groups		Predicted, %	Found, %
p-Tolyl	(Phenyl)	58	57
p-Biphenyl		42	43
m-Tolyl	(*p*-Biphenyl)	63	66
Phenyl		37	34
Anisyl	(*p*-Tolyl)	97.5	96.8
p-Biphenyl		2.5	3.2
Anisyl	(*p*-Tolyl)	99.8	98.6
Phenyl		0.2	1.4
p-Bromophenyl[a]	(Phenyl)	6.0	4.5
p-Biphenyl		94.0	95.5
p-Ethylphenyl[b]	(Phenyl)	24	25
p-Tolyl		76	75
Anisyl[b]	(*p*-Tolyl)	96.3	67
α-Naphthyl		3.7	33

[a] From results of Gomberg and Bailar, THIS JOURNAL, 51, 2229 (1929). These investigators found that predictions in two instances were verified by experiment.

[b] From results of Bailar, Table I, Ref. *a*.

It is seen that the predicted values in all but one case (anisyl-α-naphthyl) agree satisfactorily with the experimental values. Other predictions can be made and we are continuing our work of checking them by experiment.

Tiffeneau and Orékhoff assigned to the individual groups a value representing its migration aptitude with respect to the phenyl group as a standard. The series was recently amplified by Bailar. In view of our results we obtain the following order and values: anisyl, 70 or more; α-naphthyl, 18; *p*-tolyl, 15; *p*-biphenyl, 11.5; *p*-isopropylphenyl, 9; *p*-ethylphenyl, 5; *m*-tolyl, 1.95; *p*-fluorophenyl, 1.85; *p*-iodophenyl, 1; phenyl, 1; *p*-bromophenyl, 0.71; *p*-chlorophenyl, 0.66; *m*-methoxyphenyl, 0.2; *o*-tolyl, *o*- and *m*-bromophenyl and *o*- and *m*-chlorophenyl, very small. It should be noted that the series of migration aptitudes coincides well with a similar series of affinity capacities of the same groups; this is in harmony with the observation of Tiffeneau and Orekhoff that the groups that have the greatest affinity capacity migrate most easily.

Summary

A number of pinacols have been prepared by the reaction of Gomberg and Bachmann and a study has been made of the equilibrium mixture, ketyl $\leftrightarrows$ pinacolate, which is found in each case.

Twelve pinacols have been subjected to the pinacol–pinacolin rearrangement and a comparison of the migration aptitudes of the phenyl, *p*-tolyl, *p*-biphenyl, anisyl, *o*-tolyl, *m*-tolyl and *p*-chlorophenyl groups has been obtained.

The migration aptitudes of a group *in a symmetrical benzopinacol* has been shown to be a property characteristic of that group and is not dependent on the particular pinacol in which it is found.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

OXIDATION OF UNSATURATED COMPOUNDS. VI. SYNTHESIS OF 3-BROMOTHREONIC ACID. SUPPLEMENT TO THE PROOF OF CONFIGURATION OF *dl*-1,2-DIHYDROXYBUTYRIC ACIDS

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In a recent publication of this series the proof of configuration of *dl*-1,2-dihydroxybutyric acids was presented.[2] The proof was based on the fact that the 3-chlorothreonic acid could be converted into racemic tartaric acid and on the other hand it could be reduced to the *dl*-1,2-dihydroxybutyric acid (m. p. 74°), which shows clearly that the *dl*-1,2-dihydroxybutyric acid (m. p. 74°) has the same configuration as the racemic acid. It was thought necessary to complete this proof with the reactions of 3-bromothreonic acid, and the results of this investigation are reported in the present paper.

I. Synthesis of 3-Bromothreonic Acid.—The 3-bromothreonic acid is prepared by the oxidation of 3-bromocrotonic acid[3] with osmic acid activated barium chlorate in the same manner as was reported in the case of 3-chlorocrotonic acid.[2] The 3-bromothreonic acid hydrolyzes gradually in

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[2] Géza Braun, THIS JOURNAL, **52**, 3176 (1930).

[3] Géza Braun, *ibid.*, **52**, 3167 (1930).